

خدمتكم طريق خضناه لرضى الله

2021

حلول كتاب الكيمياء العامة



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CHAPTER 3

STOICHIOMETRY

3.1 One atomic mass unit is defined as a mass exactly equal to one-twelfth the mass of one carbon-12 atom. We cannot weigh a single atom, but it is possible to determine the mass of one atom relative to another experimentally. The first step is to assign a value to the mass of one atom of a given element so that it can be used as a standard.

3.2 12.00 amu. On the periodic table, the mass is listed as 12.01 amu because this is an average mass of the naturally occurring mixture of isotopes of carbon.

3.3 The value 197.0 amu is an average value (an average atomic mass). If we could examine gold atoms individually, we would not find an atom with a mass of 197.0 amu. However, the average mass of a gold atom in a typical sample of gold is 197.0 amu.

3.4 You need the mass of each isotope of the element and each isotope's relative abundance.

3.5 $(34.968 \text{ amu})(0.7553) + (36.956 \text{ amu})(0.2447) = \mathbf{35.45 \text{ amu}}$

3.6 **Strategy:** Each isotope contributes to the average atomic mass based on its relative abundance. Multiplying the mass of an isotope by its fractional abundance (not percent) will give the contribution to the average atomic mass of that particular isotope.

It would seem that there are two unknowns in this problem, the fractional abundance of ^6Li and the fractional abundance of ^7Li . However, these two quantities are not independent of each other; they are related by the fact that they must sum to 1. Start by letting x be the fractional abundance of ^6Li . Since the sum of the two abundance's must be 1, we can write

$$\text{Abundance } ^7\text{Li} = (1 - x)$$

Solution:

$$\begin{aligned} \text{Average atomic mass of Li} &= 6.941 \text{ amu} = x(6.0151 \text{ amu}) + (1 - x)(7.0160 \text{ amu}) \\ 6.941 &= -1.0009x + 7.0160 \\ 1.0009x &= 0.075 \\ x &= \mathbf{0.075} \end{aligned}$$

$x = 0.075$ corresponds to a natural abundance of ^6Li of **7.5 percent**. The natural abundance of ^7Li is $(1 - x) = 0.925$ or **92.5 percent**.

3.7 The conversion factor required is $\left(\frac{6.022 \times 10^{23} \text{ amu}}{1 \text{ g}} \right)$

$$? \text{ g} = 13.2 \cancel{\text{ amu}} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \cancel{\text{ amu}}} = \mathbf{2.19 \times 10^{-23} \text{ g}}$$

3.8 The unit factor required is $\left(\frac{6.022 \times 10^{23} \text{ amu}}{1 \text{ g}} \right)$

$$? \text{ amu} = 8.4 \cancel{\text{g}} \times \frac{6.022 \times 10^{23} \text{ amu}}{1 \cancel{\text{g}}} = 5.1 \times 10^{24} \text{ amu}$$

3.9 The mole is the amount of a substance that contains as many elementary entities (atoms, molecules, or other particles) as there are atoms in exactly 12 grams of the carbon-12 isotope. The unit for mole used in calculations is mol. A mole is a unit like a pair, dozen, or gross. A mole is the amount of substance that contains 6.022×10^{23} particles. Avogadro's number (6.022×10^{23}) is the number of atoms in exactly 12 g of the carbon-12 isotope.

3.10 The molar mass of an atom is the mass of one mole, 6.022×10^{23} atoms, of that element. Units are g/mol.

3.11 In one year:

$$(6.5 \times 10^9 \cancel{\text{people}}) \times \frac{365 \cancel{\text{days}}}{1 \text{ yr}} \times \frac{24 \cancel{\text{h}}}{1 \cancel{\text{day}}} \times \frac{3600 \cancel{\text{s}}}{1 \cancel{\text{h}}} \times \frac{2 \text{ particles}}{1 \cancel{\text{person}}} = 4.1 \times 10^{17} \text{ particles/yr}$$

$$\text{Total time} = \frac{6.022 \times 10^{23} \cancel{\text{particles}}}{4.1 \times 10^{17} \cancel{\text{particles/yr}}} = 1.5 \times 10^6 \text{ yr}$$

3.12 The thickness of the book in miles would be:

$$\frac{0.0036 \cancel{\text{in}}}{1 \cancel{\text{page}}} \times \frac{1 \cancel{\text{ft}}}{12 \cancel{\text{in}}} \times \frac{1 \text{ mi}}{5280 \cancel{\text{ft}}} \times (6.022 \times 10^{23} \cancel{\text{pages}}) = 3.4 \times 10^{16} \text{ mi}$$

The distance, in miles, traveled by light in one year is:

$$1.00 \cancel{\text{yr}} \times \frac{365 \cancel{\text{day}}}{1 \cancel{\text{yr}}} \times \frac{24 \cancel{\text{h}}}{1 \cancel{\text{day}}} \times \frac{3600 \cancel{\text{s}}}{1 \cancel{\text{h}}} \times \frac{3.00 \times 10^8 \cancel{\text{m}}}{1 \cancel{\text{s}}} \times \frac{1 \text{ mi}}{1609 \cancel{\text{m}}} = 5.88 \times 10^{12} \text{ mi}$$

The thickness of the book in light-years is:

$$(3.4 \times 10^{16} \cancel{\text{mi}}) \times \frac{1 \text{ light-yr}}{5.88 \times 10^{12} \cancel{\text{mi}}} = 5.8 \times 10^3 \text{ light-yr}$$

It will take light 5.8×10^3 years to travel from the first page to the last one!

$$\text{3.13} \quad 5.10 \cancel{\text{mol S}} \times \frac{6.022 \times 10^{23} \text{ S atoms}}{1 \cancel{\text{mol S}}} = 3.07 \times 10^{24} \text{ S atoms}$$

$$\text{3.14} \quad (6.00 \times 10^9 \cancel{\text{Co atoms}}) \times \frac{1 \text{ mol Co}}{6.022 \times 10^{23} \cancel{\text{Co atoms}}} = 9.96 \times 10^{-15} \text{ mol Co}$$

$$\text{3.15} \quad 77.4 \cancel{\text{g of Ca}} \times \frac{1 \text{ mol Ca}}{40.08 \cancel{\text{g Ca}}} = 1.93 \text{ mol Ca}$$

- 3.16 Strategy:** We are given moles of gold and asked to solve for grams of gold. What conversion factor do we need to convert between moles and grams? Arrange the appropriate conversion factor so moles cancel, and the unit grams is obtained for the answer.

Solution: The conversion factor needed to convert between moles and grams is the molar mass. In the periodic table (see inside front cover of the text), we see that the molar mass of Au is 197.0 g. This can be expressed as

$$1 \text{ mol Au} = 197.0 \text{ g Au}$$

From this equality, we can write two conversion factors.

$$\frac{1 \text{ mol Au}}{197.0 \text{ g Au}} \quad \text{and} \quad \frac{197.0 \text{ g Au}}{1 \text{ mol Au}}$$

The conversion factor on the right is the correct one. Moles will cancel, leaving the unit grams for the answer.

We write

$$? \text{ g Au} = 15.3 \cancel{\text{ mol Au}} \times \frac{197.0 \text{ g Au}}{1 \cancel{\text{ mol Au}}} = 3.01 \times 10^3 \text{ g Au}$$

Check: Does a mass of 3010 g for 15.3 moles of Au seem reasonable? What is the mass of 1 mole of Au?

3.17 (a)
$$\frac{200.6 \text{ g Hg}}{1 \cancel{\text{ mol Hg}}} \times \frac{1 \cancel{\text{ mol Hg}}}{6.022 \times 10^{23} \text{ Hg atoms}} = 3.331 \times 10^{-22} \text{ g/Hg atom}$$

(b)
$$\frac{20.18 \text{ g Ne}}{1 \cancel{\text{ mol Ne}}} \times \frac{1 \cancel{\text{ mol Ne}}}{6.022 \times 10^{23} \text{ Ne atoms}} = 3.351 \times 10^{-23} \text{ g/Ne atom}$$

3.18

(a) Strategy: We can look up the molar mass of arsenic (As) on the periodic table (74.92 g/mol). We want to find the mass of a single atom of arsenic (unit of g/atom). Therefore, we need to convert from the unit mole in the denominator to the unit atom in the denominator. What conversion factor is needed to convert between moles and atoms? Arrange the appropriate conversion factor so mole in the denominator cancels, and the unit atom is obtained in the denominator.

Solution: The conversion factor needed is Avogadro's number. We have

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ particles (atoms)}$$

From this equality, we can write two conversion factors.

$$\frac{1 \text{ mol As}}{6.022 \times 10^{23} \text{ As atoms}} \quad \text{and} \quad \frac{6.022 \times 10^{23} \text{ As atoms}}{1 \text{ mol As}}$$

The conversion factor on the left is the correct one. Moles will cancel, leaving the unit atoms in the denominator of the answer.

We write

$$? \text{ g/As atom} = \frac{74.92 \text{ g As}}{1 \cancel{\text{ mol As}}} \times \frac{1 \cancel{\text{ mol As}}}{6.022 \times 10^{23} \text{ As atoms}} = 1.244 \times 10^{-22} \text{ g/As atom}$$

(b) Follow same method as part (a).

$$? \text{ g/Ni atom} = \frac{58.69 \text{ g Ni}}{1 \cancel{\text{ mol Ni}}} \times \frac{1 \cancel{\text{ mol Ni}}}{6.022 \times 10^{23} \text{ Ni atoms}} = 9.746 \times 10^{-23} \text{ g/Ni atom}$$

Check: Should the mass of a single atom of As or Ni be a very small mass?

$$3.19 \quad 1.00 \times 10^{12} \text{ Pb atoms} \times \frac{1 \cancel{\text{ mol Pb}}}{6.022 \times 10^{23} \text{ Pb atoms}} \times \frac{207.2 \text{ g Pb}}{1 \cancel{\text{ mol Pb}}} = 3.44 \times 10^{-10} \text{ g Pb}$$

3.20 Strategy: The question asks for atoms of Cu. We cannot convert directly from grams to atoms of copper. What unit do we need to convert grams of Cu to in order to convert to atoms? What does Avogadro's number represent?

Solution: To calculate the number of Cu atoms, we first must convert grams of Cu to moles of Cu. We use the molar mass of copper as a conversion factor. Once moles of Cu are obtained, we can use Avogadro's number to convert from moles of copper to atoms of copper.

$$1 \text{ mol Cu} = 63.55 \text{ g Cu}$$

The conversion factor needed is

$$\frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}}$$

Avogadro's number is the key to the second conversion. We have

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ particles (atoms)}$$

From this equality, we can write two conversion factors.

$$\frac{1 \text{ mol Cu}}{6.022 \times 10^{23} \text{ Cu atoms}} \quad \text{and} \quad \frac{6.022 \times 10^{23} \text{ Cu atoms}}{1 \text{ mol Cu}}$$

The conversion factor on the right is the one we need because it has number of Cu atoms in the numerator, which is the unit we want for the answer.

Let's complete the two conversions in one step.

grams of Cu \rightarrow moles of Cu \rightarrow number of Cu atoms

$$? \text{ atoms of Cu} = 3.14 \cancel{\text{ g Cu}} \times \frac{1 \cancel{\text{ mol Cu}}}{63.55 \cancel{\text{ g Cu}}} \times \frac{6.022 \times 10^{23} \text{ Cu atoms}}{1 \cancel{\text{ mol Cu}}} = 2.98 \times 10^{22} \text{ Cu atoms}$$

Check: Should 3.14 g of Cu contain fewer than Avogadro's number of atoms? What mass of Cu would contain Avogadro's number of atoms?

$$3.21 \quad \text{For hydrogen: } 1.10 \cancel{\text{ g H}} \times \frac{1 \cancel{\text{ mol H}}}{1.008 \cancel{\text{ g H}}} \times \frac{6.022 \times 10^{23} \text{ H atoms}}{1 \cancel{\text{ mol H}}} = 6.57 \times 10^{23} \text{ H atoms}$$

$$\text{For chromium: } 14.7 \cancel{\text{ g Cr}} \times \frac{1 \cancel{\text{ mol Cr}}}{52.00 \cancel{\text{ g Cr}}} \times \frac{6.022 \times 10^{23} \text{ Cr atoms}}{1 \cancel{\text{ mol Cr}}} = 1.70 \times 10^{23} \text{ Cr atoms}$$

There are more hydrogen atoms than chromium atoms.

$$3.22 \quad 2 \text{ Pb atoms} \times \frac{1 \cancel{\text{mol Pb}}}{6.022 \times 10^{23} \text{ Pb atoms}} \times \frac{207.2 \text{ g Pb}}{1 \cancel{\text{mol Pb}}} = 6.881 \times 10^{-22} \text{ g Pb}$$

$$(5.1 \times 10^{-23} \cancel{\text{mol He}}) \times \frac{4.003 \text{ g He}}{1 \cancel{\text{mol He}}} = 2.0 \times 10^{-22} \text{ g He}$$

2 atoms of lead have a greater mass than 5.1×10^{-23} mol of helium.

3.23 Using the appropriate atomic masses,

- | | |
|-----------------------------------------------------|---------------------------------------------------------------|
| (a) CH ₄ | 12.01 amu + 4(1.008 amu) = 16.04 amu |
| (b) NO ₂ | 14.01 amu + 2(16.00 amu) = 46.01 amu |
| (c) SO ₃ | 32.07 amu + 3(16.00 amu) = 80.07 amu |
| (d) C ₆ H ₆ | 6(12.01 amu) + 6(1.008 amu) = 78.11 amu |
| (e) NaI | 22.99 amu + 126.9 amu = 149.9 amu |
| (f) K ₂ SO ₄ | 2(39.10 amu) + 32.07 amu + 4(16.00 amu) = 174.27 amu |
| (g) Ca ₃ (PO ₄) ₂ | 3(40.08 amu) + 2(30.97 amu) + 8(16.00 amu) = 310.2 amu |

3.24 Strategy: How do molar masses of different elements combine to give the molar mass of a compound?

Solution: To calculate the molar mass of a compound, we need to sum all the molar masses of the elements in the molecule. For each element, we multiply its molar mass by the number of moles of that element in one mole of the compound. We find molar masses for the elements in the periodic table (inside front cover of the text).

- (a) **molar mass Li₂CO₃** = 2(6.941 g) + 12.01 g + 3(16.00 g) = **73.89 g**
- (b) **molar mass CS₂** = 12.01 g + 2(32.07 g) = **76.15 g**
- (c) **molar mass CHCl₃** = 12.01 g + 1.008 g + 3(35.45 g) = **119.4 g**
- (d) **molar mass C₆H₈O₆** = 6(12.01 g) + 8(1.008 g) + 6(16.00 g) = **176.12 g**
- (e) **molar mass KNO₃** = 39.10 g + 14.01 g + 3(16.00 g) = **101.11 g**
- (f) **molar mass Mg₃N₂** = 3(24.31 g) + 2(14.01 g) = **100.95 g**

3.25 To find the molar mass (g/mol), we simply divide the mass (in g) by the number of moles.

$$\frac{152 \text{ g}}{0.372 \text{ mol}} = \mathbf{409 \text{ g/mol}}$$

3.26 The molar mass of acetone, C₃H₆O, is 58.08 g. We use the molar mass and Avogadro's number as conversion factors to convert from grams to moles to molecules of acetone.

$$0.435 \cancel{\text{g C}_3\text{H}_6\text{O}} \times \frac{1 \cancel{\text{mol C}_3\text{H}_6\text{O}}}{58.08 \cancel{\text{g C}_3\text{H}_6\text{O}}} \times \frac{6.022 \times 10^{23} \text{ molecules C}_3\text{H}_6\text{O}}{1 \cancel{\text{mol C}_3\text{H}_6\text{O}}} = \mathbf{4.51 \times 10^{21} \text{ molecules C}_3\text{H}_6\text{O}}$$

3.27 We use the molar mass of squaric acid (114.06 g), Avogadro's number, and the subscripts in the formula of squaric acid, C₄H₂O₄, to convert from grams of squaric acid to moles of squaric acid to molecules of squaric acid, and finally to atoms of C, H, or O. We first convert to molecules of squaric acid.

$$1.75 \cancel{\text{g C}_4\text{H}_2\text{O}_4} \times \frac{1 \cancel{\text{mol C}_4\text{H}_2\text{O}_4}}{114.06 \cancel{\text{g C}_4\text{H}_2\text{O}_4}} \times \frac{6.022 \times 10^{23} \text{ molecules C}_4\text{H}_2\text{O}_4}{1 \cancel{\text{mol C}_4\text{H}_2\text{O}_4}} = \mathbf{9.24 \times 10^{21} \text{ molecules C}_4\text{H}_2\text{O}_4}$$

Next, we convert to atoms of C, H, and O using the subscripts in the formula as conversion factors.

$$9.24 \times 10^{21} \text{ molecules } \text{C}_4\text{H}_2\text{O}_4 \times \frac{4 \text{ atoms C}}{1 \text{ molecule } \text{C}_4\text{H}_2\text{O}_4} = 3.70 \times 10^{22} \text{ C atoms}$$

$$9.24 \times 10^{21} \text{ molecules } \text{C}_4\text{H}_2\text{O}_4 \times \frac{2 \text{ atoms H}}{1 \text{ molecule } \text{C}_4\text{H}_2\text{O}_4} = 1.85 \times 10^{22} \text{ H atoms}$$

$$9.24 \times 10^{21} \text{ molecules } \text{C}_4\text{H}_2\text{O}_4 \times \frac{4 \text{ atoms O}}{1 \text{ molecule } \text{C}_4\text{H}_2\text{O}_4} = 3.70 \times 10^{22} \text{ O atoms}$$

3.28 Strategy: We are asked to solve for the number of N, C, O, and H atoms in 1.68×10^4 g of urea. We cannot convert directly from grams urea to atoms. What unit do we need to obtain first before we can convert to atoms? How should Avogadro's number be used here? How many atoms of N, C, O, or H are in 1 molecule of urea?

Solution: Let's first calculate the number of N atoms in 1.68×10^4 g of urea. First, we must convert grams of urea to number of molecules of urea. This calculation is similar to Problem 3.26. The molecular formula of urea shows there are two N atoms in one urea molecule, which will allow us to convert to atoms of N. We need to perform three conversions:

grams of urea \rightarrow moles of urea \rightarrow molecules of urea \rightarrow atoms of N

The conversion factors needed for each step are: 1) the molar mass of urea, 2) Avogadro's number, and 3) the number of N atoms in 1 molecule of urea.

We complete the three conversions in one calculation.

$$\begin{aligned} \text{? atoms of N} &= (1.68 \times 10^4 \text{ g urea}) \times \frac{1 \text{ mol urea}}{60.06 \text{ g urea}} \times \frac{6.022 \times 10^{23} \text{ urea molecules}}{1 \text{ mol urea}} \times \frac{2 \text{ N atoms}}{1 \text{ molecule urea}} \\ &= 3.37 \times 10^{26} \text{ N atoms} \end{aligned}$$

The above method utilizes the ratio of molecules (urea) to atoms (nitrogen). We can also solve the problem by reading the formula as the ratio of moles of urea to moles of nitrogen by using the following conversions:

grams of urea \rightarrow moles of urea \rightarrow moles of N \rightarrow atoms of N

Try it.

Check: Does the answer seem reasonable? We have 1.68×10^4 g urea. How many atoms of N would 60.06 g of urea contain?

We could calculate the number of atoms of the remaining elements in the same manner, or we can use the atom ratios from the molecular formula. The carbon atom to nitrogen atom ratio in a urea molecule is 1:2, the oxygen atom to nitrogen atom ratio is 1:2, and the hydrogen atom to nitrogen atom ratio is 4:2.

$$\text{? atoms of C} = (3.37 \times 10^{26} \text{ N atoms}) \times \frac{1 \text{ C atom}}{2 \text{ N atoms}} = 1.69 \times 10^{26} \text{ C atoms}$$

$$\text{? atoms of O} = (3.37 \times 10^{26} \text{ N atoms}) \times \frac{1 \text{ O atom}}{2 \text{ N atoms}} = 1.69 \times 10^{26} \text{ O atoms}$$

$$\text{? atoms of H} = (3.37 \times 10^{26} \text{ N atoms}) \times \frac{4 \text{ H atoms}}{2 \text{ N atoms}} = 6.74 \times 10^{26} \text{ H atoms}$$

- 3.29 The molar mass of $C_{19}H_{38}O$ is 282.5 g.

$$1.0 \times 10^{-12} \cancel{\text{g}} \times \frac{1 \cancel{\text{mol}}}{282.5 \cancel{\text{g}}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \cancel{\text{mol}}} = 2.1 \times 10^9 \text{ molecules}$$

Notice that even though 1.0×10^{-12} g is an extremely small mass, it still is comprised of over a billion pheromone molecules!

- 3.30 Mass of water = $2.56 \cancel{\text{mL}} \times \frac{1.00 \text{ g}}{1.00 \cancel{\text{mL}}} = 2.56 \text{ g}$

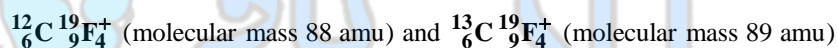
Molar mass of H_2O = $(16.00 \text{ g}) + 2(1.008 \text{ g}) = 18.02 \text{ g/mol}$

$$\begin{aligned} ? \text{ H}_2\text{O molecules} &= 2.56 \cancel{\text{g H}_2\text{O}} \times \frac{1 \cancel{\text{mol H}_2\text{O}}}{18.02 \cancel{\text{g H}_2\text{O}}} \times \frac{6.022 \times 10^{23} \text{ molecules H}_2\text{O}}{1 \cancel{\text{mol H}_2\text{O}}} \\ &= 8.56 \times 10^{22} \text{ molecules} \end{aligned}$$

- 3.31 Please see Section 3.4 of the text.

- 3.32 The relative abundance of each isotope can be determined from the area of the peak in the mass spectrum for that isotope.

- 3.33 Since there are only two isotopes of carbon, there are only two possibilities for CF_4^+ .



There would be two peaks in the mass spectrum.

- 3.34 Since there are two hydrogen isotopes, they can be paired in three ways: $^1\text{H}-^1\text{H}$, $^1\text{H}-^2\text{H}$, and $^2\text{H}-^2\text{H}$. There will then be three choices for each sulfur isotope. We can make a table showing all the possibilities (masses in amu):

	^{32}S	^{33}S	^{34}S	^{36}S
$^1\text{H}_2$	34	35	36	38
$^1\text{H } ^2\text{H}$	35	36	37	39
$^2\text{H}_2$	36	37	38	40

There will be **seven peaks** of the following mass numbers: 34, 35, 36, 37, 38, 39, and 40.

Very accurate (and expensive!) mass spectrometers can detect the mass difference between two ^1H and one ^2H . How many peaks would be detected in such a “high resolution” mass spectrum?

- 3.35 The percent composition is the percent by mass of each element in a compound. For NH_3 , we would speak of the mass % of nitrogen (N) and the mass % of hydrogen (H) in the compound. What percentage of the mass of a sample of ammonia is due to nitrogen and what percentage of the mass is due to hydrogen?
- 3.36 If you know the percent composition by mass of an unknown compound, you can determine its empirical formula.

3.37 An empirical formula tells us which elements are present and the simplest whole-number ratio of their atoms. A definition of empirical is something that is derived from experiment and observation rather than from theory. When chemists analyze an unknown compound, the first step is usually the determination of the compound's empirical formula. With additional information, it is possible to deduce the molecular formula.

3.38 The approximate molar mass.

3.39 Molar mass of $\text{SnO}_2 = (118.7 \text{ g}) + 2(16.00 \text{ g}) = 150.7 \text{ g}$

$$\% \text{Sn} = \frac{118.7 \text{ g/mol}}{150.7 \text{ g/mol}} \times 100\% = \mathbf{78.77\%}$$

$$\% \text{O} = \frac{(2)(16.00 \text{ g/mol})}{150.7 \text{ g/mol}} \times 100\% = \mathbf{21.23\%}$$

3.40 Strategy: Recall the procedure for calculating a percentage. Assume that we have 1 mole of CHCl_3 . The percent by mass of each element (C, H, and Cl) is given by the mass of that element in 1 mole of CHCl_3 divided by the molar mass of CHCl_3 , then multiplied by 100 to convert from a fractional number to a percentage.

Solution: The molar mass of $\text{CHCl}_3 = 12.01 \text{ g/mol} + 1.008 \text{ g/mol} + 3(35.45 \text{ g/mol}) = 119.4 \text{ g/mol}$. The percent by mass of each of the elements in CHCl_3 is calculated as follows:

$$\% \text{C} = \frac{12.01 \text{ g/mol}}{119.4 \text{ g/mol}} \times 100\% = \mathbf{10.06\%}$$

$$\% \text{H} = \frac{1.008 \text{ g/mol}}{119.4 \text{ g/mol}} \times 100\% = \mathbf{0.8442\%}$$

$$\% \text{Cl} = \frac{3(35.45) \text{ g/mol}}{119.4 \text{ g/mol}} \times 100\% = \mathbf{89.07\%}$$

Check: Do the percentages add to 100%? The sum of the percentages is $(10.06\% + 0.8442\% + 89.07\%) = 99.97\%$. The small discrepancy from 100% is due to the way we rounded off.

3.41 The molar mass of cinnamic alcohol, $\text{C}_9\text{H}_{10}\text{O}$, is 134.17 g/mol.

$$\text{(a)} \quad \% \text{C} = \frac{(9)(12.01 \text{ g/mol})}{134.17 \text{ g/mol}} \times 100\% = \mathbf{80.56\%}$$

$$\% \text{H} = \frac{(10)(1.008 \text{ g/mol})}{134.17 \text{ g/mol}} \times 100\% = \mathbf{7.513\%}$$

$$\% \text{O} = \frac{16.00 \text{ g/mol}}{134.17 \text{ g/mol}} \times 100\% = \mathbf{11.93\%}$$

$$\begin{aligned} \text{(b)} \quad & 0.469 \cancel{\text{g}} \text{C}_9\text{H}_{10}\text{O} \times \frac{1 \cancel{\text{mol}} \text{C}_9\text{H}_{10}\text{O}}{134.17 \cancel{\text{g}} \text{C}_9\text{H}_{10}\text{O}} \times \frac{6.022 \times 10^{23} \text{ molecules C}_9\text{H}_{10}\text{O}}{1 \cancel{\text{mol}} \text{C}_9\text{H}_{10}\text{O}} \\ &= \mathbf{2.11 \times 10^{21} \text{ molecules C}_9\text{H}_{10}\text{O}} \end{aligned}$$

3.42	<u>Compound</u>	<u>Molar mass (g)</u>	<u>N% by mass</u>
(a)	(NH ₂) ₂ CO	60.06	$\frac{2(14.01 \text{ g})}{60.06 \text{ g}} \times 100\% = 46.65\%$
(b)	NH ₄ NO ₃	80.05	$\frac{2(14.01 \text{ g})}{80.05 \text{ g}} \times 100\% = 35.00\%$
(c)	HNC(NH ₂) ₂	59.08	$\frac{3(14.01 \text{ g})}{59.08 \text{ g}} \times 100\% = 71.14\%$
(d)	NH ₃	17.03	$\frac{14.01 \text{ g}}{17.03 \text{ g}} \times 100\% = 82.27\%$

Ammonia, NH₃, is the richest source of nitrogen on a mass percentage basis.

3.43 Assume you have exactly 100 g of substance.

$$n_{\text{C}} = 44.4 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.70 \text{ mol C}$$

$$n_{\text{H}} = 6.21 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 6.16 \text{ mol H}$$

$$n_{\text{S}} = 39.5 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 1.23 \text{ mol S}$$

$$n_{\text{O}} = 9.86 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.616 \text{ mol O}$$

Thus, we arrive at the formula C_{3.70}H_{6.16}S_{1.23}O_{0.616}. Dividing by the smallest number of moles (0.616 mole) gives the empirical formula, **C₆H₁₀S₂O**.

To determine the molecular formula, divide the molar mass by the empirical mass.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{162 \text{ g}}{162.3 \text{ g}} \approx 1$$

Hence, the molecular formula and the empirical formula are the same, **C₆H₁₀S₂O**.

3.44 METHOD 1:

Step 1: Assume you have exactly 100 g of substance. 100 g is a convenient amount, because all the percentages sum to 100%. The percentage of oxygen is found by difference:

$$100\% - (19.8\% + 2.50\% + 11.6\%) = 66.1\%$$

In 100 g of PAN there will be 19.8 g C, 2.50 g H, 11.6 g N, and 66.1 g O.

Step 2: Calculate the number of moles of each element in the compound. Remember, an *empirical formula* tells us which elements are present and the simplest whole-number ratio of their atoms. This ratio is also a mole ratio. Use the molar masses of these elements as conversion factors to convert to moles.

$$n_{\text{C}} = 19.8 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 1.65 \text{ mol C}$$

$$n_{\text{H}} = 2.50 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 2.48 \text{ mol H}$$

$$n_{\text{N}} = 11.6 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.828 \text{ mol N}$$

$$n_{\text{O}} = 66.1 \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 4.13 \text{ mol O}$$

Step 3: Try to convert to whole numbers by dividing all the subscripts by the smallest subscript. The formula is $\text{C}_{1.65}\text{H}_{2.48}\text{N}_{0.828}\text{O}_{4.13}$. Dividing the subscripts by 0.828 gives the empirical formula, **$\text{C}_2\text{H}_3\text{NO}_5$** .

To determine the molecular formula, remember that the molar mass/empirical mass will be an integer greater than or equal to one.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} \geq 1 \text{ (integer values)}$$

In this case,

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{120 \text{ g}}{121.05 \text{ g}} \approx 1$$

Hence, the molecular formula and the empirical formula are the same, **$\text{C}_2\text{H}_3\text{NO}_5$** .

METHOD 2:

Step 1: Multiply the mass % (converted to a decimal) of each element by the molar mass to convert to grams of each element. Then, use the molar mass to convert to moles of each element.

$$\begin{aligned} n_{\text{C}} &= (0.198) \times (120 \cancel{\text{g}}) \times \frac{1 \text{ mol C}}{12.01 \cancel{\text{g C}}} = 1.98 \text{ mol C} \approx \mathbf{2 \text{ mol C}} \\ n_{\text{H}} &= (0.0250) \times (120 \cancel{\text{g}}) \times \frac{1 \text{ mol H}}{1.008 \cancel{\text{g H}}} = 2.98 \text{ mol H} \approx \mathbf{3 \text{ mol H}} \\ n_{\text{N}} &= (0.116) \times (120 \cancel{\text{g}}) \times \frac{1 \text{ mol N}}{14.01 \cancel{\text{g N}}} = 0.994 \text{ mol N} \approx \mathbf{1 \text{ mol N}} \\ n_{\text{O}} &= (0.661) \times (120 \cancel{\text{g}}) \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 4.96 \text{ mol O} \approx \mathbf{5 \text{ mol O}} \end{aligned}$$

Step 2: Since we used the molar mass to calculate the moles of each element present in the compound, this method directly gives the molecular formula. The formula is **$\text{C}_2\text{H}_3\text{NO}_5$** .

Step 3: Try to reduce the molecular formula to a simpler whole number ratio to determine the empirical formula. The formula is already in its simplest whole number ratio. The molecular and empirical formulas are the same. The empirical formula is **$\text{C}_2\text{H}_3\text{NO}_5$** .

$$\mathbf{3.45} \quad 24.6 \cancel{\text{g Fe}_2\text{O}_3} \times \frac{1 \cancel{\text{mol Fe}_2\text{O}_3}}{159.7 \cancel{\text{g Fe}_2\text{O}_3}} \times \frac{2 \text{ mol Fe}}{1 \cancel{\text{mol Fe}_2\text{O}_3}} = \mathbf{0.308 \text{ mol Fe}}$$

3.46 Using unit factors we convert:

$$\text{g of Hg} \rightarrow \text{mol Hg} \rightarrow \text{mol S} \rightarrow \text{g S}$$

$$\mathbf{? \text{ g S}} = 246 \cancel{\text{g Hg}} \times \frac{1 \cancel{\text{mol Hg}}}{200.6 \cancel{\text{g Hg}}} \times \frac{1 \cancel{\text{mol S}}}{1 \cancel{\text{mol Hg}}} \times \frac{32.07 \text{ g S}}{1 \cancel{\text{mol S}}} = \mathbf{39.3 \text{ g S}}$$

3.47 The balanced equation is: $2\text{Al}(s) + 3\text{I}_2(s) \longrightarrow 2\text{AlI}_3(s)$

Using unit factors, we convert: g of Al \rightarrow mol of Al \rightarrow mol of I_2 \rightarrow g of I_2

$$20.4 \cancel{\text{g Al}} \times \frac{1 \cancel{\text{mol Al}}}{26.98 \cancel{\text{g Al}}} \times \frac{3 \cancel{\text{mol I}_2}}{2 \cancel{\text{mol Al}}} \times \frac{253.8 \text{ g I}_2}{1 \cancel{\text{mol I}_2}} = \mathbf{288 \text{ g I}_2}$$

3.48 Strategy: Tin(II) fluoride is composed of Sn and F. The mass due to F is based on its percentage by mass in the compound. How do we calculate mass percent of an element?

Solution: First, we must find the mass % of fluorine in SnF_2 . Then, we convert this percentage to a fraction and multiply by the mass of the compound (24.6 g), to find the mass of fluorine in 24.6 g of SnF_2 .

The percent by mass of fluorine in tin(II) fluoride, is calculated as follows:

$$\begin{aligned} \text{mass \% F} &= \frac{\text{mass of F in 1 mol SnF}_2}{\text{molar mass of SnF}_2} \times 100\% \\ &= \frac{2(19.00 \text{ g})}{156.7 \text{ g}} \times 100\% = 24.25\% \text{ F} \end{aligned}$$

Converting this percentage to a fraction, we obtain $24.25/100 = 0.2425$.

Next, multiply the fraction by the total mass of the compound.

$$\mathbf{? \text{ g F in } 24.6 \text{ g SnF}_2 = (0.2425)(24.6 \text{ g}) = \mathbf{5.97 \text{ g F}}}$$

Check: As a ball-park estimate, note that the mass percent of F is roughly 25 percent, so that a quarter of the mass should be F. One quarter of approximately 24 g is 6 g, which is close to the answer.

Note: This problem could have been worked in a manner similar to Problem 3.46. You could complete the following conversions:

$$\text{g of SnF}_2 \rightarrow \text{mol of SnF}_2 \rightarrow \text{mol of F} \rightarrow \text{g of F}$$

3.49 In each case, assume 100 g of compound.

(a) $2.1 \cancel{\text{g H}} \times \frac{1 \text{ mol H}}{1.008 \cancel{\text{g H}}} = 2.1 \text{ mol H}$

$$65.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 4.08 \text{ mol O}$$

$$32.6 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 1.02 \text{ mol S}$$

This gives the formula $\text{H}_{2.1}\text{S}_{1.02}\text{O}_{4.08}$. Dividing by 1.02 gives the empirical formula, $\mathbf{H_2SO_4}$.

(b) $20.2 \cancel{\text{g Al}} \times \frac{1 \text{ mol Al}}{26.98 \cancel{\text{g Al}}} = 0.749 \text{ mol Al}$

$$79.8 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 2.25 \text{ mol Cl}$$

This gives the formula, $\text{Al}_{0.749}\text{Cl}_{2.25}$. Dividing by 0.749 gives the empirical formula, $\mathbf{AlCl_3}$.

3.50 (a)

Strategy: In a chemical formula, the subscripts represent the ratio of the number of moles of each element that combine to form the compound. Therefore, we need to convert from mass percent to moles in order to determine the empirical formula. If we assume an exactly 100 g sample of the compound, do we know the mass of each element in the compound? How do we then convert from grams to moles?

Solution: If we have 100 g of the compound, then each percentage can be converted directly to grams. In this sample, there will be 40.1 g of C, 6.6 g of H, and 53.3 g of O. Because the subscripts in the formula represent a mole ratio, we need to convert the grams of each element to moles. The conversion factor needed is the molar mass of each element. Let n represent the number of moles of each element so that

$$n_{\text{C}} = 40.1 \cancel{\text{g C}} \times \frac{1 \text{ mol C}}{12.01 \cancel{\text{g C}}} = 3.34 \text{ mol C}$$

$$n_{\text{H}} = 6.6 \cancel{\text{g H}} \times \frac{1 \text{ mol H}}{1.008 \cancel{\text{g H}}} = 6.5 \text{ mol H}$$

$$n_{\text{O}} = 53.3 \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 3.33 \text{ mol O}$$

Thus, we arrive at the formula $\text{C}_{3.34}\text{H}_{6.5}\text{O}_{3.33}$, which gives the identity and the mole ratios of atoms present. However, chemical formulas are written with whole numbers. Try to convert to whole numbers by dividing all the subscripts by the smallest subscript (3.33).

$$\text{C: } \frac{3.34}{3.33} \approx 1 \quad \text{H: } \frac{6.5}{3.33} \approx 2 \quad \text{O: } \frac{3.33}{3.33} = 1$$

This gives the empirical formula, **CH₂O**.

Check: Are the subscripts in CH₂O reduced to the smallest whole numbers?

(b) Following the same procedure as part (a), we find:

$$n_{\text{C}} = 18.4 \cancel{\text{g C}} \times \frac{1 \text{ mol C}}{12.01 \cancel{\text{g C}}} = 1.53 \text{ mol C}$$

$$n_{\text{N}} = 21.5 \cancel{\text{g N}} \times \frac{1 \text{ mol N}}{14.01 \cancel{\text{g N}}} = 1.53 \text{ mol N}$$

$$n_{\text{K}} = 60.1 \cancel{\text{g K}} \times \frac{1 \text{ mol K}}{39.10 \cancel{\text{g K}}} = 1.54 \text{ mol K}$$

Dividing by the smallest number of moles (1.53 mol) gives the empirical formula, **KCN**.

3.51 The molar mass of CaSiO₃ is 116.17 g/mol.

$$\% \text{Ca} = \frac{40.08 \text{ g}}{116.17 \text{ g}} \times 100\% = \mathbf{34.50\%}$$

$$\% \text{Si} = \frac{28.09 \text{ g}}{116.17 \text{ g}} \times 100\% = \mathbf{24.18\%}$$

$$\% \text{O} = \frac{(3)(16.00 \text{ g})}{116.17 \text{ g}} \times 100\% = \mathbf{41.32\%}$$

Check to see that the percentages sum to 100%. (34.50% + 24.18% + 41.32%) = 100.00%

- 3.52** The empirical molar mass of CH is approximately 13.02 g. Let's compare this to the molar mass to determine the molecular formula.

Recall that the molar mass divided by the empirical mass will be an integer greater than or equal to one.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} \geq 1 \text{ (integer values)}$$

In this case,

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{78 \text{ g}}{13.02 \text{ g}} \approx 6$$

Thus, there are six CH units in each molecule of the compound, so the molecular formula is (CH)₆, or **C₆H₆**.

- 3.53** Find the molar mass corresponding to each formula.

$$\text{For C}_4\text{H}_5\text{N}_2\text{O:} \quad 4(12.01 \text{ g}) + 5(1.008 \text{ g}) + 2(14.01 \text{ g}) + (16.00 \text{ g}) = 97.10 \text{ g}$$

$$\text{For C}_8\text{H}_{10}\text{N}_4\text{O}_2: \quad 8(12.01 \text{ g}) + 10(1.008 \text{ g}) + 4(14.01 \text{ g}) + 2(16.00 \text{ g}) = 194.20 \text{ g}$$

The molecular formula is **C₈H₁₀N₄O₂**.

3.54 METHOD 1:

Step 1: Assume you have exactly 100 g of substance. 100 g is a convenient amount, because all the percentages sum to 100%. In 100 g of MSG there will be 35.51 g C, 4.77 g H, 37.85 g O, 8.29 g N, and 13.60 g Na.

Step 2: Calculate the number of moles of each element in the compound. Remember, an *empirical formula* tells us which elements are present and the simplest whole-number ratio of their atoms. This ratio is also a mole ratio. Let n_{C} , n_{H} , n_{O} , n_{N} , and n_{Na} be the number of moles of elements present. Use the molar masses of these elements as conversion factors to convert to moles.

$$n_{\text{C}} = 35.51 \cancel{\text{g C}} \times \frac{1 \text{ mol C}}{12.01 \cancel{\text{g C}}} = 2.957 \text{ mol C}$$

$$n_{\text{H}} = 4.77 \cancel{\text{g H}} \times \frac{1 \text{ mol H}}{1.008 \cancel{\text{g H}}} = 4.73 \text{ mol H}$$

$$n_{\text{O}} = 37.85 \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 2.366 \text{ mol O}$$

$$n_{\text{N}} = 8.29 \cancel{\text{g N}} \times \frac{1 \text{ mol N}}{14.01 \cancel{\text{g N}}} = 0.592 \text{ mol N}$$

$$n_{\text{Na}} = 13.60 \cancel{\text{g Na}} \times \frac{1 \text{ mol Na}}{22.99 \cancel{\text{g Na}}} = 0.5916 \text{ mol Na}$$

Thus, we arrive at the formula C_{2.957}H_{4.73}O_{2.366}N_{0.592}Na_{0.5916}, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers.

Step 3: Try to convert to whole numbers by dividing all the subscripts by the smallest subscript.

$$\begin{array}{lll} \text{C: } \frac{2.957}{0.5916} = 4.998 \approx 5 & \text{H: } \frac{4.73}{0.5916} = 8.00 & \text{O: } \frac{2.366}{0.5916} = 3.999 \approx 4 \\ \text{N: } \frac{0.592}{0.5916} = 1.00 & \text{Na: } \frac{0.5916}{0.5916} = 1 & \end{array}$$

This gives us the empirical formula for MSG, C₅H₈O₄NNa.

To determine the molecular formula, remember that the molar mass/empirical mass will be an integer greater than or equal to one.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} \geq 1 \text{ (integer values)}$$

In this case,

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{169 \text{ g}}{169.11 \text{ g}} \approx 1$$

Hence, the molecular formula and the empirical formula are the same, **C₅H₈O₄NNa**. It should come as no surprise that the empirical and molecular formulas are the same since MSG stands for *monosodium*glutamate.

METHOD 2:

Step 1: Multiply the mass % (converted to a decimal) of each element by the molar mass to convert to grams of each element. Then, use the molar mass to convert to moles of each element.

$$n_{\text{C}} = (0.3551) \times (169 \text{ g}) \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 5.00 \text{ mol C}$$

$$n_{\text{H}} = (0.0477) \times (169 \text{ g}) \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 8.00 \text{ mol H}$$

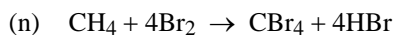
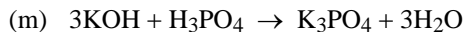
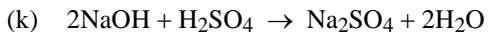
$$n_{\text{O}} = (0.3785) \times (169 \text{ g}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 4.00 \text{ mol O}$$

$$n_{\text{N}} = (0.0829) \times (169 \text{ g}) \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.00 \text{ mol N}$$

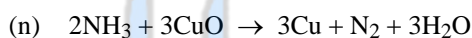
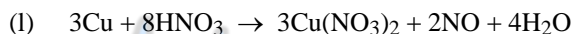
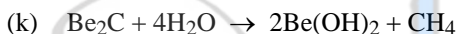
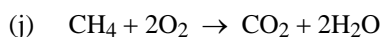
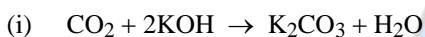
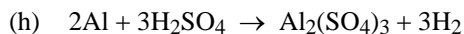
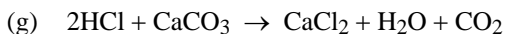
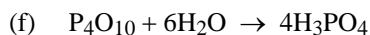
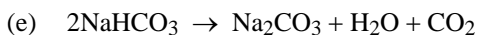
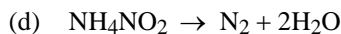
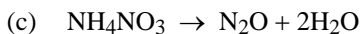
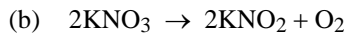
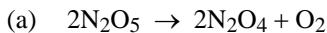
$$n_{\text{Na}} = (0.1360) \times (169 \text{ g}) \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 1.00 \text{ mol Na}$$

Step 2: Since we used the molar mass to calculate the moles of each element present in the compound, this method directly gives the molecular formula. The formula is **C₅H₈O₄NNa**.

- 3.55** A chemical reaction is a process in which a substance (or substances) is changed into one or more new substances. In this reaction, hydrogen and oxygen, the reactants, are changed into the product, water.
- 3.56** A chemical equation uses chemical symbols to show what happens during a chemical reaction. A chemical reaction is a process in which a substance (or substances) is changed into one or more new substances.
- 3.57** To accurately show what happens during a chemical reaction, a chemical equation must be balanced. The Law of Conservation of Mass is obeyed by a balanced chemical equation.
- 3.58** (g), (l), (s), (aq).
- 3.59** The balanced equations are as follows:
- | | |
|----------------------------------------------------------------------------|--------------------------------------------------------------------------|
| (a) $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ | (f) $2\text{O}_3 \rightarrow 3\text{O}_2$ |
| (b) $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ | (g) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ |
| (c) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ | (h) $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ |
| (d) $2\text{K} + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2$ | (i) $\text{Zn} + 2\text{AgCl} \rightarrow \text{ZnCl}_2 + 2\text{Ag}$ |
| (e) $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ | (j) $\text{S}_8 + 8\text{O}_2 \rightarrow 8\text{SO}_2$ |



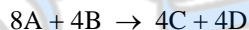
3.60 The balanced equations are as follows:



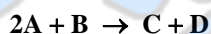
3.61 Stoichiometry is the quantitative study of reactants and products in a chemical reaction; therefore, it is based on the Law of Conservation of Mass. A balanced chemical equation is essential to solving stoichiometric problems so that the “mole method” can be applied correctly.

3.62 The steps of the mole method are shown in Figure 3.8 of the text.

3.63 On the reactants side there are 8 A atoms and 4 B atoms. On the products side, there are 4 C atoms and 4 D atoms. Writing an equation,

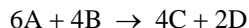


Chemical equations are typically written with the smallest set of whole number coefficients. Dividing the equation by four gives,

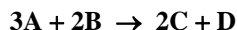


The correct answer is choice (c).

3.64 On the reactants side there are 6 A atoms and 4 B atoms. On the products side, there are 4 C atoms and 2 D atoms. Writing an equation,



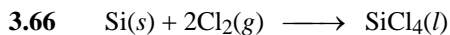
Chemical equations are typically written with the smallest set of whole number coefficients. Dividing the equation by two gives,



The correct answer is choice (d).

3.65 The mole ratio from the balanced equation is 2 moles CO_2 : 2 moles CO .

$$3.60 \cancel{\text{mol CO}} \times \frac{2 \text{ mol CO}_2}{2 \cancel{\text{mol CO}}} = 3.60 \text{ mol CO}_2$$



Strategy: Looking at the balanced equation, how do we compare the amounts of Cl_2 and SiCl_4 ? We can compare them based on the mole ratio from the balanced equation.

Solution: Because the balanced equation is given in the problem, the mole ratio between Cl_2 and SiCl_4 is known: 2 moles Cl_2 *f* 1 mole SiCl_4 . From this relationship, we have two conversion factors.

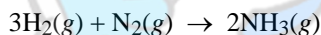
$$\frac{2 \text{ mol Cl}_2}{1 \text{ mol SiCl}_4} \quad \text{and} \quad \frac{1 \text{ mol SiCl}_4}{2 \text{ mol Cl}_2}$$

Which conversion factor is needed to convert from moles of SiCl_4 to moles of Cl_2 ? The conversion factor on the left is the correct one. Moles of SiCl_4 will cancel, leaving units of "mol Cl_2 " for the answer. We calculate moles of Cl_2 reacted as follows:

$$\text{? mol Cl}_2 \text{ reacted} = 0.507 \cancel{\text{ mol SiCl}_4} \times \frac{2 \text{ mol Cl}_2}{1 \cancel{\text{ mol SiCl}_4}} = \mathbf{1.01 \text{ mol Cl}_2}$$

Check: Does the answer seem reasonable? Should the moles of Cl_2 reacted be *double* the moles of SiCl_4 produced?

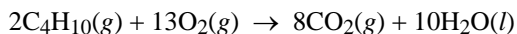
- 3.67** Starting with the amount of ammonia produced (6.0 moles), we can use the mole ratio from the balanced equation to calculate the moles of H_2 and N_2 that reacted to produce 6.0 moles of NH_3 .



$$\text{? mol H}_2 = 6.0 \cancel{\text{ mol NH}_3} \times \frac{3 \text{ mol H}_2}{2 \cancel{\text{ mol NH}_3}} = \mathbf{9.0 \text{ mol H}_2}$$

$$\text{? mol N}_2 = 6.0 \cancel{\text{ mol NH}_3} \times \frac{1 \text{ mol N}_2}{2 \cancel{\text{ mol NH}_3}} = \mathbf{3.0 \text{ mol N}_2}$$

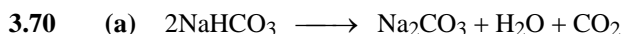
- 3.68** Starting with the 5.0 moles of C_4H_{10} , we can use the mole ratio from the balanced equation to calculate the moles of CO_2 formed.



$$\text{? mol CO}_2 = 5.0 \cancel{\text{ mol C}_4\text{H}_{10}} \times \frac{8 \text{ mol CO}_2}{2 \cancel{\text{ mol C}_4\text{H}_{10}}} = 20 \text{ mol CO}_2 = \mathbf{2.0 \times 10^1 \text{ mol CO}_2}$$

- 3.69** It is convenient to use the unit ton-mol in this problem. We normally use a g-mol. 1 g-mol SO_2 has a mass of 64.07 g. In a similar manner, 1 ton-mol of SO_2 has a mass of 64.07 tons. We need to complete the following conversions: tons $\text{SO}_2 \rightarrow$ ton-mol $\text{SO}_2 \rightarrow$ ton-mol $\text{S} \rightarrow$ ton S .

$$(2.6 \times 10^7 \cancel{\text{ tons SO}_2}) \times \frac{1 \cancel{\text{ ton-mol SO}_2}}{64.07 \cancel{\text{ ton SO}_2}} \times \frac{1 \cancel{\text{ ton-mol S}}}{1 \cancel{\text{ ton-mol SO}_2}} \times \frac{32.07 \text{ ton S}}{1 \cancel{\text{ ton-mol S}}} = \mathbf{1.3 \times 10^7 \text{ tons S}}$$



- (b) Molar mass $\text{NaHCO}_3 = 22.99 \text{ g} + 1.008 \text{ g} + 12.01 \text{ g} + 3(16.00 \text{ g}) = 84.01 \text{ g}$
 Molar mass $\text{CO}_2 = 12.01 \text{ g} + 2(16.00 \text{ g}) = 44.01 \text{ g}$

The balanced equation shows one mole of CO_2 formed from two moles of NaHCO_3 .

$$\begin{aligned} \text{mass NaHCO}_3 &= 20.5 \cancel{\text{g CO}_2} \times \frac{1 \cancel{\text{mol CO}_2}}{44.01 \cancel{\text{g CO}_2}} \times \frac{2 \cancel{\text{mol NaHCO}_3}}{1 \cancel{\text{mol CO}_2}} \times \frac{84.01 \text{ g NaHCO}_3}{1 \cancel{\text{mol NaHCO}_3}} \\ &= \mathbf{78.3 \text{ g NaHCO}_3} \end{aligned}$$

- 3.71 The balanced equation shows a mole ratio of 1 mole HCN : 1 mole KCN .

$$0.140 \cancel{\text{g KCN}} \times \frac{1 \cancel{\text{mol KCN}}}{65.12 \cancel{\text{g KCN}}} \times \frac{1 \cancel{\text{mol HCN}}}{1 \cancel{\text{mol KCN}}} \times \frac{27.03 \text{ g HCN}}{1 \cancel{\text{mol HCN}}} = \mathbf{0.0581 \text{ g HCN}}$$

- 3.72 $\text{C}_6\text{H}_{12}\text{O}_6 \longrightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$
 glucose ethanol

Strategy: We compare glucose and ethanol based on the *mole ratio* in the balanced equation. Before we can determine moles of ethanol produced, we need to convert to moles of glucose. What conversion factor is needed to convert from grams of glucose to moles of glucose? Once moles of ethanol are obtained, another conversion factor is needed to convert from moles of ethanol to grams of ethanol.

Solution: The molar mass of glucose will allow us to convert from grams of glucose to moles of glucose. The molar mass of glucose = $6(12.01 \text{ g}) + 12(1.008 \text{ g}) + 6(16.00 \text{ g}) = 180.16 \text{ g}$. The balanced equation is given, so the mole ratio between glucose and ethanol is known; that is 1 mole glucose *f* 2 moles ethanol. Finally, the molar mass of ethanol will convert moles of ethanol to grams of ethanol. This sequence of three conversions is summarized as follows:

grams of glucose \rightarrow moles of glucose \rightarrow moles of ethanol \rightarrow grams of ethanol

$$\begin{aligned} ? \text{ g C}_2\text{H}_5\text{OH} &= 500.4 \cancel{\text{g C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6}}{180.16 \cancel{\text{g C}_6\text{H}_{12}\text{O}_6}} \times \frac{2 \cancel{\text{mol C}_2\text{H}_5\text{OH}}}{1 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6}} \times \frac{46.07 \text{ g C}_2\text{H}_5\text{OH}}{1 \cancel{\text{mol C}_2\text{H}_5\text{OH}}} \\ &= \mathbf{255.9 \text{ g C}_2\text{H}_5\text{OH}} \end{aligned}$$

Check: Does the answer seem reasonable? Should the mass of ethanol produced be approximately half the mass of glucose reacted? Twice as many moles of ethanol are produced compared to the moles of glucose reacted, but the molar mass of ethanol is about one-fourth that of glucose.

The liters of ethanol can be calculated from the density and the mass of ethanol.

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

$$\text{Volume of ethanol obtained} = \frac{255.9 \cancel{\text{g}}}{0.789 \cancel{\text{g/mL}}} = 324 \text{ mL} = \mathbf{0.324 \text{ L}}$$

- 3.73 The mass of water lost is just the difference between the initial and final masses.

$$\text{Mass H}_2\text{O lost} = 15.01 \text{ g} - 9.60 \text{ g} = 5.41 \text{ g}$$

$$\text{moles of H}_2\text{O} = 5.41 \cancel{\text{g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \cancel{\text{g H}_2\text{O}}} = \mathbf{0.300 \text{ mol H}_2\text{O}}$$

- 3.74** The balanced equation shows that eight moles of KCN are needed to combine with four moles of Au.

$$? \text{ mol KCN} = 29.0 \cancel{\text{ g Au}} \times \frac{1 \cancel{\text{ mol Au}}}{197.0 \cancel{\text{ g Au}}} \times \frac{8 \text{ mol KCN}}{4 \cancel{\text{ mol Au}}} = \mathbf{0.294 \text{ mol KCN}}$$

- 3.75** The balanced equation is: $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$

$$1.0 \cancel{\text{ kg CaCO}_3} \times \frac{1000 \cancel{\text{ g}}}{1 \cancel{\text{ kg}}} \times \frac{1 \cancel{\text{ mol CaCO}_3}}{100.09 \cancel{\text{ g CaCO}_3}} \times \frac{1 \cancel{\text{ mol CaO}}}{1 \cancel{\text{ mol CaCO}_3}} \times \frac{56.08 \text{ g CaO}}{1 \cancel{\text{ mol CaO}}} = \mathbf{5.6 \times 10^2 \text{ g CaO}}$$

- 3.76** (a) $\text{NH}_4\text{NO}_3(s) \longrightarrow \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g)$

- (b) Starting with moles of NH_4NO_3 , we can use the mole ratio from the balanced equation to find moles of N_2O . Once we have moles of N_2O , we can use the molar mass of N_2O to convert to grams of N_2O . Combining the two conversions into one calculation, we have:

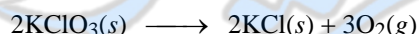
$$\text{mol NH}_4\text{NO}_3 \rightarrow \text{mol N}_2\text{O} \rightarrow \text{g N}_2\text{O}$$

$$? \text{ g N}_2\text{O} = 0.46 \cancel{\text{ mol NH}_4\text{NO}_3} \times \frac{1 \cancel{\text{ mol N}_2\text{O}}}{1 \cancel{\text{ mol NH}_4\text{NO}_3}} \times \frac{44.02 \text{ g N}_2\text{O}}{1 \cancel{\text{ mol N}_2\text{O}}} = \mathbf{2.0 \times 10^1 \text{ g N}_2\text{O}}$$

- 3.77** The quantity of ammonia needed is:

$$1.00 \times 10^8 \cancel{\text{ g (NH}_4)_2\text{SO}_4} \times \frac{1 \cancel{\text{ mol (NH}_4)_2\text{SO}_4}}{132.15 \cancel{\text{ g (NH}_4)_2\text{SO}_4}} \times \frac{2 \cancel{\text{ mol NH}_3}}{1 \cancel{\text{ mol (NH}_4)_2\text{SO}_4}} \times \frac{17.03 \cancel{\text{ g NH}_3}}{1 \cancel{\text{ mol NH}_3}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{ g}}} \\ = \mathbf{2.58 \times 10^4 \text{ kg NH}_3}$$

- 3.78** The balanced equation for the decomposition is :



$$? \text{ g O}_2 = 46.0 \cancel{\text{ g KClO}_3} \times \frac{1 \cancel{\text{ mol KClO}_3}}{122.55 \cancel{\text{ g KClO}_3}} \times \frac{3 \cancel{\text{ mol O}_2}}{2 \cancel{\text{ mol KClO}_3}} \times \frac{32.00 \text{ g O}_2}{1 \cancel{\text{ mol O}_2}} = \mathbf{18.0 \text{ g O}_2}$$

- 3.79** The reactant used up first in a reaction is called the limiting reagent. Excess reagents are the reactants present in quantities greater than necessary to react with the quantity of the limiting reagent. The maximum amount of product formed depends on how much of the limiting reagent is present. When this reactant is used up, no more product can be formed. In a reaction with one reactant, the one reactant is by definition the limiting reagent.

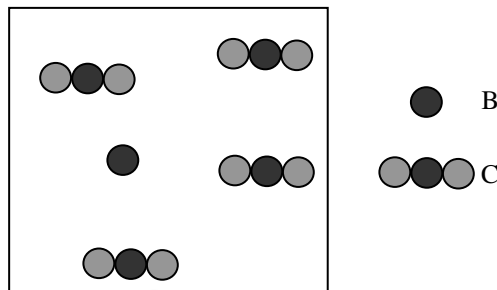
- 3.80** If you are making sandwiches and have four pieces of bread, you can only make two sandwiches, no matter how much mayonnaise, mustard, sandwich meat, etc. that you have. The bread limits the number of sandwiches that you can make.

- 3.81** $2\text{A} + \text{B} \rightarrow \text{C}$

- (a) The number of B atoms shown in the diagram is 5. The balanced equation shows 2 moles A f 1 mole B. Therefore, we need 10 atoms of A to react completely with 5 atoms of B. There are only 8 atoms of A present in the diagram. There are not enough atoms of A to react completely with B.

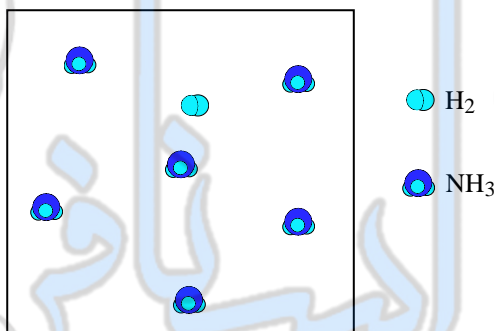
A is the limiting reagent.

- (b) There are 8 atoms of A. Since the mole ratio between A and B is 2:1, 4 atoms of B will react with 8 atoms of A, leaving 1 atom of B in excess. The mole ratio between A and C is also 2:1. When 8 atoms of A react, 4 molecules of C will be produced.

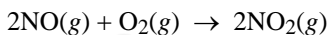


3.82 $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

9 moles of H_2 will react with 3 moles of N_2 , leaving **1 mole of H_2 in excess**. The mole ratio between N_2 and NH_3 is 1:2. When 3 moles of N_2 react, **6 moles of NH_3 will be produced**.



3.83 This is a limiting reagent problem. Let's calculate the moles of NO_2 produced assuming complete reaction for each reactant.



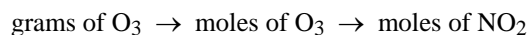
$$0.886 \cancel{\text{mol NO}} \times \frac{2 \text{ mol NO}_2}{2 \cancel{\text{mol NO}}} = 0.886 \text{ mol NO}_2$$

$$0.503 \cancel{\text{mol O}_2} \times \frac{2 \text{ mol NO}_2}{1 \cancel{\text{mol O}_2}} = 1.01 \text{ mol NO}_2$$

NO is the **limiting reagent**; it limits the amount of product produced. The amount of product produced is **0.886 mole NO_2** .

3.84 Strategy: Note that this reaction gives the amounts of both reactants, so it is likely to be a limiting reagent problem. The reactant that produces fewer moles of product is the limiting reagent because it limits the amount of product that can be produced. How do we convert from the amount of reactant to amount of product? Perform this calculation for each reactant, then compare the moles of product, NO_2 , formed by the given amounts of O_3 and NO to determine which reactant is the limiting reagent.

Solution: We carry out two separate calculations. First, starting with 0.740 g O_3 , we calculate the number of moles of NO_2 that could be produced if all the O_3 reacted. We complete the following conversions.



Combining these two conversions into one calculation, we write

$$? \text{ mol NO}_2 = 0.740 \cancel{\text{g O}_3} \times \frac{1 \cancel{\text{mol O}_3}}{48.00 \cancel{\text{g O}_3}} \times \frac{1 \text{ mol NO}_2}{1 \cancel{\text{mol O}_3}} = 0.0154 \text{ mol NO}_2$$

Second, starting with 0.670 g of NO, we complete similar conversions.

grams of NO \rightarrow moles of NO \rightarrow moles of NO₂

Combining these two conversions into one calculation, we write

$$? \text{ mol NO}_2 = 0.670 \cancel{\text{g NO}} \times \frac{1 \cancel{\text{mol NO}}}{30.01 \cancel{\text{g NO}}} \times \frac{1 \text{ mol NO}_2}{1 \cancel{\text{mol NO}}} = 0.0223 \text{ mol NO}_2$$

The initial amount of O₃ limits the amount of product that can be formed; therefore, it is the **limiting reagent**.

The problem asks for grams of NO₂ produced. We already know the moles of NO₂ produced, 0.0154 mole. Use the molar mass of NO₂ as a conversion factor to convert to grams (Molar mass NO₂ = 46.01 g).

$$? \text{ g NO}_2 = 0.0154 \cancel{\text{mol NO}_2} \times \frac{46.01 \text{ g NO}_2}{1 \cancel{\text{mol NO}_2}} = \mathbf{0.709 \text{ g NO}_2}$$

Check: Does your answer seem reasonable? 0.0154 mole of product is formed. What is the mass of 1 mole of NO₂?

Strategy: Working backwards, we can determine the amount of NO that reacted to produce 0.0154 mole of NO₂. The amount of NO left over is the difference between the initial amount and the amount reacted.

Solution: Starting with 0.0154 mole of NO₂, we can determine the moles of NO that reacted using the mole ratio from the balanced equation. We can calculate the initial moles of NO starting with 0.670 g and using molar mass of NO as a conversion factor.

$$\text{mol NO reacted} = 0.0154 \cancel{\text{mol NO}_2} \times \frac{1 \text{ mol NO}}{1 \cancel{\text{mol NO}_2}} = 0.0154 \text{ mol NO}$$

$$\text{mol NO initial} = 0.670 \cancel{\text{g NO}} \times \frac{1 \text{ mol NO}}{30.01 \cancel{\text{g NO}}} = 0.0223 \text{ mol NO}$$

$$\text{mol NO remaining} = \text{mol NO initial} - \text{mol NO reacted.}$$

$$\mathbf{\text{mol NO remaining} = 0.0223 \text{ mol NO} - 0.0154 \text{ mol NO} = \mathbf{0.0069 \text{ mol NO}}}$$

3.85 (a) The balanced equation is: $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$

(b) The balanced equation shows a mole ratio of 3 moles CO₂ : 1 mole C₃H₈. The mass of CO₂ produced is:

$$3.65 \cancel{\text{mol C}_3\text{H}_8} \times \frac{3 \cancel{\text{mol CO}_2}}{1 \cancel{\text{mol C}_3\text{H}_8}} \times \frac{44.01 \text{ g CO}_2}{1 \cancel{\text{mol CO}_2}} = \mathbf{482 \text{ g CO}_2}$$

3.86 This is a limiting reagent problem. Let's calculate the moles of Cl₂ produced assuming complete reaction for each reactant.

$$0.86 \cancel{\text{mol MnO}_2} \times \frac{1 \text{ mol Cl}_2}{1 \cancel{\text{mol MnO}_2}} = 0.86 \text{ mol Cl}_2$$

$$48.2 \cancel{\text{g HCl}} \times \frac{1 \cancel{\text{mol HCl}}}{36.46 \cancel{\text{g HCl}}} \times \frac{1 \text{ mol Cl}_2}{4 \cancel{\text{mol HCl}}} = 0.330 \text{ mol Cl}_2$$

HCl is the limiting reagent; it limits the amount of product produced. It will be used up first. The amount of product produced is 0.330 mole Cl_2 . Let's convert this to grams.

$$? \text{ g Cl}_2 = 0.330 \cancel{\text{mol Cl}_2} \times \frac{70.90 \text{ g Cl}_2}{1 \cancel{\text{mol Cl}_2}} = \mathbf{23.4 \text{ g Cl}_2}$$

3.87 The theoretical yield of a reaction is the amount of product that would result if all the limiting reagent reacted. When the limiting reactant is used up, no more product can be formed.

3.88 There are many reasons why the actual yield is less than the theoretical yield. Some reactions are reversible, so they do not proceed 100% from reactants to product.. There could be impurities in the starting materials. Sometimes it is difficult to recover all the product. There may be side reactions that lead to additional products.

3.89 The balanced equation is given: $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{HF}$

The balanced equation shows a mole ratio of 2 moles HF : 1 mole CaF_2 . The theoretical yield of HF is:

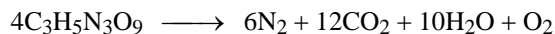
$$(6.00 \times 10^3 \cancel{\text{g CaF}_2}) \times \frac{1 \cancel{\text{mol CaF}_2}}{78.08 \cancel{\text{g CaF}_2}} \times \frac{2 \cancel{\text{mol HF}}}{1 \cancel{\text{mol CaF}_2}} \times \frac{20.01 \cancel{\text{g HF}}}{1 \cancel{\text{mol HF}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 3.08 \text{ kg HF}$$

The actual yield is given in the problem (2.86 kg HF).

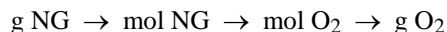
$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

$$\% \text{ yield} = \frac{2.86 \text{ kg}}{3.08 \text{ kg}} \times 100\% = \mathbf{92.9\%}$$

3.90 (a) Start with a balanced chemical equation. It's given in the problem. We use NG as an abbreviation for nitroglycerin. The molar mass of NG = 227.1 g/mol.



Map out the following strategy to solve this problem.



Calculate the grams of O_2 using the strategy above.

$$? \text{ g O}_2 = 2.00 \times 10^2 \cancel{\text{g NG}} \times \frac{1 \cancel{\text{mol NG}}}{227.1 \cancel{\text{g NG}}} \times \frac{1 \cancel{\text{mol O}_2}}{4 \cancel{\text{mol NG}}} \times \frac{32.00 \text{ g O}_2}{1 \cancel{\text{mol O}_2}} = \mathbf{7.05 \text{ g O}_2}$$

(b) The theoretical yield was calculated in part (a), and the actual yield is given in the problem (6.55 g). The percent yield is:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

$$\% \text{ yield} = \frac{6.55 \text{ g O}_2}{7.05 \text{ g O}_2} \times 100\% = \mathbf{92.9\%}$$

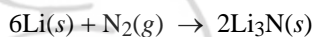
- 3.91** The balanced equation shows a mole ratio of 1 mole TiO_2 : 1 mole FeTiO_3 . The molar mass of FeTiO_3 is 151.73 g/mol, and the molar mass of TiO_2 is 79.88 g/mol. The theoretical yield of TiO_2 is:

$$8.00 \times 10^6 \cancel{\text{g FeTiO}_3} \times \frac{1 \cancel{\text{mol FeTiO}_3}}{151.73 \cancel{\text{g FeTiO}_3}} \times \frac{1 \cancel{\text{mol TiO}_2}}{1 \cancel{\text{mol FeTiO}_3}} \times \frac{79.88 \cancel{\text{g TiO}_2}}{1 \cancel{\text{mol TiO}_2}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} \\ = 4.21 \times 10^3 \text{ kg TiO}_2$$

The actual yield is given in the problem ($3.67 \times 10^3 \text{ kg TiO}_2$).

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{3.67 \times 10^3 \text{ kg}}{4.21 \times 10^3 \text{ kg}} \times 100\% = 87.2\%$$

- 3.92** This is a limiting reagent problem. Let's calculate the moles of Li_3N produced assuming complete reaction for each reactant.



$$12.3 \cancel{\text{g Li}} \times \frac{1 \cancel{\text{mol Li}}}{6.941 \cancel{\text{g Li}}} \times \frac{2 \text{ mol Li}_3\text{N}}{6 \cancel{\text{mol Li}}} = 0.591 \text{ mol Li}_3\text{N}$$

$$33.6 \cancel{\text{g N}_2} \times \frac{1 \cancel{\text{mol N}_2}}{28.02 \cancel{\text{g N}_2}} \times \frac{2 \text{ mol Li}_3\text{N}}{1 \cancel{\text{mol N}_2}} = 2.40 \text{ mol Li}_3\text{N}$$

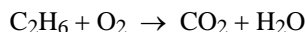
Li is the limiting reagent; it limits the amount of product produced. The amount of product produced is 0.591 mole Li_3N . Let's convert this to grams.

$$? \text{ g Li}_3\text{N} = 0.591 \cancel{\text{mol Li}_3\text{N}} \times \frac{34.83 \text{ g Li}_3\text{N}}{1 \cancel{\text{mol Li}_3\text{N}}} = 20.6 \text{ g Li}_3\text{N}$$

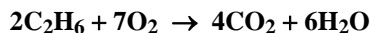
This is the theoretical yield of Li_3N . The actual yield is given in the problem (5.89 g). The percent yield is:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{5.89 \text{ g}}{20.6 \text{ g}} \times 100\% = 28.6\%$$

- 3.93** All the carbon from the hydrocarbon reactant ends up in CO_2 , and all the hydrogen from the hydrocarbon reactant ends up in water. In the diagram, we find 4 CO_2 molecules and 6 H_2O molecules. This gives a ratio between carbon and hydrogen of 4:12. We write the formula C_4H_{12} , which reduces to the empirical formula CH_3 . The empirical molar mass equals approximately 15 g, which is half the molar mass of the hydrocarbon. Thus, the molecular formula is double the empirical formula or C_2H_6 . Since this is a combustion reaction, the other reactant is O_2 . We write:



Balancing the equation,



- 3.94** $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$

We start with 8 molecules of H_2 and 3 molecules of O_2 . The balanced equation shows 2 moles H_2 f 1 mole O_2 . If 3 molecules of O_2 react, 6 molecules of H_2 will react, leaving 2 molecules of H_2 in excess. The balanced equation also shows 1 mole O_2 f 2 moles H_2O . If 3 molecules of O_2 react, 6 molecules of H_2O will be produced.

After complete reaction, there will be **2 molecules of H₂** and **6 molecules of H₂O**. The correct diagram is choice **(b)**.

3.95 First, let's convert to moles of HNO₃ produced.

$$1.00 \cancel{\text{ton}} \text{ HNO}_3 \times \frac{2000 \cancel{\text{lb}}}{1 \cancel{\text{ton}}} \times \frac{453.6 \cancel{\text{g}}}{1 \cancel{\text{lb}}} \times \frac{1 \text{ mol HNO}_3}{63.02 \cancel{\text{g HNO}_3}} = 1.44 \times 10^4 \text{ mol HNO}_3$$

Now, we will work in the reverse direction to calculate the amount of reactant needed to produce 1.44×10^3 mol of HNO₃. Realize that since the problem says to assume an 80% yield for each step, the amount of reactant needed in each step will be **larger** by a factor of $\frac{100\%}{80\%}$, compared to a standard stoichiometry calculation where a 100% yield is assumed.

Referring to the balanced equation in the **last step**, we calculate the moles of NO₂.

$$(1.44 \times 10^4 \cancel{\text{mol HNO}_3}) \times \frac{2 \text{ mol NO}_2}{1 \cancel{\text{mol HNO}_3}} \times \frac{100\%}{80\%} = 3.60 \times 10^4 \text{ mol NO}_2$$

Now, let's calculate the amount of NO needed to produce 3.60×10^4 mol NO₂. Following the same procedure as above, and referring to the balanced equation in the **middle step**, we calculate the moles of NO.

$$(3.60 \times 10^4 \cancel{\text{mol NO}_2}) \times \frac{1 \text{ mol NO}}{1 \cancel{\text{mol NO}_2}} \times \frac{100\%}{80\%} = 4.50 \times 10^4 \text{ mol NO}$$

Now, let's calculate the amount of NH₃ needed to produce 4.5×10^4 mol NO. Referring to the balanced equation in the **first step**, the moles of NH₃ is:

$$(4.50 \times 10^4 \cancel{\text{mol NO}}) \times \frac{4 \text{ mol NH}_3}{4 \cancel{\text{mol NO}}} \times \frac{100\%}{80\%} = 5.63 \times 10^4 \text{ mol NH}_3$$

Finally, converting to grams of NH₃:

$$5.63 \times 10^4 \cancel{\text{mol NH}_3} \times \frac{17.03 \text{ g NH}_3}{1 \cancel{\text{mol NH}_3}} = 9.59 \times 10^5 \text{ g NH}_3$$

3.96 We assume that all the Cl in the compound ends up as HCl and all the O ends up as H₂O. Therefore, we need to find the number of moles of Cl in HCl and the number of moles of O in H₂O.

$$\text{mol Cl} = 0.233 \cancel{\text{g HCl}} \times \frac{1 \cancel{\text{mol HCl}}}{36.46 \cancel{\text{g HCl}}} \times \frac{1 \text{ mol Cl}}{1 \cancel{\text{mol HCl}}} = 0.00639 \text{ mol Cl}$$

$$\text{mol O} = 0.403 \cancel{\text{g H}_2\text{O}} \times \frac{1 \cancel{\text{mol H}_2\text{O}}}{18.02 \cancel{\text{g H}_2\text{O}}} \times \frac{1 \text{ mol O}}{1 \cancel{\text{mol H}_2\text{O}}} = 0.0224 \text{ mol O}$$

Dividing by the smallest number of moles (0.00639 mole) gives the formula, ClO_{3.5}. Multiplying both subscripts by two gives the empirical formula, **Cl₂O₇**.

3.97 The number of moles of Y in 84.10 g of Y is:

$$27.22 \cancel{\text{g X}} \times \frac{1 \cancel{\text{mol X}}}{33.42 \cancel{\text{g X}}} \times \frac{1 \text{ mol Y}}{1 \cancel{\text{mol X}}} = 0.8145 \text{ mol Y}$$

The molar mass of Y is:

$$\text{molar mass Y} = \frac{84.10 \text{ g Y}}{0.8145 \text{ mol Y}} = 103.3 \text{ g/mol}$$

The atomic mass of Y is **103.3 amu**.

3.98 This is a calculation involving percent composition. Remember,

$$\text{percent by mass of each element} = \frac{\text{mass of element in 1 mol of compound}}{\text{molar mass of compound}} \times 100\%$$

The molar masses are: Al, 26.98 g/mol; $\text{Al}_2(\text{SO}_4)_3$, 342.2 g/mol; H_2O , 18.02 g/mol. Thus, using x as the number of H_2O molecules,

$$\text{mass \% Al} = \left(\frac{2(\text{molar mass of Al})}{\text{molar mass of Al}_2(\text{SO}_4)_3 + x(\text{molar mass of H}_2\text{O})} \right) \times 100\%$$

$$8.20\% = \left(\frac{2(26.98 \text{ g})}{342.2 \text{ g} + x(18.02 \text{ g})} \right) \times 100\%$$

$$x = 17.53$$

Rounding off to a whole number of water molecules, $x = 18$. Therefore, the formula is **$\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}$** .

3.99 The amount of Fe that reacted is: $\frac{1}{8} \times 664 \text{ g} = 83.0 \text{ g}$ reacted

The amount of Fe remaining is: $664 \text{ g} - 83.0 \text{ g} = 581 \text{ g}$ remaining

Thus, 83.0 g of Fe reacts to form the compound Fe_2O_3 , which has two moles of Fe atoms per 1 mole of compound. The mass of Fe_2O_3 produced is:

$$83.0 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \times \frac{159.7 \text{ g Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} = 119 \text{ g Fe}_2\text{O}_3$$

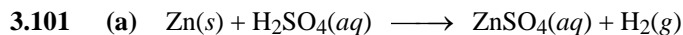
The final mass of the iron bar and rust is: $581 \text{ g Fe} + 119 \text{ g Fe}_2\text{O}_3 = 7.00 \times 10^2 \text{ g}$

3.100 The mass of oxygen in MO is $39.46 \text{ g} - 31.70 \text{ g} = 7.76 \text{ g O}$. Therefore, for every 31.70 g of M, there is 7.76 g of O in the compound MO. The molecular formula shows a mole ratio of 1 mole M : 1 mole O. First, calculate moles of M that react with 7.76 g O.

$$\text{mol M} = 7.76 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} \times \frac{1 \text{ mol M}}{1 \text{ mol O}} = 0.485 \text{ mol M}$$

$$\text{molar mass M} = \frac{31.70 \text{ g M}}{0.485 \text{ mol M}} = 65.4 \text{ g/mol}$$

Thus, the atomic mass of M is **65.4 amu**. The metal is most likely **Zn**.



(b) We assume that a pure sample would produce the theoretical yield of H_2 . The balanced equation shows a mole ratio of 1 mole H_2 : 1 mole Zn . The theoretical yield of H_2 is:

$$3.86 \cancel{\text{g Zn}} \times \frac{1 \cancel{\text{mol Zn}}}{65.39 \cancel{\text{g Zn}}} \times \frac{1 \cancel{\text{mol H}_2}}{1 \cancel{\text{mol Zn}}} \times \frac{2.016 \text{ g H}_2}{1 \cancel{\text{mol H}_2}} = 0.119 \text{ g H}_2$$

$$\text{percent purity} = \frac{0.0764 \text{ g H}_2}{0.119 \text{ g H}_2} \times 100\% = \mathbf{64.2\%}$$

(c) We assume that the impurities are inert and do not react with the sulfuric acid to produce hydrogen.

3.102 The wording of the problem suggests that the actual yield is less than the theoretical yield. The percent yield will be equal to the percent purity of the iron(III) oxide. We find the theoretical yield:

$$\begin{aligned} (2.62 \times 10^3 \cancel{\text{kg Fe}_2\text{O}_3}) \times \frac{1000 \cancel{\text{g Fe}_2\text{O}_3}}{1 \cancel{\text{kg Fe}_2\text{O}_3}} \times \frac{1 \cancel{\text{mol Fe}_2\text{O}_3}}{159.7 \cancel{\text{g Fe}_2\text{O}_3}} \times \frac{2 \cancel{\text{mol Fe}}}{1 \cancel{\text{mol Fe}_2\text{O}_3}} \times \frac{55.85 \cancel{\text{g Fe}}}{1 \cancel{\text{mol Fe}}} \times \frac{1 \text{ kg Fe}}{1000 \cancel{\text{g Fe}}} \\ = 1.83 \times 10^3 \text{ kg Fe} \end{aligned}$$

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

$$\text{percent yield} = \frac{1.64 \times 10^3 \text{ kg Fe}}{1.83 \times 10^3 \text{ kg Fe}} \times 100\% = \mathbf{89.6\% = \text{purity of Fe}_2\text{O}_3}$$

3.103 The balanced equation is: $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \longrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

$$\begin{aligned} \frac{5.0 \times 10^2 \cancel{\text{g glucose}}}{1 \cancel{\text{day}}} \times \frac{1 \cancel{\text{mol glucose}}}{180.16 \cancel{\text{g glucose}}} \times \frac{6 \cancel{\text{mol CO}_2}}{1 \cancel{\text{mol glucose}}} \times \frac{44.01 \text{ g CO}_2}{1 \cancel{\text{mol CO}_2}} \times \frac{365 \cancel{\text{days}}}{1 \cancel{\text{yr}}} \times (6.5 \times 10^9 \cancel{\text{people}}) \\ = \mathbf{1.7 \times 10^{15} \text{ g CO}_2/\text{yr}} \end{aligned}$$

3.104 The carbohydrate contains 40 percent carbon; therefore, the remaining 60 percent is hydrogen and oxygen. The problem states that the hydrogen to oxygen ratio is 2:1. We can write this 2:1 ratio as H_2O .

Assume 100 g of compound.

$$40.0 \cancel{\text{g C}} \times \frac{1 \text{ mol C}}{12.01 \cancel{\text{g C}}} = 3.33 \text{ mol C}$$

$$60.0 \cancel{\text{g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \cancel{\text{g H}_2\text{O}}} = 3.33 \text{ mol H}_2\text{O}$$

Dividing by 3.33 gives CH_2O for the empirical formula.

To find the molecular formula, divide the molar mass by the empirical mass.

$$\frac{\text{molar mass}}{\text{empirical mass}} = \frac{178 \text{ g}}{30.03 \text{ g}} \approx 6$$

Thus, there are six CH_2O units in each molecule of the compound, so the molecular formula is $(\text{CH}_2\text{O})_6$, or $\text{C}_6\text{H}_{12}\text{O}_6$.

- 3.105** The mass of the metal (X) in the metal oxide is 1.68 g. The mass of oxygen in the metal oxide is 2.40 g – 1.68 g = 0.72 g oxygen. Next, find the number of moles of the metal and of the oxygen.

$$\text{moles X} = 1.68 \cancel{\text{g}} \times \frac{1 \text{ mol X}}{55.9 \cancel{\text{g X}}} = 0.0301 \text{ mol X}$$

$$\text{moles O} = 0.72 \cancel{\text{g}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 0.045 \text{ mol O}$$

This gives the formula $\text{X}_{0.0301}\text{O}_{0.045}$. Dividing by the smallest number of moles (0.0301 moles) gives the formula $\text{X}_{1.00}\text{O}_{1.5}$. Multiplying by two gives the empirical formula, **X_2O_3** .

The balanced equation is: **$\text{X}_2\text{O}_3(s) + 3\text{CO}(g) \longrightarrow 2\text{X}(s) + 3\text{CO}_2(g)$**

- 3.106** Both compounds contain only Mn and O. When the first compound is heated, oxygen gas is evolved. Let's calculate the empirical formulas for the two compounds, then we can write a balanced equation.

(a) Compound X: Assume 100 g of compound.

$$63.3 \cancel{\text{g Mn}} \times \frac{1 \text{ mol Mn}}{54.94 \cancel{\text{g Mn}}} = 1.15 \text{ mol Mn}$$

$$36.7 \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 2.29 \text{ mol O}$$

Dividing by the smallest number of moles (1.15 moles) gives the empirical formula, **MnO_2** .

Compound Y: Assume 100 g of compound.

$$72.0 \cancel{\text{g Mn}} \times \frac{1 \text{ mol Mn}}{54.94 \cancel{\text{g Mn}}} = 1.31 \text{ mol Mn}$$

$$28.0 \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 1.75 \text{ mol O}$$

Dividing by the smallest number of moles gives $\text{MnO}_{1.33}$. Recall that an empirical formula must have whole number coefficients. Multiplying by a factor of 3 gives the empirical formula **Mn_3O_4** .

(b) The unbalanced equation is: **$\text{MnO}_2 \longrightarrow \text{Mn}_3\text{O}_4 + \text{O}_2$**

Balancing by inspection gives: **$3\text{MnO}_2 \longrightarrow \text{Mn}_3\text{O}_4 + \text{O}_2$**

- 3.107** We carry an additional significant figure throughout this calculation to avoid rounding errors.

Assume 100 g of sample. Then,

$$\text{mol Na} = 32.08 \cancel{\text{g Na}} \times \frac{1 \text{ mol Na}}{22.99 \cancel{\text{g Na}}} = 1.3954 \text{ mol Na}$$

$$\text{mol O} = 36.01 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.2506 \text{ mol O}$$

$$\text{mol Cl} = 19.51 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.55035 \text{ mol Cl}$$

Since Cl is only contained in NaCl, the moles of Cl equals the moles of Na contained in NaCl.

$$\text{mol Na (in NaCl)} = 0.55035 \text{ mol}$$

The number of moles of Na in the remaining two compounds is: $1.3954 \text{ mol} - 0.55035 \text{ mol} = 0.84505 \text{ mol Na}$.

To solve for moles of the remaining two compounds, let

$$x = \text{moles of Na}_2\text{SO}_4$$

$$y = \text{moles of NaNO}_3$$

Then, from the mole ratio of Na and O in each compound, we can write

$$2x + y = \text{mol Na} = 0.84505 \text{ mol}$$

$$4x + 3y = \text{mol O} = 2.2506 \text{ mol}$$

Solving two equations with two unknowns gives

$$x = 0.14228 = \text{mol Na}_2\text{SO}_4 \quad \text{and} \quad y = 0.56050 = \text{mol NaNO}_3$$

Finally, we convert to mass of each compound to calculate the mass percent of each compound in the sample. Remember, the sample size is 100 g.

$$\text{mass \% NaCl} = 0.55035 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} \times \frac{1}{100 \text{ g sample}} \times 100\% = \mathbf{32.16\% NaCl}$$

$$\text{mass \% Na}_2\text{SO}_4 = 0.14228 \text{ mol Na}_2\text{SO}_4 \times \frac{142.05 \text{ g Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4} \times \frac{1}{100 \text{ g sample}} \times 100\% = \mathbf{20.21\% Na}_2\text{SO}_4$$

$$\text{mass \% NaNO}_3 = 0.56050 \text{ mol NaNO}_3 \times \frac{85.00 \text{ g NaNO}_3}{1 \text{ mol NaNO}_3} \times \frac{1}{100 \text{ g sample}} \times 100\% = \mathbf{47.64\% NaNO}_3$$

3.108 We assume that the increase in mass results from the element nitrogen. The mass of nitrogen is:

$$0.378 \text{ g} - 0.273 \text{ g} = 0.105 \text{ g N}$$

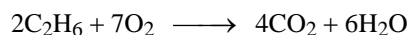
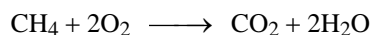
The empirical formula can now be calculated. Convert to moles of each element.

$$0.273 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} = 0.0112 \text{ mol Mg}$$

$$0.105 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.00749 \text{ mol N}$$

Dividing by the smallest number of moles gives $\text{Mg}_{1.5}\text{N}$. Recall that an empirical formula must have whole number coefficients. Multiplying by a factor of 2 gives the empirical formula $\mathbf{Mg_3N_2}$. The name of this compound is **magnesium nitride**.

3.109 The balanced equations are:



If we let $x = \text{mass of CH}_4$, then the mass of C_2H_6 is $(13.43 - x) \text{ g}$.

Next, we need to calculate the mass of CO_2 and the mass of H_2O produced by both CH_4 and C_2H_6 . The sum of the masses of CO_2 and H_2O will add up to 64.84 g.

$$? \text{ g CO}_2 \text{ (from CH}_4\text{)} = x \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} = 2.744x \text{ g CO}_2$$

$$? \text{ g H}_2\text{O (from CH}_4\text{)} = x \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol CH}_4} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 2.247x \text{ g H}_2\text{O}$$

$$\begin{aligned} ? \text{ g CO}_2 \text{ (from C}_2\text{H}_6\text{)} &= (13.43 - x) \text{ g C}_2\text{H}_6 \times \frac{1 \text{ mol C}_2\text{H}_6}{30.07 \text{ g C}_2\text{H}_6} \times \frac{4 \text{ mol CO}_2}{2 \text{ mol C}_2\text{H}_6} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \\ &= 2.927(13.43 - x) \text{ g CO}_2 \end{aligned}$$

$$\begin{aligned} ? \text{ g H}_2\text{O (from C}_2\text{H}_6\text{)} &= (13.43 - x) \text{ g C}_2\text{H}_6 \times \frac{1 \text{ mol C}_2\text{H}_6}{30.07 \text{ g C}_2\text{H}_6} \times \frac{6 \text{ mol H}_2\text{O}}{2 \text{ mol C}_2\text{H}_6} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \\ &= 1.798(13.43 - x) \text{ g H}_2\text{O} \end{aligned}$$

Summing the masses of CO₂ and H₂O:

$$2.744x \text{ g} + 2.247x \text{ g} + 2.927(13.43 - x) \text{ g} + 1.798(13.43 - x) \text{ g} = 64.84 \text{ g}$$

$$0.266x = 1.383$$

$$x = 5.20 \text{ g}$$

The fraction of CH₄ in the mixture is $\frac{5.20 \text{ g}}{13.43 \text{ g}} = \mathbf{0.387}$

3.110 The molecular formula of cysteine is **C₃H₇NO₂S**. The mass percentage of each element is:

$$\% \text{C} = \frac{(3)(12.01 \text{ g})}{121.17 \text{ g}} \times 100\% = \mathbf{29.74\%}$$

$$\% \text{H} = \frac{(7)(1.008 \text{ g})}{121.17 \text{ g}} \times 100\% = \mathbf{5.823\%}$$

$$\% \text{N} = \frac{14.01 \text{ g}}{121.17 \text{ g}} \times 100\% = \mathbf{11.56\%}$$

$$\% \text{O} = \frac{(2)(16.00 \text{ g})}{121.17 \text{ g}} \times 100\% = \mathbf{26.41\%}$$

$$\% \text{S} = \frac{32.07 \text{ g}}{121.17 \text{ g}} \times 100\% = \mathbf{26.47\%}$$

Check: 29.74% + 5.823% + 11.56% + 26.41% + 26.47% = 100.00%

3.111 The molecular formula of isoflurane is **C₃H₂ClF₅O**. The mass percentage of each element is:

$$\% \text{C} = \frac{(3)(12.01 \text{ g})}{184.50 \text{ g}} \times 100\% = \mathbf{19.53\%}$$

$$\% \text{H} = \frac{(2)(1.008 \text{ g})}{184.50 \text{ g}} \times 100\% = \mathbf{1.093\%}$$

$$\% \text{Cl} = \frac{35.45 \text{ g}}{184.50 \text{ g}} \times 100\% = \mathbf{19.21\%}$$

$$\% \text{F} = \frac{(5)(19.00 \text{ g})}{184.50 \text{ g}} \times 100\% = \mathbf{51.49\%}$$

$$\% \text{O} = \frac{16.00 \text{ g}}{184.50 \text{ g}} \times 100\% = \mathbf{8.672\%}$$

Check: $19.53\% + 1.093\% + 19.21\% + 51.49\% + 8.672\% = 100.00\%$

- 3.112** For the first step of the synthesis, the yield is 90% or 0.9. For the second step, the yield will be 90% of 0.9 or $(0.9 \times 0.9) = 0.81$. For the third step, the yield will be 90% of 0.81 or $(0.9 \times 0.9 \times 0.9) = 0.73$. We see that the yield will be:

$$\text{Yield} = (0.9)^n$$

where n = number of steps in the reaction. For 30 steps,

$$\text{Yield} = (0.9)^{30} = 0.04 = \mathbf{4\%}$$

- 3.113** The mass of water lost upon heating the mixture is $(5.020 \text{ g} - 2.988 \text{ g}) = 2.032 \text{ g}$ water. Next, if we let x = mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, then the mass of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is $(5.020 - x)\text{g}$. We can calculate the amount of water lost by each salt based on the mass % of water in each hydrate. We can write:

$$(\text{mass CuSO}_4 \cdot 5\text{H}_2\text{O})(\% \text{H}_2\text{O}) + (\text{mass MgSO}_4 \cdot 7\text{H}_2\text{O})(\% \text{H}_2\text{O}) = \text{total mass H}_2\text{O} = 2.032 \text{ g H}_2\text{O}$$

Calculate the % H_2O in each hydrate.

$$\% \text{H}_2\text{O} (\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = \frac{(5)(18.02 \text{ g})}{249.7 \text{ g}} \times 100\% = 36.08\% \text{H}_2\text{O}$$

$$\% \text{H}_2\text{O} (\text{MgSO}_4 \cdot 7\text{H}_2\text{O}) = \frac{(7)(18.02 \text{ g})}{246.5 \text{ g}} \times 100\% = 51.17\% \text{H}_2\text{O}$$

Substituting into the equation above gives:

$$(x)(0.3608) + (5.020 - x)(0.5117) = 2.032 \text{ g}$$

$$0.1509x = 0.5367$$

$$x = 3.557 \text{ g} = \text{mass of CuSO}_4 \cdot 5\text{H}_2\text{O}$$

Finally, the percent by mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the mixture is:

$$\frac{3.557 \text{ g}}{5.020 \text{ g}} \times 100\% = \mathbf{70.86\%}$$

- 3.114** (a) The observations mean either that the amount of the more abundant isotope was increasing or the amount of the less abundant isotope was decreasing. One possible explanation is that the less abundant isotope was undergoing radioactive decay, and thus its mass would decrease with time.
- (b) 16 amu, CH_4 17 amu, NH_3 18 amu, H_2O 64 amu, SO_2
- (c) The formula C_3H_8 can also be written as $\text{CH}_3\text{CH}_2\text{CH}_3$. A CH_3 fragment could break off from this molecule giving a peak at 15 amu. No fragment of CO_2 can have a mass of 15 amu. Therefore, the substance responsible for the mass spectrum is most likely **C_3H_8** .

- (d) First, let's calculate the masses of CO_2 and C_3H_8 .

$$\text{molecular mass CO}_2 = 12.00000 \text{ amu} + 2(15.99491 \text{ amu}) = 43.98982 \text{ amu}$$

$$\text{molecular mass C}_3\text{H}_8 = 3(12.00000 \text{ amu}) + 8(1.00797 \text{ amu}) = 44.06376 \text{ amu}$$

These masses differ by only 0.07394 amu. The measurements must be precise to ± 0.030 amu.

$$43.98982 + 0.030 \text{ amu} = 44.02 \text{ amu}$$

$$44.06376 - 0.030 \text{ amu} = 44.03 \text{ amu}$$

- (e) To analyze a gold sample, scientists first heat a tiny spot (about 0.01 cm in diameter and in depth) of the sample with a high-power laser. The vaporized gold and its trace elements are swept by a stream of argon gas into a mass spectrometer. Comparison of the mass spectrum with a library of mass spectra of gold from known origins will identify the source of the gold, much as fingerprints are used to identify individuals. This technique can be used on large objects like bullion and nuggets as well as on small articles of jewelry.

- 3.115** (a) We need to compare the mass % of K in both KCl and K_2SO_4 .

$$\% \text{K in KCl} = \frac{39.10 \text{ g}}{74.55 \text{ g}} \times 100\% = 52.45\% \text{ K}$$

$$\% \text{K in K}_2\text{SO}_4 = \frac{2(39.10 \text{ g})}{174.27 \text{ g}} \times 100\% = 44.87\% \text{ K}$$

The price is dependent on the %K.

$$\frac{\text{Price of K}_2\text{SO}_4}{\text{Price of KCl}} = \frac{\% \text{K in K}_2\text{SO}_4}{\% \text{K in KCl}}$$

$$\text{Price of K}_2\text{SO}_4 = \text{Price of KCl} \times \frac{\% \text{K in K}_2\text{SO}_4}{\% \text{K in KCl}}$$

$$\text{Price of K}_2\text{SO}_4 = \frac{\$0.055}{\text{kg}} \times \frac{44.87\%}{52.45\%} = \$0.047/\text{kg}$$

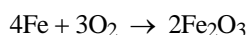
- (b) First, calculate the number of moles of K in 1.00 kg of KCl.

$$(1.00 \times 10^3 \text{ g KCl}) \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{1 \text{ mol K}}{1 \text{ mol KCl}} = 13.4 \text{ mol K}$$

Next, calculate the amount of K_2O needed to supply 13.4 mol K.

$$13.4 \text{ mol K} \times \frac{1 \text{ mol K}_2\text{O}}{2 \text{ mol K}} \times \frac{94.20 \text{ g K}_2\text{O}}{1 \text{ mol K}_2\text{O}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.631 \text{ kg K}_2\text{O}$$

- 3.116** The decomposition of KClO_3 produces oxygen gas (O_2) which reacts with Fe to produce Fe_2O_3 .



When the 15.0 g of Fe is heated in the presence of O_2 gas, any increase in mass is due to oxygen. The mass of oxygen reacted is:

$$17.9 \text{ g} - 15.0 \text{ g} = 2.9 \text{ g O}_2$$

From this mass of O_2 , we can now calculate the mass of Fe_2O_3 produced and the mass of $KClO_3$ decomposed.

$$2.9 \cancel{g O_2} \times \frac{1 \cancel{mol O_2}}{32.00 \cancel{g O_2}} \times \frac{2 \cancel{mol Fe_2O_3}}{3 \cancel{mol O_2}} \times \frac{159.7 \text{ g } Fe_2O_3}{1 \cancel{mol Fe_2O_3}} = \mathbf{9.6 \text{ g } Fe_2O_3}$$

The balanced equation for the decomposition of $KClO_3$ is: $2KClO_3 \rightarrow 2KCl + 3O_2$. The mass of $KClO_3$ decomposed is:

$$2.9 \cancel{g O_2} \times \frac{1 \cancel{mol O_2}}{32.00 \cancel{g O_2}} \times \frac{2 \cancel{mol KClO_3}}{3 \cancel{mol O_2}} \times \frac{122.55 \text{ g } KClO_3}{1 \cancel{mol KClO_3}} = \mathbf{7.4 \text{ g } KClO_3}$$

- 3.117** Possible formulas for the metal bromide could be MBr , MBr_2 , MBr_3 , etc. Assuming 100 g of compound, the moles of Br in the compound can be determined. From the mass and moles of the metal for each possible formula, we can calculate a molar mass for the metal. The molar mass that matches a metal on the periodic table would indicate the correct formula.

Assuming 100 g of compound, we have 53.79 g Br and 46.21 g of the metal (M). The moles of Br in the compound are:

$$53.79 \cancel{g Br} \times \frac{1 \text{ mol Br}}{79.90 \cancel{g Br}} = 0.67322 \text{ mol Br}$$

If the formula is MBr , the moles of M are also 0.67322 mole. If the formula is MBr_2 , the moles of M are $0.67322/2 = 0.33661$ mole, and so on. For each formula (MBr , MBr_2 , and MBr_3), we calculate the molar mass of the metal.

$$MBr: \frac{46.21 \text{ g M}}{0.67322 \text{ mol M}} = 68.64 \text{ g/mol (no such metal)}$$

$$MBr_2: \frac{46.21 \text{ g M}}{0.33661 \text{ mol M}} = 137.3 \text{ g/mol (The metal is Ba. The formula is } \mathbf{BaBr_2})$$

$$MBr_3: \frac{46.21 \text{ g M}}{0.22441 \text{ mol M}} = 205.9 \text{ g/mol (no such metal)}$$

4.3 The process in which an ion is surrounded by water molecules arranged in a specific manner is called hydration. Water has a positive end (the H atoms) and a negative end (the O atom), or positive and negative “poles”, which can interact with ions in solution.

4.4 The symbol “ \rightarrow ” means that the reaction proceeds to completion. The symbol “ \rightleftharpoons ” means that the reaction is reversible. The system eventually reaches equilibrium where the rate at which reactants go to products is equal to the rate at which products return to reactants. In some reactions, the equilibrium position favors reactants, in others, the equilibrium position favors products.

4.5 There are dissolved ions in the water; therefore, the solution conducts electricity.

4.6 $\text{Li}^+(aq)$, $\text{F}^-(aq)$, and $\text{H}_2\text{O}(l)$

4.7 (a) is a strong electrolyte. The compound dissociates completely into ions in solution.
(b) is a nonelectrolyte. The compound dissolves in water, but the molecules remain intact.
(c) is a weak electrolyte. A small amount of the compound dissociates into ions in water.

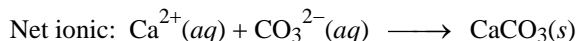
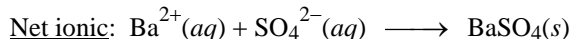
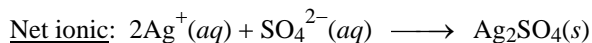
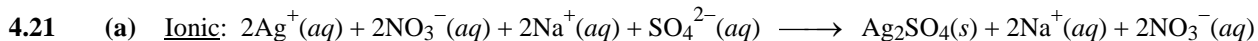
4.8 When NaCl dissolves in water it dissociates into Na^+ and Cl^- ions. When the ions are hydrated, the

- 4.1** In dissolving a solid in a liquid, the solid is typically the solute, the substance present in a smaller amount, and the liquid is the solvent, the substance present in a larger amount. The two substances together form a solution, a homogeneous mixture of two or more substances.
- 4.2** A nonelectrolyte is a solution that does not conduct electricity. A strong electrolyte solution contains a large number of ions and therefore the solution conducts electricity. A weak electrolyte solution contains a small number of ions, so the solution conducts electricity, but not as strongly as a strong electrolyte.
- 4.3** The process in which an ion is surrounded by water molecules arranged in a specific manner is called hydration. Water has a positive end (the H atoms) and a negative end (the O atom), or positive and negative “poles”, which can interact with ions in solution.
- 4.4** The symbol “ \rightarrow ” means that the reaction proceeds to completion. The symbol “ \rightleftharpoons ” means that the reaction is reversible. The system eventually reaches equilibrium where the rate at which reactants go to products is equal to the rate at which products return to reactants. In some reactions, the equilibrium position favors reactants, in others, the equilibrium position favors products.
- 4.5** There are dissolved ions in the water; therefore, the solution conducts electricity.
- 4.6** $\text{Li}^+(\text{aq})$, $\text{F}^-(\text{aq})$, and $\text{H}_2\text{O}(l)$
- 4.7** (a) is a strong electrolyte. The compound dissociates completely into ions in solution.
(b) is a nonelectrolyte. The compound dissolves in water, but the molecules remain intact.
(c) is a weak electrolyte. A small amount of the compound dissociates into ions in water.
- 4.8** When NaCl dissolves in water it dissociates into Na^+ and Cl^- ions. When the ions are hydrated, the water molecules will be oriented so that the negative end of the water dipole interacts with the positive sodium ion, and the positive end of the water dipole interacts with the negative chloride ion. The negative end of the water dipole is near the oxygen atom, and the positive end of the water dipole is near the hydrogen atoms. The diagram that best represents the hydration of NaCl when dissolved in water is choice (c).
- 4.9** Ionic compounds, strong acids, and strong bases (metal hydroxides) are strong electrolytes. Weak acids and weak bases are weak electrolytes. Molecular substances other than acids or bases are nonelectrolytes.
- (a) very weak electrolyte (b) strong electrolyte (ionic compound)
(c) strong electrolyte (strong acid) (d) weak electrolyte (weak acid)
(e) nonelectrolyte (molecular compound - neither acid nor base)
- 4.10** Ionic compounds, strong acids, and strong bases (metal hydroxides) are strong electrolytes. Weak acids and weak bases are weak electrolytes. Molecular substances other than acids or bases are nonelectrolytes.
- (a) strong electrolyte (ionic) (b) nonelectrolyte
(c) weak electrolyte (weak base) (d) strong electrolyte (strong base)

- 4.11** Since solutions must be electrically neutral, any flow of positive species (cations) must be balanced by the flow of negative species (anions). Therefore, the correct answer is **(d)**.
- 4.12** (a) Solid NaCl does not conduct. The ions are locked in a rigid lattice structure.
(b) Molten NaCl conducts. The ions can move around in the liquid state.
(c) Aqueous NaCl conducts. NaCl dissociates completely to $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$ in water.
- 4.13** Measure the conductance to see if the solution carries an electrical current. If the solution is conducting, then you can determine whether the solution is a strong or weak electrolyte by comparing its conductance with that of a known strong electrolyte.
- 4.14** Since HCl dissolved in water conducts electricity, then $\text{HCl}(aq)$ must actually exist as $\text{H}^+(aq)$ cations and $\text{Cl}^-(aq)$ anions. Since HCl dissolved in benzene solvent does not conduct electricity, then we must assume that the HCl molecules in benzene solvent do not ionize, but rather exist as un-ionized molecules.
- 4.15** In a molecular equation, the formulas of the compounds are written as though all species existed as molecules or whole units; whereas, an ionic equation shows dissolved species as free ions.
- 4.16** The advantage of writing a net ionic equation is that the equation only shows the species that actually take part in the reaction.
- 4.17** Refer to Table 4.2 of the text to solve this problem. AgCl is insoluble in water. It will precipitate from solution. NaNO_3 is soluble in water and will remain as Na^+ and NO_3^- ions in solution. Diagram (c) best represents the mixture.
- 4.18** Refer to Table 4.2 of the text to solve this problem. $\text{Mg}(\text{OH})_2$ is insoluble in water. It will precipitate from solution. KCl is soluble in water and will remain as K^+ and Cl^- ions in solution. Diagram (b) best represents the mixture.
- 4.19** Refer to Table 4.2 of the text to solve this problem.
(a) $\text{Ca}_3(\text{PO}_4)_2$ is **insoluble**.
(b) $\text{Mn}(\text{OH})_2$ is **insoluble**.
(c) AgClO_3 is **soluble**.
(d) K_2S is **soluble**.
- 4.20** **Strategy:** Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations, the ammonium ion, and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, refer to Table 4.2 of the text.

Solution:

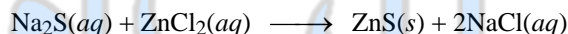
- (a) CaCO_3 is **insoluble**. Most carbonate compounds are insoluble.
(b) ZnSO_4 is **soluble**. Most sulfate compounds are soluble.
(c) $\text{Hg}(\text{NO}_3)_2$ is **soluble**. All nitrate compounds are soluble.
(d) HgSO_4 is **insoluble**. Most sulfate compounds are soluble, but those containing Ag^+ , Ca^{2+} , Ba^{2+} , Hg^{2+} , and Pb^{2+} are insoluble.
(e) NH_4ClO_4 is **soluble**. All ammonium compounds are soluble.



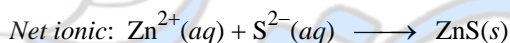
4.22 (a)

Strategy: Recall that an *ionic equation* shows dissolved ionic compounds in terms of their free ions. A *net ionic equation* shows only the species that actually take part in the reaction. What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of Na_2S and ZnCl_2 ? What happens when the cations encounter the anions in solution?

Solution: In solution, Na_2S dissociates into Na^+ and S^{2-} ions and ZnCl_2 dissociates into Zn^{2+} and Cl^- ions. According to Table 4.2 of the text, zinc ions (Zn^{2+}) and sulfide ions (S^{2-}) will form an insoluble compound, zinc sulfide (ZnS), while the other product, NaCl , is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:



The ionic and net ionic equations are:

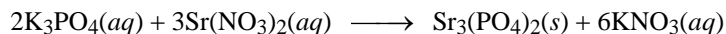


Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

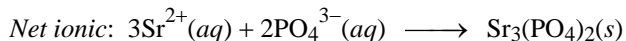
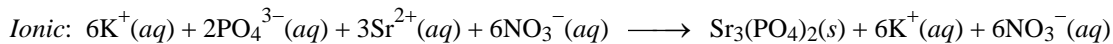
(b)

Strategy: What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of K_3PO_4 and $\text{Sr}(\text{NO}_3)_2$? What happens when the cations encounter the anions in solution?

Solution: In solution, K_3PO_4 dissociates into K^+ and PO_4^{3-} ions and $\text{Sr}(\text{NO}_3)_2$ dissociates into Sr^{2+} and NO_3^- ions. According to Table 4.2 of the text, strontium ions (Sr^{2+}) and phosphate ions (PO_4^{3-}) will form an insoluble compound, strontium phosphate [$\text{Sr}_3(\text{PO}_4)_2$], while the other product, KNO_3 , is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:



The ionic and net ionic equations are:

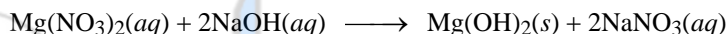


Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

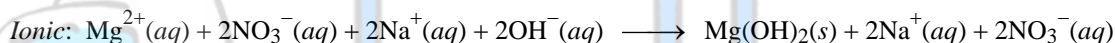
(c)

Strategy: What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of $\text{Mg}(\text{NO}_3)_2$ and NaOH ? What happens when the cations encounter the anions in solution?

Solution: In solution, $\text{Mg}(\text{NO}_3)_2$ dissociates into Mg^{2+} and NO_3^- ions and NaOH dissociates into Na^+ and OH^- ions. According to Table 4.2 of the text, magnesium ions (Mg^{2+}) and hydroxide ions (OH^-) will form an insoluble compound, magnesium hydroxide [$\text{Mg}(\text{OH})_2$], while the other product, NaNO_3 , is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:

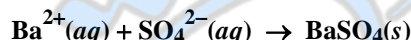


The ionic and net ionic equations are:



Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

- 4.23 (a) Both reactants are soluble ionic compounds. The other possible ion combinations, Na_2SO_4 and $\text{Cu}(\text{NO}_3)_2$, are also soluble.
- (b) Both reactants are soluble. Of the other two possible ion combinations, KCl is soluble, but BaSO_4 is insoluble and will precipitate.



- 4.24 (a) Add chloride ions. KCl is soluble, but AgCl is not.
- (b) Add hydroxide ions. $\text{Ba}(\text{OH})_2$ is soluble, but $\text{Pb}(\text{OH})_2$ is insoluble.
- (c) Add carbonate ions. $(\text{NH}_4)_2\text{CO}_3$ is soluble, but CaCO_3 is insoluble.
- (d) Add sulfate ions. CuSO_4 is soluble, but BaSO_4 is insoluble.

4.25 Please see Section 4.3 of the text.

4.26 Arrhenius acids produce H^+ in water. Arrhenius bases produce OH^- in water. A Brønsted acid is a proton (H^+) donor. A Brønsted base is a proton (H^+) acceptor. The Brønsted definitions do not require acids and bases to be in aqueous solution.

4.27 Hydrochloric acid (HCl) is a monoprotic acid, sulfuric acid (H_2SO_4) is a diprotic acid, and phosphoric acid (H_3PO_4) is a triprotic acid.

4.28 In general, an acid-base neutralization reaction produces salt and water. At the neutralization point, the correct amount of base has been added to completely react with the acid. The resulting solution only contains salt and water.

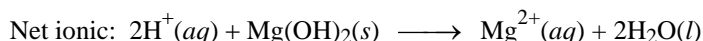
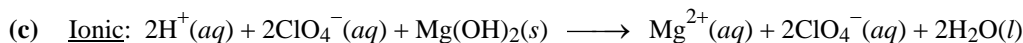
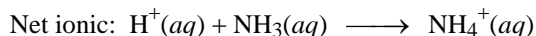
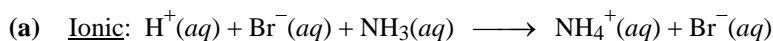
- 4.29** A salt is an ionic compound made up of a cation (other than H^+) and an anion (other than OH^- and O^{2-}). NaF , BaSO_4 , and KBr are salts.
- 4.30** (a) weak base (b) weak acid (c) strong base (d) weak acid
(e) strong acid (first stage of ionization) (f) weak acid (g) strong base
- 4.31** (a) HI dissolves in water to produce H^+ and I^- , so HI is a **Brønsted acid**.
(b) CH_3COO^- can accept a proton to become acetic acid CH_3COOH , so it is a **Brønsted base**.
(c) H_2PO_4^- can either accept a proton, H^+ , to become H_3PO_4 and thus behaves as a **Brønsted base**, or can donate a proton in water to yield H^+ and HPO_4^{2-} , thus behaving as a **Brønsted acid**.
(d) HSO_4^- can either accept a proton, H^+ , to become H_2SO_4 and thus behaves as a **Brønsted base**, or can donate a proton in water to yield H^+ and SO_4^{2-} , thus behaving as a **Brønsted acid**.
- 4.32 Strategy:** What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

Solution:

- (a) PO_4^{3-} in water can accept a proton to become HPO_4^{2-} , and is thus a **Brønsted base**.
(b) ClO_2^- in water can accept a proton to become HClO_2 , and is thus a **Brønsted base**.
(c) NH_4^+ dissolved in water can donate a proton H^+ , thus behaving as a **Brønsted acid**.
(d) HCO_3^- can either accept a proton to become H_2CO_3 , thus behaving as a **Brønsted base**. Or, HCO_3^- can donate a proton to yield H^+ and CO_3^{2-} , thus behaving as a **Brønsted acid**.

Comment: The HCO_3^- species is said to be *amphoteric* because it possesses both acidic and basic properties.

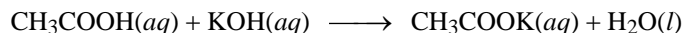
- 4.33** Recall that strong acids and strong bases are strong electrolytes. They are completely ionized in solution. An *ionic equation* will show strong acids and strong bases in terms of their free ions. A *net ionic equation* shows only the species that actually take part in the reaction.



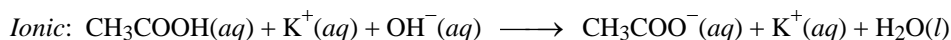
- 4.34 Strategy:** Recall that strong acids and strong bases are strong electrolytes. They are completely ionized in solution. An *ionic equation* will show strong acids and strong bases in terms of their free ions. Weak acids and weak bases are weak electrolytes. They only ionize to a small extent in solution. Weak acids and weak bases are shown as molecules in ionic and net ionic equations. A *net ionic equation* shows only the species that actually take part in the reaction.

(a)

Solution: CH_3COOH is a weak acid. It will be shown as a molecule in the ionic equation. KOH is a strong base. It completely ionizes to K^+ and OH^- ions. Since CH_3COOH is an acid, it donates an H^+ to the base, OH^- , producing water. The other product is the salt, CH_3COOK , which is soluble and remains in solution. The balanced molecular equation is:

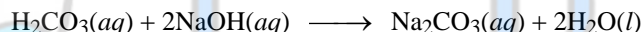


The ionic and net ionic equations are:

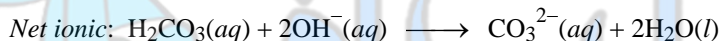
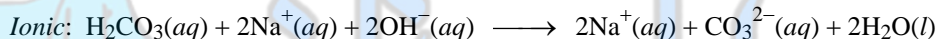


(b)

Solution: H_2CO_3 is a weak acid. It will be shown as a molecule in the ionic equation. NaOH is a strong base. It completely ionizes to Na^+ and OH^- ions. Since H_2CO_3 is an acid, it donates an H^+ to the base, OH^- , producing water. The other product is the salt, Na_2CO_3 , which is soluble and remains in solution. The balanced molecular equation is:

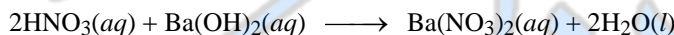


The ionic and net ionic equations are:

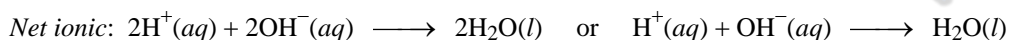


(c)

Solution: HNO_3 is a strong acid. It completely ionizes to H^+ and NO_3^- ions. $\text{Ba}(\text{OH})_2$ is a strong base. It completely ionizes to Ba^{2+} and OH^- ions. Since HNO_3 is an acid, it donates an H^+ to the base, OH^- , producing water. The other product is the salt, $\text{Ba}(\text{NO}_3)_2$, which is soluble and remains in solution. The balanced molecular equation is:



The ionic and net ionic equations are:



- 4.35** A half-reaction explicitly shows the electrons involved in a redox reaction. An oxidation reaction refers to the half-reaction that involves a loss of electrons. A reduction reaction is a half-reaction that involves a gain of electrons. A reducing agent is a substance that can donate electrons to another substance, thereby reducing this other substance. An oxidizing agent is a substance that can accept electrons from another substance, thereby oxidizing this other substance. Redox reactions are electron-transfer reactions.
- 4.36** An oxidation number signifies the number of charges that an atom would have in a molecule (or an ionic compound) if electrons were transferred completely. For other than ionic compounds, the oxidation number is used simply to track electrons in redox reactions. The oxidation numbers are not actual charges in the molecule.
- 4.37** (a) +1 and +2, respectively. (b) +3, +4, +5, +6, and +7, respectively.
- 4.38** No. Oxidation and reduction go together. One substance loses electrons and another gains those electrons.

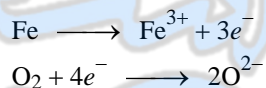
- 4.39** Even though the problem doesn't ask you to assign oxidation numbers, you need to be able to do so in order to determine what is being oxidized or reduced.

	<u>(i) Half Reactions</u>	<u>(ii) Oxidizing Agent</u>	<u>(iii) Reducing Agent</u>
(a)	$\text{Sr} \rightarrow \text{Sr}^{2+} + 2e^{-}$ $\text{O}_2 + 4e^{-} \rightarrow 2\text{O}^{2-}$	O_2	Sr
(b)	$\text{Li} \rightarrow \text{Li}^{+} + e^{-}$ $\text{H}_2 + 2e^{-} \rightarrow 2\text{H}^{-}$	H_2	Li
(c)	$\text{Cs} \rightarrow \text{Cs}^{+} + e^{-}$ $\text{Br}_2 + 2e^{-} \rightarrow 2\text{Br}^{-}$	Br_2	Cs
(d)	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^{-}$ $\text{N}_2 + 6e^{-} \rightarrow 2\text{N}^{3-}$	N_2	Mg

- 4.40 Strategy:** In order to break a redox reaction down into an oxidation half-reaction and a reduction half-reaction, you should first assign oxidation numbers to all the atoms in the reaction. In this way, you can determine which element is oxidized (loses electrons) and which element is reduced (gains electrons).

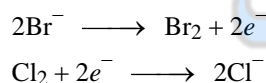
Solution: In each part, the reducing agent is the reactant in the first half-reaction and the oxidizing agent is the reactant in the second half-reaction. The coefficients in each half-reaction have been reduced to smallest whole numbers.

- (a) The product is an ionic compound whose ions are Fe^{3+} and O^{2-} .



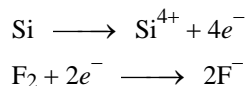
O_2 is the oxidizing agent; Fe is the reducing agent.

- (b) Na^{+} does not change in this reaction. It is a "spectator ion."



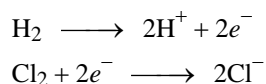
Cl_2 is the oxidizing agent; Br^{-} is the reducing agent.

- (c) Assume SiF_4 is made up of Si^{4+} and F^{-} .



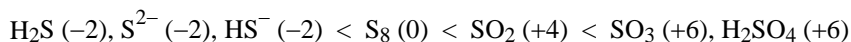
F_2 is the oxidizing agent; Si is the reducing agent.

- (d) Assume HCl is made up of H^{+} and Cl^{-} .



Cl_2 is the oxidizing agent; H_2 is the reducing agent.

- 4.41** The oxidation number for hydrogen is +1 (rule 4), and for oxygen is -2 (rule 3). The oxidation number for sulfur in S_8 is zero (rule 1). Remember that in a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero, and in an ion the sum of oxidation numbers of all elements in the ion must equal the net charge of the ion (rule 6).



The number in parentheses denotes the oxidation number of sulfur.

- 4.42 Strategy:** In general, we follow the rules listed in Section 4.4 of the text for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1 in ionic compounds, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2 in their compounds.

Solution: All the compounds listed are neutral compounds, so the oxidation numbers must sum to zero (Rule 6, Section 4.4 of the text).

Let the oxidation number of P = x .

- | | |
|-----------------------------------------|----------------------------------------------------|
| (a) $x + 1 + (3)(-2) = 0, x = +5$ | (d) $x + (3)(+1) + (4)(-2) = 0, x = +5$ |
| (b) $x + (3)(+1) + (2)(-2) = 0, x = +1$ | (e) $2x + (4)(+1) + (7)(-2) = 0, 2x = 10, x = +5$ |
| (c) $x + (3)(+1) + (3)(-2) = 0, x = +3$ | (f) $3x + (5)(+1) + (10)(-2) = 0, 3x = 15, x = +5$ |

The molecules in part (a), (e), and (f) can be made by strongly heating the compound in part (d). Are these oxidation-reduction reactions?

Check: In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species, in this case zero?

- 4.43** See Section 4.4 of the text.

- | | |
|------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| (a) $\underline{Cl}F$: F -1 (rule 5), Cl +1 (rule 6) | (b) $\underline{I}F_7$: F -1 (rule 5), I +7 (rules 5 and 6) |
| (c) $\underline{C}H_4$: H +1 (rule 4), C -4 (rule 6) | (d) \underline{C}_2H_2 : H +1 (rule 4), C -1 (rule 6) |
| (e) \underline{C}_2H_4 : H +1 (rule 4), C -2 (rule 6), | (f) $K_2\underline{Cr}O_4$: K +1 (rule 2), O -2 (rule 3), Cr +6 (rule 6) |
| (g) $K_2\underline{Cr}_2O_7$: K +1 (rule 2), O -2 (rule 3), Cr +6 (rule 6) | |
| (h) $K\underline{Mn}O_4$: K +1 (rule 2), O -2 (rule 3), Mn +7 (rule 6) | |
| (i) $NaH\underline{C}O_3$: Na +1 (rule 2), H +1 (rule 4), O -2 (rule 3), C +4 (rule 6) | |
| (j) \underline{Li}_2 : Li 0 (rule 1) | (k) $Na\underline{I}O_3$: Na +1 (rule 2), O -2 (rule 3), I +5 (rule 6) |
| (l) $K\underline{O}_2$: K +1 (rule 2), O -1/2 (rule 6) | (m) $\underline{P}F_6^-$: F -1 (rule 5), P +5 (rule 6) |
| (n) $K\underline{Au}Cl_4$: K +1 (rule 2), Cl -1 (rule 5), Au +3 (rule 6) | |

- 4.44** All are free elements, so all have an oxidation number of **zero**.

- | | | | | |
|-----------------------------------|------------------------------------|------------------------------------|---------------------------------|------------------------------|
| (a) \underline{Cs}_2O , +1 | (b) $Ca\underline{I}_2$, -1 | (c) \underline{Al}_2O_3 , +3 | (d) $H_3\underline{As}O_3$, +3 | (e) $\underline{Ti}O_2$, +4 |
| (f) $\underline{Mo}O_4^{2-}$, +6 | (g) $\underline{Pt}Cl_4^{2-}$, +2 | (h) $\underline{Pt}Cl_6^{2-}$, +4 | (i) $\underline{Sn}F_2$, +2 | (j) $\underline{Cl}F_3$, +3 |
| (k) $\underline{Sb}F_6^-$, +5 | | | | |

- | | | | |
|-----------|-------------|-----------|-----------|
| (a) N: -3 | (b) O: -1/2 | (c) C: -1 | (d) C: +4 |
| (e) C: +3 | (f) O: -2 | (g) B: +3 | (h) W: +6 |

4.47 If nitric acid is a strong oxidizing agent and zinc is a strong reducing agent, then zinc metal will probably reduce nitric acid when the two react; that is, N will gain electrons and the oxidation number of N must decrease. Since the oxidation number of nitrogen in nitric acid is +5 (verify!), then the nitrogen-containing product must have a smaller oxidation number for nitrogen. The only compound in the list that doesn't have a nitrogen oxidation number less than +5 is N_2O_5 , (what is the oxidation number of N in N_2O_5 ?). This is never a product of the reduction of nitric acid.

4.48 **Strategy:** *Hydrogen displacement:* Any metal above hydrogen in the activity series will displace it from water or from an acid. Metals below hydrogen will *not* react with either water or an acid.

Solution: Only (b) Li and (d) Ca are above hydrogen in the activity series, so they are the only metals in this problem that will react with water.

4.49 In order to work this problem, you need to assign the oxidation numbers to all the elements in the compounds. In each case oxygen has an oxidation number of -2 (rule 3). These oxidation numbers should then be compared to the range of possible oxidation numbers that each element can have. Molecular oxygen is a powerful oxidizing agent. In SO_3 alone, the oxidation number of the element bound to oxygen (S) is at its maximum value (+6); the sulfur cannot be oxidized further. The other elements bound to oxygen in this problem have less than their maximum oxidation number and can undergo further oxidation.

4.50 (a) $\text{Cu}(s) + \text{HCl}(aq) \rightarrow$ no reaction, since $\text{Cu}(s)$ is less reactive than the hydrogen from acids.

(b) $\text{I}_2(s) + \text{NaBr}(aq) \rightarrow$ no reaction, since $\text{I}_2(s)$ is less reactive than $\text{Br}_2(l)$.

(c) $\text{Mg}(s) + \text{CuSO}_4(aq) \rightarrow \text{MgSO}_4(aq) + \text{Cu}(s)$, since $\text{Mg}(s)$ is more reactive than $\text{Cu}(s)$.

Net ionic equation: $\text{Mg}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s)$

(d) $\text{Cl}_2(g) + 2\text{KBr}(aq) \rightarrow \text{Br}_2(l) + 2\text{KCl}(aq)$, since $\text{Cl}_2(g)$ is more reactive than $\text{Br}_2(l)$

Net ionic equation: $\text{Cl}_2(g) + 2\text{Br}^-(aq) \rightarrow 2\text{Cl}^-(aq) + \text{Br}_2(l)$

4.51 $\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$. Because moles of solute are in the equation, molarity is a convenient unit for performing solution stoichiometry calculations. Also, because the denominator is the volume of solution, it is easy to prepare a solution of a given molarity. See Figure 4.15 of the text.

4.52 The steps are shown in Figure 4.15 of the text.

4.53 First, calculate the moles of KI needed to prepare the solution.

$$\text{mol KI} = \frac{2.80 \text{ mol KI}}{1000 \text{ mL soln}} \times (5.00 \times 10^2 \text{ mL soln}) = 1.40 \text{ mol KI}$$

Converting to grams of KI:

$$1.40 \text{ mol KI} \times \frac{166.0 \text{ g KI}}{1 \text{ mol KI}} = 232 \text{ g KI}$$

4.54 **Strategy:** How many moles of NaNO_3 does 250 mL of a 0.707 M solution contain? How would you convert moles to grams?

Solution: From the molarity (0.707 *M*), we can calculate the moles of NaNO₃ needed to prepare 250 mL of solution.

$$\text{Moles NaNO}_3 = \frac{0.707 \text{ mol NaNO}_3}{1000 \text{ mL soln}} \times 250 \text{ mL soln} = 0.177 \text{ mol}$$

Next, we use the molar mass of NaNO₃ as a conversion factor to convert from moles to grams.

$\mathcal{M}(\text{NaNO}_3) = 85.00 \text{ g/mol}$.

$$0.177 \text{ mol NaNO}_3 \times \frac{85.00 \text{ g NaNO}_3}{1 \text{ mol NaNO}_3} = 15.0 \text{ g NaNO}_3$$

To make the solution, **dissolve 15.0 g of NaNO₃ in enough water to make 250 mL of solution.**

Check: As a ball-park estimate, the mass should be given by [molarity (mol/L) \times volume (L) = moles \times molar mass (g/mol) = grams]. Let's round the molarity to 1 *M* and the molar mass to 80 g, because we are simply making an estimate. This gives: [1 mol/L \times (1/4)L \times 80 g = 20 g]. This is close to our answer of 15.0 g.

4.55 $\text{mol} = M \times L$

$$60.0 \text{ mL} = 0.0600 \text{ L}$$

$$\text{mol MgCl}_2 = \frac{0.100 \text{ mol MgCl}_2}{1 \text{ L soln}} \times 0.0600 \text{ L soln} = \mathbf{6.00 \times 10^{-3} \text{ mol MgCl}_2}$$

4.56 Since the problem asks for grams of solute (KOH), you should be thinking that you can calculate moles of solute from the molarity and volume of solution. Then, you can convert moles of solute to grams of solute.

$$? \text{ moles KOH solute} = \frac{5.50 \text{ moles solute}}{1000 \text{ mL solution}} \times 35.0 \text{ mL solution} = 0.193 \text{ mol KOH}$$

The molar mass of KOH is 56.11 g/mol. Use this conversion factor to calculate grams of KOH.

$$? \text{ grams KOH} = 0.193 \text{ mol KOH} \times \frac{56.11 \text{ g KOH}}{1 \text{ mol KOH}} = \mathbf{10.8 \text{ g KOH}}$$

4.57 Molar mass of C₂H₅OH = 46.07 g/mol; molar mass of C₁₂H₂₂O₁₁ = 342.3 g/mol; molar mass of NaCl = 58.44 g/mol.

$$(a) \quad ? \text{ mol C}_2\text{H}_5\text{OH} = 29.0 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} = 0.629 \text{ mol C}_2\text{H}_5\text{OH}$$

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L of soln}} = \frac{0.629 \text{ mol C}_2\text{H}_5\text{OH}}{0.545 \text{ L soln}} = \mathbf{1.15 \text{ M}}$$

$$(b) \quad ? \text{ mol C}_{12}\text{H}_{22}\text{O}_{11} = 15.4 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = 0.0450 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$$

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L of soln}} = \frac{0.0450 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{74.0 \times 10^{-3} \text{ L soln}} = \mathbf{0.608 \text{ M}}$$

$$(c) \quad ? \text{ mol NaCl} = 9.00 \cancel{\text{g NaCl}} \times \frac{1 \text{ mol NaCl}}{58.44 \cancel{\text{g NaCl}}} = 0.154 \text{ mol NaCl}$$

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L of soln}} = \frac{0.154 \text{ mol NaCl}}{86.4 \times 10^{-3} \text{ L soln}} = \mathbf{1.78 \text{ M}}$$

$$\mathbf{4.58} \quad (a) \quad ? \text{ mol CH}_3\text{OH} = 6.57 \cancel{\text{g CH}_3\text{OH}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \cancel{\text{g CH}_3\text{OH}}} = 0.205 \text{ mol CH}_3\text{OH}$$

$$\mathbf{M} = \frac{0.205 \text{ mol CH}_3\text{OH}}{0.150 \text{ L}} = \mathbf{1.37 \text{ M}}$$

$$(b) \quad ? \text{ mol CaCl}_2 = 10.4 \cancel{\text{g CaCl}_2} \times \frac{1 \text{ mol CaCl}_2}{110.98 \cancel{\text{g CaCl}_2}} = 0.0937 \text{ mol CaCl}_2$$

$$\mathbf{M} = \frac{0.0937 \text{ mol CaCl}_2}{0.220 \text{ L}} = \mathbf{0.426 \text{ M}}$$

$$(c) \quad ? \text{ mol C}_{10}\text{H}_8 = 7.82 \cancel{\text{g C}_{10}\text{H}_8} \times \frac{1 \text{ mol C}_{10}\text{H}_8}{128.2 \cancel{\text{g C}_{10}\text{H}_8}} = 0.0610 \text{ mol C}_{10}\text{H}_8$$

$$\mathbf{M} = \frac{0.0610 \text{ mol C}_{10}\text{H}_8}{0.0852 \text{ L}} = \mathbf{0.716 \text{ M}}$$

4.59 First, calculate the moles of each solute. Then, you can calculate the volume (in L) from the molarity and the number of moles of solute.

$$(a) \quad ? \text{ mol NaCl} = 2.14 \cancel{\text{g NaCl}} \times \frac{1 \text{ mol NaCl}}{58.44 \cancel{\text{g NaCl}}} = 0.0366 \text{ mol NaCl}$$

$$\text{L soln} = \frac{\text{mol solute}}{\text{Molarity}} = \frac{0.0366 \cancel{\text{mol NaCl}}}{0.270 \cancel{\text{mol/L}}} = 0.136 \text{ L} = \mathbf{136 \text{ mL soln}}$$

$$(b) \quad ? \text{ mol C}_2\text{H}_5\text{OH} = 4.30 \cancel{\text{g C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \cancel{\text{g C}_2\text{H}_5\text{OH}}} = 0.0933 \text{ mol C}_2\text{H}_5\text{OH}$$

$$\text{L soln} = \frac{\text{mol solute}}{\text{Molarity}} = \frac{0.0933 \cancel{\text{mol C}_2\text{H}_5\text{OH}}}{1.50 \cancel{\text{mol/L}}} = 0.0622 \text{ L} = \mathbf{62.2 \text{ mL soln}}$$

$$(c) \quad ? \text{ mol CH}_3\text{COOH} = 0.85 \cancel{\text{g CH}_3\text{COOH}} \times \frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \cancel{\text{g CH}_3\text{COOH}}} = 0.014 \text{ mol CH}_3\text{COOH}$$

$$\text{L soln} = \frac{\text{mol solute}}{\text{Molarity}} = \frac{0.014 \cancel{\text{mol CH}_3\text{COOH}}}{0.30 \cancel{\text{mol/L}}} = 0.047 \text{ L} = \mathbf{47 \text{ mL soln}}$$

4.60 A 250 mL sample of 0.100 M solution contains 0.0250 mol of solute ($\text{mol} = M \times L$). The computation in each case is the same:

$$(a) \quad 0.0250 \cancel{\text{mol CsI}} \times \frac{259.8 \text{ g CsI}}{1 \cancel{\text{mol CsI}}} = \mathbf{6.50 \text{ g CsI}}$$

$$(b) \quad 0.0250 \cancel{\text{mol}} \text{H}_2\text{SO}_4 \times \frac{98.09 \text{ g H}_2\text{SO}_4}{1 \cancel{\text{mol}} \text{H}_2\text{SO}_4} = \mathbf{2.45 \text{ g H}_2\text{SO}_4}$$

$$(c) \quad 0.0250 \cancel{\text{mol}} \text{Na}_2\text{CO}_3 \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{1 \cancel{\text{mol}} \text{Na}_2\text{CO}_3} = \mathbf{2.65 \text{ g Na}_2\text{CO}_3}$$

$$(d) \quad 0.0250 \cancel{\text{mol}} \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g K}_2\text{Cr}_2\text{O}_7}{1 \cancel{\text{mol}} \text{K}_2\text{Cr}_2\text{O}_7} = \mathbf{7.36 \text{ g K}_2\text{Cr}_2\text{O}_7}$$

$$(e) \quad 0.0250 \cancel{\text{mol}} \text{KMnO}_4 \times \frac{158.04 \text{ g KMnO}_4}{1 \cancel{\text{mol}} \text{KMnO}_4} = \mathbf{3.95 \text{ g KMnO}_4}$$

4.61 A pipet is used to transfer a known amount of the solution to a volumetric flask. Water is then added to the mark on the flask to dilute the solution.

4.62 The equation is: $M_1V_1 = M_2V_2$. The units of molarity (M) are mol solute/L of solution. The units of volume (V) must be the same (usually mL or L).

4.63 $M_{\text{initial}}V_{\text{initial}} = M_{\text{final}}V_{\text{final}}$

You can solve the equation algebraically for V_{initial} . Then substitute in the given quantities to solve for the volume of 2.00 M HCl needed to prepare 1.00 L of a 0.646 M HCl solution.

$$V_{\text{initial}} = \frac{M_{\text{final}} \times V_{\text{final}}}{M_{\text{initial}}} = \frac{0.646 \cancel{M} \times 1.00 \text{ L}}{2.00 \cancel{M}} = \mathbf{0.323 \text{ L} = 323 \text{ mL}}$$

To prepare the 0.646 M solution, you would dilute 323 mL of the 2.00 M HCl solution to a final volume of 1.00 L.

4.64 Strategy: Because the volume of the final solution is greater than the original solution, this is a dilution process. Keep in mind that in a dilution, the concentration of the solution decreases, but the number of moles of the solute remains the same.

Solution: We prepare for the calculation by tabulating our data.

$$M_i = 0.866 \text{ M} \quad M_f = ?$$

$$V_i = 25.0 \text{ mL} \quad V_f = 500 \text{ mL}$$

We substitute the data into Equation (4.3) of the text.

$$M_iV_i = M_fV_f$$

$$(0.866 \text{ M})(25.0 \text{ mL}) = M_f(500 \text{ mL})$$

$$M_f = \frac{(0.866 \text{ M})(25.0 \cancel{\text{mL}})}{500 \cancel{\text{mL}}} = \mathbf{0.0433 \text{ M}}$$

4.65 $M_{\text{initial}}V_{\text{initial}} = M_{\text{final}}V_{\text{final}}$

You can solve the equation algebraically for V_{initial} . Then substitute in the given quantities to solve for the volume of 4.00 M HNO_3 needed to prepare 60.0 mL of a 0.200 M HNO_3 solution.

$$V_{\text{initial}} = \frac{M_{\text{final}} \times V_{\text{final}}}{M_{\text{initial}}} = \frac{0.200 \cancel{M} \times 60.00 \text{ mL}}{4.00 \cancel{M}} = \mathbf{3.00 \text{ mL}}$$

To prepare the 0.200 *M* solution, you would dilute 3.00 mL of the 4.00 *M* HNO₃ solution to a final volume of 60.0 mL.

- 4.66** You need to calculate the final volume of the dilute solution. Then, you can subtract 505 mL from this volume to calculate the amount of water that should be added. We assume that the volumes are additive.

$$V_{\text{final}} = \frac{M_{\text{initial}} V_{\text{initial}}}{M_{\text{final}}} = \frac{(0.125 \cancel{M})(505 \text{ mL})}{(0.100 \cancel{M})} = 631 \text{ mL}$$

$$(631 - 505) \text{ mL} = \mathbf{126 \text{ mL of water}}$$

- 4.67** Moles of KMnO₄ in the first solution:

$$\frac{1.66 \text{ mol}}{1000 \cancel{\text{mL}} \text{ soln}} \times 35.2 \cancel{\text{mL}} = 0.0584 \text{ mol KMnO}_4$$

Moles of KMnO₄ in the second solution:

$$\frac{0.892 \text{ mol}}{1000 \cancel{\text{mL}} \text{ soln}} \times 16.7 \cancel{\text{mL}} = 0.0149 \text{ mol KMnO}_4$$

The total volume is 35.2 mL + 16.7 mL = 51.9 mL. The concentration of the final solution is:

$$M = \frac{(0.0584 + 0.0149) \text{ mol}}{51.9 \times 10^{-3} \text{ L}} = \mathbf{1.41 \text{ M}}$$

- 4.68** Moles of calcium nitrate in the first solution:

$$\frac{0.568 \text{ mol}}{1000 \cancel{\text{mL}} \text{ soln}} \times 46.2 \cancel{\text{mL}} \text{ soln} = 0.0262 \text{ mol Ca(NO}_3)_2$$

Moles of calcium nitrate in the second solution:

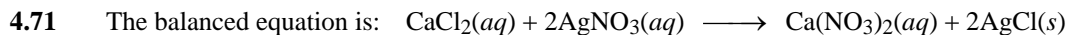
$$\frac{1.396 \text{ mol}}{1000 \cancel{\text{mL}} \text{ soln}} \times 80.5 \cancel{\text{mL}} \text{ soln} = 0.112 \text{ mol Ca(NO}_3)_2$$

The volume of the combined solutions = 46.2 mL + 80.5 mL = 126.7 mL. The concentration of the final solution is:

$$M = \frac{(0.0262 + 0.112) \text{ mol}}{0.1267 \text{ L}} = \mathbf{1.09 \text{ M}}$$

- 4.69** A sample of a substance of unknown composition is dissolved in water and allowed to react with another substance to form a precipitate. The precipitate is filtered off, dried, and weighed. Knowing the mass and chemical formula of the precipitate formed, we can calculate the mass of a particular chemical component (that is, the anion or cation) of the original sample. From the mass of the component and the mass of the original sample, we can determine the percent composition by mass of the component in the original compound.

- 4.70** Chloride ions are present in tap water and therefore distilled water must be used in gravimetric analysis of chlorides.



We need to determine the limiting reagent. Ag^+ and Cl^- combine in a 1:1 mole ratio to produce AgCl . Let's calculate the amount of Ag^+ and Cl^- in solution.

$$\text{mol Ag}^+ = \frac{0.100 \text{ mol Ag}^+}{1000 \text{ mL soln}} \times 15.0 \text{ mL soln} = 1.50 \times 10^{-3} \text{ mol Ag}^+$$

$$\text{mol Cl}^- = \frac{0.150 \text{ mol CaCl}_2}{1000 \text{ mL soln}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol CaCl}_2} \times 30.0 \text{ mL soln} = 9.00 \times 10^{-3} \text{ mol Cl}^-$$

Since Ag^+ and Cl^- combine in a 1:1 mole ratio, AgNO_3 is the limiting reagent. Only 1.50×10^{-3} mole of AgCl can form. Converting to grams of AgCl :

$$1.50 \times 10^{-3} \text{ mol AgCl} \times \frac{143.4 \text{ g AgCl}}{1 \text{ mol AgCl}} = \mathbf{0.215 \text{ g AgCl}}$$

4.72 Strategy: We want to calculate the mass % of Ba in the original compound. Let's start with the definition of mass %.

$$\text{mass \% Ba} = \frac{\text{mass Ba}}{\text{mass of sample}} \times 100\%$$

want to calculate need to find
 ↓ ↓
 mass % Ba mass Ba
 ↓
 mass of sample
 ↓
 given

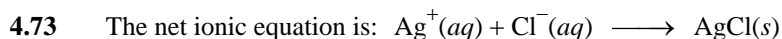
The mass of the sample is given in the problem (0.6760 g). Therefore we need to find the mass of Ba in the original sample. We assume the precipitation is quantitative, that is, that all of the barium in the sample has been precipitated as barium sulfate. From the mass of BaSO_4 produced, we can calculate the mass of Ba. There is 1 mole of Ba in 1 mole of BaSO_4 .

Solution: First, we calculate the mass of Ba in 0.4105 g of the BaSO_4 precipitate. The molar mass of BaSO_4 is 233.4 g/mol.

$$\begin{aligned} ? \text{ mass of Ba} &= 0.4105 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.4 \text{ g BaSO}_4} \times \frac{1 \text{ mol Ba}}{1 \text{ mol BaSO}_4} \times \frac{137.3 \text{ g Ba}}{1 \text{ mol Ba}} \\ &= 0.2415 \text{ g Ba} \end{aligned}$$

Next, we calculate the mass percent of Ba in the unknown compound.

$$\mathbf{\% \text{Ba by mass}} = \frac{0.2415 \text{ g}}{0.6760 \text{ g}} \times 100\% = \mathbf{35.72\%}$$



One mole of Cl^- is required per mole of Ag^+ . First, find the number of moles of Ag^+ .

$$\text{mol Ag}^+ = \frac{0.0113 \text{ mol Ag}^+}{1000 \text{ mL soln}} \times (2.50 \times 10^2 \text{ mL soln}) = 2.83 \times 10^{-3} \text{ mol Ag}^+$$

Now, calculate the mass of NaCl using the mole ratio from the balanced equation.

$$(2.83 \times 10^{-3} \cancel{\text{mol Ag}^+}) \times \frac{1 \cancel{\text{mol Cl}^-}}{1 \cancel{\text{mol Ag}^+}} \times \frac{1 \cancel{\text{mol NaCl}}}{1 \cancel{\text{mol Cl}^-}} \times \frac{58.44 \text{ g NaCl}}{1 \cancel{\text{mol NaCl}}} = \mathbf{0.165 \text{ g NaCl}}$$

4.74 The net ionic equation is: $\text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \longrightarrow \text{CuS}(\text{s})$

The answer sought is the molar concentration of Cu^{2+} , that is, moles of Cu^{2+} ions per liter of solution. The dimensional analysis method is used to convert, in order:

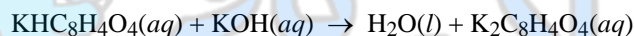
g of CuS \rightarrow moles CuS \rightarrow moles Cu^{2+} \rightarrow moles Cu^{2+} per liter soln

$$[\text{Cu}^{2+}] = 0.0177 \cancel{\text{g CuS}} \times \frac{1 \cancel{\text{mol CuS}}}{95.62 \cancel{\text{g CuS}}} \times \frac{1 \text{ mol Cu}^{2+}}{1 \cancel{\text{mol CuS}}} \times \frac{1}{0.800 \text{ L}} = \mathbf{2.31 \times 10^{-4} \text{ M}}$$

4.75 In a titration experiment, a solution of accurately known concentration, called a standard solution, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution. There are many chemistry applications that involve acid-base titrations.

4.76 Indicators are substances that have distinctly different colors in acidic and basic media.

4.77 The reaction between KHP ($\text{KHC}_8\text{H}_4\text{O}_4$) and KOH is:



We know the volume of the KOH solution, and we want to calculate the molarity of the KOH solution.

$$M \text{ of KOH} = \frac{\text{mol KOH}}{\text{L of KOH soln}}$$

want to calculate \swarrow \nwarrow need to find
 \nwarrow given

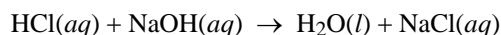
If we can determine the moles of KOH in the solution, we can then calculate the molarity of the solution. From the mass of KHP and its molar mass, we can calculate moles of KHP. Then, using the mole ratio from the balanced equation, we can calculate moles of KOH.

$$? \text{ mol KOH} = 0.4218 \cancel{\text{g KHP}} \times \frac{1 \cancel{\text{mol KHP}}}{204.2 \cancel{\text{g KHP}}} \times \frac{1 \text{ mol KOH}}{1 \cancel{\text{mol KHP}}} = 2.066 \times 10^{-3} \text{ mol KOH}$$

From the moles and volume of KOH, we calculate the molarity of the KOH solution.

$$M \text{ of KOH} = \frac{\text{mol KOH}}{\text{L of KOH soln}} = \frac{2.066 \times 10^{-3} \text{ mol KOH}}{18.68 \times 10^{-3} \text{ L soln}} = \mathbf{0.1106 \text{ M}}$$

4.78 The reaction between HCl and NaOH is:



We know the volume of the NaOH solution, and we want to calculate the molarity of the NaOH solution.

$$\begin{array}{ccc}
 \text{want to calculate} & & \text{need to find} \\
 \downarrow & & \downarrow \\
 M \text{ of NaOH} = \frac{\text{mol NaOH}}{\text{L of NaOH soln}} & & \\
 & \uparrow & \\
 & \text{given} &
 \end{array}$$

If we can determine the moles of NaOH in the solution, we can then calculate the molarity of the solution. From the volume and molarity of HCl, we can calculate moles of HCl. Then, using the mole ratio from the balanced equation, we can calculate moles of NaOH.

$$? \text{ mol NaOH} = 17.4 \text{ mL HCl} \times \frac{0.312 \text{ mol HCl}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} = 5.43 \times 10^{-3} \text{ mol NaOH}$$

From the moles and volume of NaOH, we calculate the molarity of the NaOH solution.

$$M \text{ of NaOH} = \frac{\text{mol NaOH}}{\text{L of NaOH soln}} = \frac{5.43 \times 10^{-3} \text{ mol NaOH}}{25.0 \times 10^{-3} \text{ L soln}} = \mathbf{0.217 \text{ M}}$$

- 4.79 (a)** In order to have the correct mole ratio to solve the problem, you must start with a balanced chemical equation.



From the molarity and volume of the HCl solution, you can calculate moles of HCl. Then, using the mole ratio from the balanced equation above, you can calculate moles of NaOH.

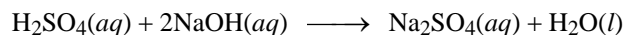
$$? \text{ mol NaOH} = 25.00 \text{ mL} \times \frac{2.430 \text{ mol HCl}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} = 6.075 \times 10^{-2} \text{ mol NaOH}$$

Solving for the volume of NaOH:

$$\text{liters of solution} = \frac{\text{moles of solute}}{M}$$

$$\mathbf{\text{volume of NaOH}} = \frac{6.075 \times 10^{-2} \text{ mol NaOH}}{1.420 \text{ mol/L}} = 4.278 \times 10^{-2} \text{ L} = \mathbf{42.78 \text{ mL}}$$

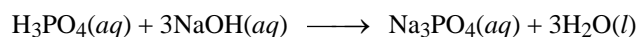
- (b)** This problem is similar to part (a). The difference is that the mole ratio between base and acid is 2:1.



$$? \text{ mol NaOH} = 25.00 \text{ mL} \times \frac{4.500 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} = 0.2250 \text{ mol NaOH}$$

$$\mathbf{\text{volume of NaOH}} = \frac{0.2250 \text{ mol NaOH}}{1.420 \text{ mol/L}} = 0.1585 \text{ L} = \mathbf{158.5 \text{ mL}}$$

- (c)** This problem is similar to parts (a) and (b). The difference is that the mole ratio between base and acid is 3:1.



$$? \text{ mol NaOH} = 25.00 \text{ mL} \times \frac{1.500 \text{ mol H}_3\text{PO}_4}{1000 \text{ mL soln}} \times \frac{3 \text{ mol NaOH}}{1 \text{ mol H}_3\text{PO}_4} = 0.1125 \text{ mol NaOH}$$

$$\text{volume of NaOH} = \frac{0.1125 \text{ mol NaOH}}{1.420 \text{ mol/L}} = 0.07923 \text{ L} = \mathbf{79.23 \text{ mL}}$$

4.80 Strategy: We know the molarity of the HCl solution, and we want to calculate the volume of the HCl solution.

$$M \text{ of HCl} = \frac{\text{mol HCl}}{\text{L of HCl soln}}$$

given need to find
 ↓ ↓
 want to calculate

If we can determine the moles of HCl, we can then use the definition of molarity to calculate the volume of HCl needed. From the volume and molarity of NaOH or Ba(OH)₂, we can calculate moles of NaOH or Ba(OH)₂. Then, using the mole ratio from the balanced equation, we can calculate moles of HCl.

Solution:

(a) In order to have the correct mole ratio to solve the problem, you must start with a balanced chemical equation.



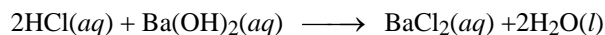
$$? \text{ mol HCl} = 10.0 \text{ mL} \times \frac{0.300 \text{ mol NaOH}}{1000 \text{ mL of solution}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 3.00 \times 10^{-3} \text{ mol HCl}$$

From the molarity and moles of HCl, we calculate volume of HCl required to neutralize the NaOH.

$$\text{liters of solution} = \frac{\text{moles of solute}}{M}$$

$$\text{volume of HCl} = \frac{3.00 \times 10^{-3} \text{ mol HCl}}{0.500 \text{ mol/L}} = \mathbf{6.00 \times 10^{-3} \text{ L} = 6.00 \text{ mL}}$$

(b) This problem is similar to part (a). The difference is that the mole ratio between acid and base is 2:1.



$$? \text{ mol HCl} = 10.0 \text{ mL} \times \frac{0.200 \text{ mol Ba}(\text{OH})_2}{1000 \text{ mL of solution}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Ba}(\text{OH})_2} = 4.00 \times 10^{-3} \text{ mol HCl}$$

$$\text{volume of HCl} = \frac{4.00 \times 10^{-3} \text{ mol HCl}}{0.500 \text{ mol/L}} = \mathbf{8.00 \times 10^{-3} \text{ L} = 8.00 \text{ mL}}$$

4.81 In redox reactions the oxidation numbers of elements change. To test whether an equation represents a redox process, assign the oxidation numbers to each of the elements in the reactants and products. If oxidation numbers change, it is a redox reaction.

- (a) On the left the oxidation number of chlorine in Cl_2 is zero (rule 1). On the right it is -1 in Cl^- (rule 2) and $+1$ in OCl^- (rules 3 and 5). Since chlorine is both oxidized and reduced, this is a disproportionation **redox reaction**.
- (b) The oxidation numbers of calcium and carbon do not change. This is not a redox reaction; it is a **precipitation reaction**.
- (c) The oxidation numbers of nitrogen and hydrogen do not change. This is not a redox reaction; it is an **acid-base reaction**.
- (d) The oxidation numbers of carbon, chlorine, chromium, and oxygen do not change. This is not a redox reaction; it doesn't fit easily into any category, but could be considered a **combination reaction**.
- (e) The oxidation number of calcium changes from 0 to $+2$, and the oxidation number of fluorine changes from 0 to -1 . This is a combination **redox reaction**.

The remaining parts (f) through (j) can be worked the same way.

(f) **Redox** (g) **Precipitation** (h) **Redox** (i) **Redox** (j) **Redox**

- 4.82** Since both of the original solutions were strong electrolytes, you would expect a mixture of the two solutions to also be a strong electrolyte. However, since the light dims, the mixture must contain fewer ions than the original solution. Indeed, H^+ from the sulfuric acid reacts with the OH^- from the barium hydroxide to form water. The barium cations react with the sulfate anions to form insoluble barium sulfate.

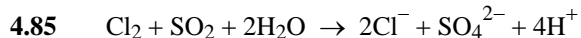


Thus, the reaction depletes the solution of ions and the conductivity decreases.

- 4.83** The three chemical tests might include:

- (1) Electrolysis to ascertain if hydrogen and oxygen were produced,
- (2) The reaction with an alkali metal to see if a base and hydrogen gas were produced, and
- (3) The dissolution of a metal oxide to see if a base was produced (or a nonmetal oxide to see if an acid was produced).

- 4.84** You could test the conductivity of the solutions. Sugar is a nonelectrolyte and an aqueous sugar solution will not conduct electricity; whereas, NaCl is a strong electrolyte when dissolved in water. Silver nitrate could be added to the solutions to see if silver chloride precipitated. In this particular case, the solutions could also be tasted.



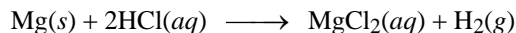
- 4.86** You would choose a more active metal than Al . Looking at the activity series (Figure 4.14 of the text), metals higher in the activity series than Al are Mg , Na , Ca , Ba , K , Li . All of these metals could be used to reduce Al^{3+} to Al .

- 4.87** First, the gases could be tested to see if they supported combustion. O_2 would support combustion, CO_2 would not. Second, if CO_2 is bubbled through a solution of calcium hydroxide $[\text{Ca}(\text{OH})_2]$, a white precipitate of CaCO_3 forms. No reaction occurs when O_2 is bubbled through a calcium hydroxide solution.

- 4.88** Using the rules of assigning oxidation numbers, we find that the oxidation number for C in CO_2 is $+4$, which is the maximum oxidation number that carbon can have. Thus it cannot be further oxidized and CO_2 will not burn. In contrast, the oxidation number of C in CO is $+2$. The carbon in CO can be further oxidized (to what?) and therefore will burn.

- 4.89** Choice **(d)**, $0.20\text{ M Mg(NO}_3)_2$, should be the best conductor of electricity; the total ion concentration in this solution is 0.60 M . The total ion concentrations for solutions **(a)** and **(c)** are 0.40 M and 0.50 M , respectively. We can rule out choice **(b)**, because acetic acid is a weak electrolyte.

- 4.90** Starting with a balanced chemical equation:



From the mass of Mg, you can calculate moles of Mg. Then, using the mole ratio from the balanced equation above, you can calculate moles of HCl reacted.

$$4.47\text{ g Mg} \times \frac{1\text{ mol Mg}}{24.31\text{ g Mg}} \times \frac{2\text{ mol HCl}}{1\text{ mol Mg}} = 0.368\text{ mol HCl reacted}$$

Next we can calculate the number of moles of HCl in the original solution.

$$\frac{2.00\text{ mol HCl}}{1000\text{ mL soln}} \times (5.00 \times 10^2\text{ mL}) = 1.00\text{ mol HCl}$$

$$\text{Moles HCl remaining} = 1.00\text{ mol} - 0.368\text{ mol} = 0.632\text{ mol HCl}$$

$$\text{conc. of HCl after reaction} = \frac{\text{mol HCl}}{\text{L soln}} = \frac{0.632\text{ mol HCl}}{0.500\text{ L}} = 1.26\text{ mol/L} = \mathbf{1.26\text{ M}}$$

- 4.91** We carry additional significant figures in this calculation to avoid rounding errors.

The balanced equation for the displacement reaction is:



The moles of CuSO_4 reacted with 7.89 g of zinc are:

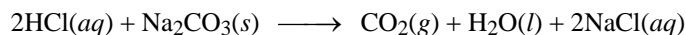
$$7.89\text{ g Zn} \times \frac{1\text{ mol Zn}}{65.39\text{ g Zn}} \times \frac{1\text{ mol CuSO}_4}{1\text{ mol Zn}} = 0.12066\text{ mol CuSO}_4$$

The volume of the 0.156 M CuSO_4 solution needed to react with 7.89 g Zn is:

$$\text{L of soln} = \frac{\text{mole solute}}{\text{M}} = \frac{0.12066\text{ mol CuSO}_4}{0.156\text{ mol/L}} = \mathbf{0.773\text{ L}}$$

Would you expect Zn to displace Cu^{2+} from solution, as shown in the equation?

- 4.92** The balanced equation is:



The mole ratio from the balanced equation is 2 moles HCl : 1 mole Na_2CO_3 . The moles of HCl needed to react with 0.256 g of Na_2CO_3 are:

$$0.256\text{ g Na}_2\text{CO}_3 \times \frac{1\text{ mol Na}_2\text{CO}_3}{105.99\text{ g Na}_2\text{CO}_3} \times \frac{2\text{ mol HCl}}{1\text{ mol Na}_2\text{CO}_3} = 4.83 \times 10^{-3}\text{ mol HCl}$$

$$\text{Molarity HCl} = \frac{\text{moles HCl}}{\text{L soln}} = \frac{4.83 \times 10^{-3}\text{ mol HCl}}{0.0283\text{ L soln}} = 0.171\text{ mol/L} = \mathbf{0.171\text{ M}}$$

4.93 The neutralization reaction is: $\text{HA}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaA}(aq) + \text{H}_2\text{O}(l)$

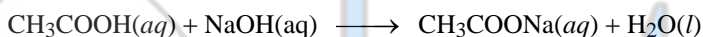
The mole ratio between the acid and NaOH is 1:1. The moles of HA that react with NaOH are:

$$20.27 \cancel{\text{mL}} \text{ soln} \times \frac{0.1578 \cancel{\text{mol}} \text{ NaOH}}{1000 \cancel{\text{mL}} \text{ soln}} \times \frac{1 \text{ mol HA}}{1 \cancel{\text{mol}} \text{ NaOH}} = 3.199 \times 10^{-3} \text{ mol HA}$$

3.664 g of the acid reacted with the base. The molar mass of the acid is:

$$\text{Molar mass} = \frac{3.664 \text{ g HA}}{3.199 \times 10^{-3} \text{ mol HA}} = \mathbf{1145 \text{ g/mol}}$$

4.94 Starting with a balanced chemical equation:



From the molarity and volume of the NaOH solution, you can calculate moles of NaOH. Then, using the mole ratio from the balanced equation above, you can calculate moles of CH_3COOH .

$$5.75 \cancel{\text{mL}} \text{ solution} \times \frac{1.00 \cancel{\text{mol}} \text{ NaOH}}{1000 \cancel{\text{mL}} \text{ of solution}} \times \frac{1 \text{ mol CH}_3\text{COOH}}{1 \cancel{\text{mol}} \text{ NaOH}} = 5.75 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$

$$\text{Molarity CH}_3\text{COOH} = \frac{5.75 \times 10^{-3} \text{ mol CH}_3\text{COOH}}{0.0500 \text{ L}} = \mathbf{0.115 \text{ M}}$$

4.95 The balanced equation is: $\text{Ba}(\text{OH})_2(aq) + \text{Na}_2\text{SO}_4(aq) \longrightarrow \text{BaSO}_4(s) + 2\text{NaOH}(aq)$

$$\text{moles Ba}(\text{OH})_2: (2.27 \cancel{\text{L}})(0.0820 \cancel{\text{mol}}/\cancel{\text{L}}) = 0.186 \text{ mol Ba}(\text{OH})_2$$

$$\text{moles Na}_2\text{SO}_4: (3.06 \text{ L})(0.0664 \text{ mol/L}) = 0.203 \text{ mol Na}_2\text{SO}_4$$

Since the mole ratio between $\text{Ba}(\text{OH})_2$ and Na_2SO_4 is 1:1, $\text{Ba}(\text{OH})_2$ is the limiting reagent. The mass of BaSO_4 formed is:

$$0.186 \cancel{\text{mol}} \text{ Ba}(\text{OH})_2 \times \frac{1 \cancel{\text{mol}} \text{ BaSO}_4}{1 \cancel{\text{mol}} \text{ Ba}(\text{OH})_2} \times \frac{233.4 \text{ g BaSO}_4}{1 \cancel{\text{mol}} \text{ BaSO}_4} = \mathbf{43.4 \text{ g BaSO}_4}$$

4.96 The balanced equation is: $2\text{HCl} + \text{Mg}(\text{OH})_2 \longrightarrow \text{MgCl}_2 + 2\text{H}_2\text{O}$

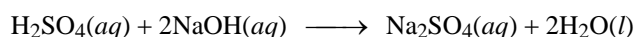
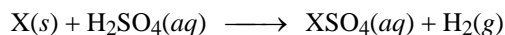
The moles of $\text{Mg}(\text{OH})_2$ in 10 mL of milk of magnesia are:

$$10 \cancel{\text{mL}} \text{ soln} \times \frac{0.080 \cancel{\text{g}} \text{ Mg}(\text{OH})_2}{1 \cancel{\text{mL}} \text{ soln}} \times \frac{1 \text{ mol Mg}(\text{OH})_2}{58.33 \cancel{\text{g}} \text{ Mg}(\text{OH})_2} = 0.014 \text{ mol Mg}(\text{OH})_2$$

$$\text{Moles of HCl reacted} = 0.014 \cancel{\text{mol}} \text{ Mg}(\text{OH})_2 \times \frac{2 \text{ mol HCl}}{1 \cancel{\text{mol}} \text{ Mg}(\text{OH})_2} = 0.028 \text{ mol HCl}$$

$$\text{Volume of HCl} = \frac{\text{mol solute}}{M} = \frac{0.028 \text{ mol HCl}}{0.035 \text{ mol/L}} = \mathbf{0.80 \text{ L}}$$

4.97 The balanced equations for the two reactions are:



First, let's find the number of moles of excess acid from the reaction with NaOH.

$$0.0334 \cancel{\text{L}} \times \frac{0.500 \cancel{\text{mol NaOH}}}{1 \cancel{\text{L soln}}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \cancel{\text{mol NaOH}}} = 8.35 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

The original number of moles of acid was:

$$0.100 \cancel{\text{L}} \times \frac{0.500 \text{ mol H}_2\text{SO}_4}{1 \cancel{\text{L soln}}} = 0.0500 \text{ mol H}_2\text{SO}_4$$

The amount of sulfuric acid that reacted with the metal, X, is:

$$(0.0500 \text{ mol H}_2\text{SO}_4) - (8.35 \times 10^{-3} \text{ mol H}_2\text{SO}_4) = 0.0417 \text{ mol H}_2\text{SO}_4.$$

Since the mole ratio from the balanced equation is 1 mole X : 1 mole H₂SO₄, then the amount of X that reacted is 0.0417 mole X.

$$\text{molar mass X} = \frac{1.00 \text{ g X}}{0.0417 \text{ mol X}} = \mathbf{24.0 \text{ g/mol}}$$

The element is **magnesium**.

4.98 First, calculate the number of moles of glucose present.

$$\frac{0.513 \text{ mol glucose}}{1000 \cancel{\text{mL soln}}} \times 60.0 \cancel{\text{mL}} = 0.0308 \text{ mol glucose}$$

$$\frac{2.33 \text{ mol glucose}}{1000 \cancel{\text{mL soln}}} \times 120.0 \cancel{\text{mL}} = 0.280 \text{ mol glucose}$$

Add the moles of glucose, then divide by the total volume of the combined solutions to calculate the molarity.

$$60.0 \text{ mL} + 120.0 \text{ mL} = 180.0 \text{ mL} = 0.180 \text{ L}$$

$$\text{Molarity of final solution} = \frac{(0.0308 + 0.280) \text{ mol glucose}}{0.180 \text{ L}} = 1.73 \text{ mol/L} = \mathbf{1.73 \text{ M}}$$

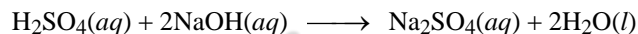
- 4.99**
- (a) Check with litmus paper, react with carbonate or bicarbonate to see if CO₂ gas is produced, react with a base and check with an indicator.
 - (b) Titrate a known quantity of acid with a standard NaOH solution. Since it is a monoprotic acid, the moles of NaOH reacted equals the moles of the acid. Dividing the mass of acid by the number of moles gives the molar mass of the acid.
 - (c) Visually compare the conductivity of the acid with a standard NaCl solution of the same molar concentration. A strong acid will have a similar conductivity to the NaCl solution. The conductivity of a weak acid will be considerably less than the NaCl solution.

- 4.100** The solid sodium bicarbonate would be the better choice. The hydrogen carbonate ion, HCO_3^- , behaves as a Brønsted base to accept a proton from the acid.



The heat generated during the reaction of hydrogen carbonate with the acid causes the carbonic acid, H_2CO_3 , that was formed to decompose to water and carbon dioxide.

The reaction of the spilled sulfuric acid with sodium hydroxide would produce sodium sulfate, Na_2SO_4 , and water. There is a possibility that the Na_2SO_4 could precipitate. Also, the sulfate ion, SO_4^{2-} is a weak base; therefore, the “neutralized” solution would actually be *basic*.

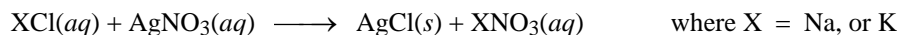


Also, NaOH is a caustic substance and therefore is not safe to use in this manner.

- 4.101**
- (a) Table salt, NaCl, is very soluble in water and is a strong electrolyte. Addition of AgNO_3 will precipitate AgCl.
 - (b) Table sugar or sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is soluble in water and is a nonelectrolyte.
 - (c) Aqueous acetic acid, CH_3COOH , the primary ingredient of vinegar, is a weak electrolyte. It exhibits all of the properties of acids (Section 4.3 of the text).
 - (d) Baking soda, NaHCO_3 , is a water-soluble strong electrolyte. It reacts with acid to release CO_2 gas. Addition of $\text{Ca}(\text{OH})_2$ results in the precipitation of CaCO_3 .
 - (e) Washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, is a water soluble strong electrolyte. It reacts with acids to release CO_2 gas. Addition of a soluble alkaline-earth salt will precipitate the alkaline-earth carbonate. Aqueous washing soda is also slightly basic (Section 4.3 of the text).
 - (f) Boric acid, H_3BO_3 , is weak electrolyte and a weak acid.
 - (g) Epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, is a water soluble strong electrolyte. Addition of $\text{Ba}(\text{NO}_3)_2$ results in the precipitation of BaSO_4 . Addition of hydroxide precipitates $\text{Mg}(\text{OH})_2$.
 - (h) Sodium hydroxide, NaOH, is a strong electrolyte and a strong base. Addition of $\text{Ca}(\text{NO}_3)_2$ results in the precipitation of $\text{Ca}(\text{OH})_2$.
 - (i) Ammonia, NH_3 , is a sharp-odored gas that when dissolved in water is a weak electrolyte and a weak base. NH_3 in the gas phase reacts with HCl gas to produce solid NH_4Cl .
 - (j) Milk of magnesia, $\text{Mg}(\text{OH})_2$, is an insoluble, strong base that reacts with acids. The resulting magnesium salt may be soluble or insoluble.
 - (k) CaCO_3 is an insoluble salt that reacts with acid to release CO_2 gas.

With the exception of NH_3 and vinegar, all the compounds in this problem are white solids.

- 4.102** We carry an additional significant figure throughout this calculation to minimize rounding errors. The balanced equation for the reaction is:



From the amount of AgCl produced, we can calculate the moles of XCl reacted (X = Na, or K).

$$1.913 \cancel{\text{g AgCl}} \times \frac{1 \cancel{\text{mol AgCl}}}{143.35 \cancel{\text{g AgCl}}} \times \frac{1 \text{ mol XCl}}{1 \cancel{\text{mol AgCl}}} = 0.013345 \text{ mol XCl}$$

Let x = number of moles NaCl. Then, the number of moles of KCl = $0.013345 \text{ mol} - x$. The sum of the NaCl and KCl masses must equal the mass of the mixture, 0.8870 g. We can write:

$$\text{mass NaCl} + \text{mass KCl} = 0.8870 \text{ g}$$

$$\left[x \cancel{\text{mol NaCl}} \times \frac{58.44 \text{ g NaCl}}{1 \cancel{\text{mol NaCl}}} \right] + \left[(0.013345 - x) \cancel{\text{mol KCl}} \times \frac{74.55 \text{ g KCl}}{1 \cancel{\text{mol KCl}}} \right] = 0.8870 \text{ g}$$

$$x = 6.6958 \times 10^{-3} = \text{moles NaCl}$$

$$\text{mol KCl} = 0.013345 - x = 0.013345 \text{ mol} - (6.6958 \times 10^{-3} \text{ mol}) = 6.6492 \times 10^{-3} \text{ mol KCl}$$

Converting moles to grams:

$$\text{mass NaCl} = (6.6958 \times 10^{-3} \cancel{\text{mol NaCl}}) \times \frac{58.44 \text{ g NaCl}}{1 \cancel{\text{mol NaCl}}} = 0.3913 \text{ g NaCl}$$

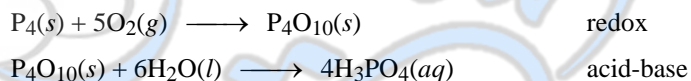
$$\text{mass KCl} = (6.6492 \times 10^{-3} \cancel{\text{mol KCl}}) \times \frac{74.55 \text{ g KCl}}{1 \cancel{\text{mol KCl}}} = 0.4957 \text{ g KCl}$$

The percentages by mass for each compound are:

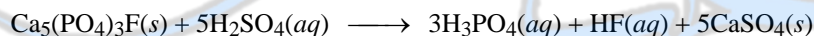
$$\% \text{ NaCl} = \frac{0.3913 \text{ g}}{0.8870 \text{ g}} \times 100\% = \mathbf{44.11\% \text{ NaCl}}$$

$$\% \text{ KCl} = \frac{0.4957 \text{ g}}{0.8870 \text{ g}} \times 100\% = \mathbf{55.89\% \text{ KCl}}$$

4.103 Electric furnace method:

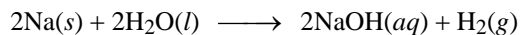


Wet process:



This is a precipitation and an acid-base reaction.

- 4.104** (a) The precipitate CaSO_4 formed over Ca preventing the Ca from reacting with the sulfuric acid.
 (b) Aluminum is protected by a tenacious oxide layer with the composition Al_2O_3 .
 (c) These metals react more readily with water.



- (d) The metal should be placed below Fe and above H.

- 4.105** Metals that can have more than *one* oxidation state are more likely to participate in redox reactions of biological systems. Of the choices given, the metals that can have more than one oxidation state are: **Mn, Fe, Co, and Cu**. The only oxidation state of Na and K is +1, and the only oxidation state of Mg, Ca, and Zn is +2.

4.106 (a)**First Solution:**

$$0.8214 \cancel{\text{g KMnO}_4} \times \frac{1 \text{ mol KMnO}_4}{158.04 \cancel{\text{g KMnO}_4}} = 5.197 \times 10^{-3} \text{ mol KMnO}_4$$

$$M = \frac{\text{mol solute}}{\text{L of soln}} = \frac{5.197 \times 10^{-3} \text{ mol KMnO}_4}{0.5000 \text{ L}} = 1.039 \times 10^{-2} M$$

Second Solution:

$$M_1 V_1 = M_2 V_2$$

$$(1.039 \times 10^{-2} M)(2.000 \text{ mL}) = M_2(1000 \text{ mL})$$

$$M_2 = 2.078 \times 10^{-5} M$$

Third Solution:

$$M_1 V_1 = M_2 V_2$$

$$(2.078 \times 10^{-5} M)(10.00 \text{ mL}) = M_2(250.0 \text{ mL})$$

$$M_2 = 8.312 \times 10^{-7} M$$

- (b)** From the molarity and volume of the final solution, we can calculate the moles of KMnO_4 . Then, the mass can be calculated from the moles of KMnO_4 .

$$\frac{8.312 \times 10^{-7} \text{ mol KMnO}_4}{1000 \cancel{\text{ mL of soln}}} \times 250 \cancel{\text{ mL}} = 2.078 \times 10^{-7} \text{ mol KMnO}_4$$

$$2.078 \times 10^{-7} \cancel{\text{ mol KMnO}_4} \times \frac{158.04 \text{ g KMnO}_4}{1 \cancel{\text{ mol KMnO}_4}} = 3.284 \times 10^{-5} \text{ g KMnO}_4$$

This mass is too small to directly weigh accurately.

4.107 There are two moles of Cl^- per one mole of CaCl_2 .

$$\text{(a)} \quad 25.3 \cancel{\text{ g CaCl}_2} \times \frac{1 \cancel{\text{ mol CaCl}_2}}{110.98 \cancel{\text{ g CaCl}_2}} \times \frac{2 \text{ mol Cl}^-}{1 \cancel{\text{ mol CaCl}_2}} = 0.456 \text{ mol Cl}^-$$

$$\text{Molarity Cl}^- = \frac{0.456 \text{ mol Cl}^-}{0.325 \text{ L soln}} = 1.40 \text{ mol/L} = \mathbf{1.40 M}$$

- (b)** We need to convert from mol/L to grams in 0.100 L.

$$\frac{1.40 \cancel{\text{ mol Cl}^-}}{1 \cancel{\text{ L soln}}} \times \frac{35.45 \text{ g Cl}}{1 \cancel{\text{ mol Cl}^-}} \times 0.100 \cancel{\text{ L soln}} = \mathbf{4.96 \text{ g Cl}^-}$$

4.108 Since aspirin is a monoprotic acid, it will react with NaOH in a 1:1 mole ratio.

First, calculate the moles of aspirin in the tablet.

$$12.25 \cancel{\text{ mL soln}} \times \frac{0.1466 \cancel{\text{ mol NaOH}}}{1000 \cancel{\text{ mL soln}}} \times \frac{1 \text{ mol aspirin}}{1 \cancel{\text{ mol NaOH}}} = 1.796 \times 10^{-3} \text{ mol aspirin}$$

Next, convert from moles of aspirin to grains of aspirin.

$$1.796 \times 10^{-3} \cancel{\text{mol aspirin}} \times \frac{180.2 \cancel{\text{g aspirin}}}{1 \cancel{\text{mol aspirin}}} \times \frac{1 \text{ grain}}{0.0648 \cancel{\text{g}}} = \mathbf{4.99 \text{ grains aspirin in one tablet}}$$

4.109 (a) The balanced equations are:

- | | |
|-------------------------------------------------------------------------------------------------------------------------------|---------------|
| 1. $\text{Cu}(s) + 4\text{HNO}_3(aq) \longrightarrow \text{Cu}(\text{NO}_3)_2(aq) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}(l)$ | Redox |
| 2. $\text{Cu}(\text{NO}_3)_2(aq) + 2\text{NaOH}(aq) \longrightarrow \text{Cu}(\text{OH})_2(s) + 2\text{NaNO}_3(aq)$ | Precipitation |
| 3. $\text{Cu}(\text{OH})_2(s) \xrightarrow{\text{heat}} \text{CuO}(s) + \text{H}_2\text{O}(g)$ | Decomposition |
| 4. $\text{CuO}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{CuSO}_4(aq) + \text{H}_2\text{O}(l)$ | Acid-Base |
| 5. $\text{CuSO}_4(aq) + \text{Zn}(s) \longrightarrow \text{Cu}(s) + \text{ZnSO}_4(aq)$ | Redox |
| 6. $\text{Zn}(s) + 2\text{HCl}(aq) \longrightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$ | Redox |

(b) We start with 65.6 g Cu which is $65.6 \cancel{\text{g Cu}} \times \frac{1 \text{ mol Cu}}{63.55 \cancel{\text{g Cu}}} = 1.03 \text{ mol Cu}$. The mole ratio between product and reactant in each reaction is 1:1. Therefore, the theoretical yield in each reaction is 1.03 moles.

- 1) $1.03 \cancel{\text{mol}} \times \frac{187.57 \text{ g Cu}(\text{NO}_3)_2}{1 \cancel{\text{mol Cu}(\text{NO}_3)_2}} = \mathbf{193 \text{ g Cu}(\text{NO}_3)_2}$
- 2) $1.03 \text{ mol} \times \frac{97.57 \text{ g Cu}(\text{OH})_2}{1 \text{ mol Cu}(\text{OH})_2} = \mathbf{1.00 \times 10^2 \text{ g Cu}(\text{OH})_2}$
- 3) $1.03 \text{ mol} \times \frac{79.55 \text{ g CuO}}{1 \text{ mol CuO}} = \mathbf{81.9 \text{ g CuO}}$
- 4) $1.03 \text{ mol} \times \frac{159.62 \text{ g CuSO}_4}{1 \text{ mol CuSO}_4} = \mathbf{164 \text{ g CuSO}_4}$
- 5) $1.03 \text{ mol} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = \mathbf{65.5 \text{ g Cu}}$

(c) All of the reaction steps are clean and almost quantitative; therefore, the recovery yield should be high.

4.110 (a) $\text{NH}_4^+(aq) + \text{OH}^-(aq) \longrightarrow \text{NH}_3(aq) + \text{H}_2\text{O}(l)$

(b) From the amount of NaOH needed to neutralize the 0.2041 g sample, we can find the amount of the 0.2041 g sample that is NH_4NO_3 .

First, calculate the moles of NaOH.

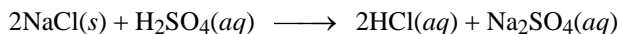
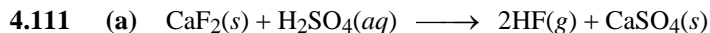
$$\frac{0.1023 \text{ mol NaOH}}{1000 \cancel{\text{mL of soln}}} \times 24.42 \cancel{\text{mL soln}} = 2.498 \times 10^{-3} \text{ mol NaOH}$$

Using the mole ratio from the balanced equation, we can calculate the amount of NH_4NO_3 that reacted.

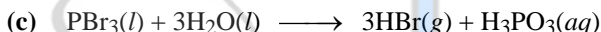
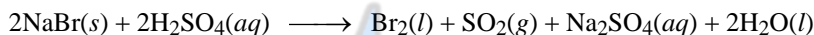
$$(2.498 \times 10^{-3} \cancel{\text{mol NaOH}}) \times \frac{1 \cancel{\text{mol NH}_4\text{NO}_3}}{1 \cancel{\text{mol NaOH}}} \times \frac{80.05 \text{ g NH}_4\text{NO}_3}{1 \cancel{\text{mol NH}_4\text{NO}_3}} = 0.2000 \text{ g NH}_4\text{NO}_3$$

The purity of the NH_4NO_3 sample is:

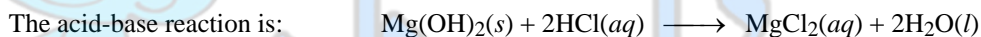
$$\% \text{ purity} = \frac{0.2000 \text{ g}}{0.2041 \text{ g}} \times 100\% = 97.99\%$$



(b) HBr and HI **cannot** be prepared similarly, because Br^- and I^- would be oxidized to the element, Br_2 and I_2 , respectively.



4.112 Because the volume of the solution changes (increases or decreases) when the solid dissolves.



(b) NaOH is much more expensive than CaO .

(c) Dolomite has the advantage of being an additional source of magnesium that can also be recovered.

(d) It is less expensive to “mine” magnesium metal from the ocean than from Earth’s crust. Also, it is less destructive, because you do not have to dig a mine to obtain the mineral.

4.114 To determine the formula of the iron chloride hydrate, we need to calculate the moles of each component in the compound (Fe , Cl , and H_2O). The subscripts in a chemical formula represent the mole ratio of the components in the compound.

First, we determine the moles of H_2O in the hydrate.

$$\text{mass H}_2\text{O} = 5.012 \text{ g} - 3.195 \text{ g} = 1.817 \text{ g}$$

$$\text{mol H}_2\text{O} = 1.817 \cancel{\text{g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \cancel{\text{g H}_2\text{O}}} = 0.1008 \text{ mol}$$

Next, from the mass of the AgCl precipitate, we can determine the moles of Cl and then the mass of Cl in the iron chloride hydrate.

$$7.225 \cancel{\text{g AgCl}} \times \frac{1 \cancel{\text{mol AgCl}}}{143.4 \cancel{\text{g AgCl}}} \times \frac{1 \text{ mol Cl}}{1 \cancel{\text{mol AgCl}}} = 0.05038 \cancel{\text{mol Cl}} \times \frac{35.45 \text{ g Cl}}{1 \cancel{\text{mol Cl}}} = 1.786 \text{ g Cl}$$

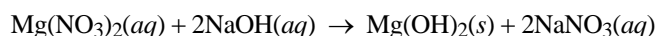
Subtracting the mass of Cl from the mass of the anhydrous compound will give the mass of iron in the compound. We can then convert to moles of iron.

$$\text{mass Fe} = 3.195 \text{ g} - 1.786 \text{ g} = 1.409 \text{ g Fe}$$

$$\text{mol Fe} = 1.409 \cancel{\text{g Fe}} \times \frac{1 \text{ mol Fe}}{55.85 \cancel{\text{g Fe}}} = 0.02523 \text{ mol}$$

This gives the formula, $\text{Fe}_{0.02523}\text{Cl}_{0.05038} \cdot 0.1008 \text{H}_2\text{O}$, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers. Dividing by the smallest number of moles (0.02523) gives the formula, **$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$** .

4.115 The reaction between $\text{Mg}(\text{NO}_3)_2$ and NaOH is:



Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, precipitates from solution. Na^+ and NO_3^- are spectator ions. This is most likely a limiting reagent problem as the amounts of both reactants are given. Let's first determine which reactant is the limiting reagent before we try to determine the concentration of ions remaining in the solution.

$$1.615 \cancel{\text{g Mg}(\text{NO}_3)_2} \times \frac{1 \text{ mol Mg}(\text{NO}_3)_2}{148.33 \cancel{\text{g Mg}(\text{NO}_3)_2}} = 0.01089 \text{ mol Mg}(\text{NO}_3)_2$$

$$1.073 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 0.02683 \text{ mol NaOH}$$

From the balanced equation, we need twice as many moles of NaOH compared to $\text{Mg}(\text{NO}_3)_2$. We have more than twice as much NaOH ($2 \times 0.01089 \text{ mol} = 0.02178 \text{ mol}$) and therefore $\text{Mg}(\text{NO}_3)_2$ is the limiting reagent. NaOH is in excess and ions of Na^+ , OH^- , and NO_3^- will remain in solution. Because Na^+ and NO_3^- are spectator ions, the number of moles after reaction will equal the initial number of moles. The excess moles of OH^- need to be calculated based on the amount that reacts with Mg^{2+} . The combined volume of the two solutions is: $22.02 \text{ mL} + 28.64 \text{ mL} = 50.66 \text{ mL} = 0.05066 \text{ L}$.

$$[\text{Na}^+] = 0.02683 \cancel{\text{mol NaOH}} \times \frac{1 \text{ mol Na}^+}{1 \cancel{\text{mol NaOH}}} \times \frac{1}{0.05066 \text{ L}} = \mathbf{0.5296 \text{ M}}$$

$$[\text{NO}_3^-] = 0.01089 \text{ mol Mg}(\text{NO}_3)_2 \times \frac{2 \text{ mol NO}_3^-}{1 \text{ mol Mg}(\text{NO}_3)_2} \times \frac{1}{0.05066 \text{ L}} = \mathbf{0.4299 \text{ M}}$$

The moles of OH^- reacted are:

$$0.01089 \cancel{\text{mol Mg}^{2+}} \times \frac{2 \text{ mol OH}^-}{1 \cancel{\text{mol Mg}^{2+}}} = 0.02178 \text{ mol OH}^- \text{ reacted}$$

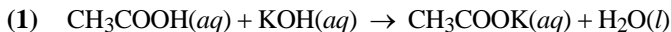
The moles of excess OH^- are:

$$0.02683 \text{ mol} - 0.02178 \text{ mol} = 0.00505 \text{ mol OH}^-$$

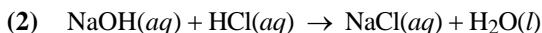
$$[\text{OH}^-] = \frac{0.00505 \text{ mol}}{0.05066 \text{ L}} = \mathbf{0.0997 \text{ M}}$$

The concentration of Mg^{2+} is approximately zero as almost all of it will precipitate as $\text{Mg}(\text{OH})_2$.

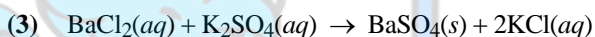
4.116 Let's set up a table showing each reaction, the volume of solution added, and the species responsible for any electrical conductance of the solution. Note that if a substance completely dissociates into +1 ions and -1 ions in solution, its conductance unit will be twice its molarity. Similarly, if a substance completely dissociates into +2 ions and -2 ions in solution, its conductance unit will be four times its molarity.



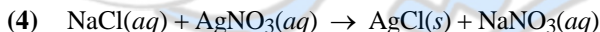
<u>Volume (added)</u>	<u>Conductance unit</u>	
0 L, KOH	$[\text{CH}_3\text{COOH}] = 1.0 \text{ M}$, (negligible ions, weak acid)	0 unit
1 L, KOH	$[\text{CH}_3\text{COOK}] = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M}$, $(\text{CH}_3\text{COO}^-, \text{K}^+)$	1 unit
2 L, KOH	$[\text{CH}_3\text{COOK}] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $[\text{KOH}] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $(\text{K}^+, \text{OH}^-)$	1.3 units



<u>Volume (added)</u>	<u>Conductance unit</u>	
0 L, NaOH	$[\text{HCl}] = 1.0 \text{ M}$, $(\text{H}^+, \text{Cl}^-)$	2 units
1 L, NaOH	$[\text{NaCl}] = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M}$, $(\text{Na}^+, \text{Cl}^-)$	1 unit
2 L, NaOH	$[\text{NaCl}] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $[\text{NaOH}] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $(\text{Na}^+, \text{OH}^-)$	1.3 units



<u>Volume (added)</u>	<u>Conductance unit</u>	
0 L, BaCl_2	$[\text{K}_2\text{SO}_4] = 1.0 \text{ M}$, $(2\text{K}^+, \text{SO}_4^{2-})$	4 units
1 L, BaCl_2	$[\text{KCl}] = \frac{2.0 \text{ mol}}{2.0 \text{ L}} = 1.0 \text{ M}$, $(\text{K}^+, \text{Cl}^-)$	2 units
2 L, BaCl_2	$[\text{KCl}] = \frac{2.0 \text{ mol}}{3.0 \text{ L}} = \frac{2}{3} \text{ M}$, $[\text{BaCl}_2] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $(\text{Ba}^{2+}, 2\text{Cl}^-)$	2.7 units



<u>Volume (added)</u>	<u>Conductance unit</u>	
0 L, NaCl	$[\text{AgNO}_3] = 1.0 \text{ M}$, $(\text{Ag}^+, \text{NO}_3^-)$	2 units
1 L, NaCl	$[\text{NaNO}_3] = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M}$, $(\text{Na}^+, \text{NO}_3^-)$	1 unit
2 L, NaCl	$[\text{NaNO}_3] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $[\text{NaCl}] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$, $(\text{Na}^+, \text{Cl}^-)$	1.3 units



<u>Volume (added)</u>	<u>Conductance unit</u>	
0 L, CH_3COOH	$[\text{NH}_3] = 1.0 \text{ M}$, (negligible ions, weak base)	0 unit
1 L, CH_3COOH	$[\text{CH}_3\text{COONH}_4] = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M}$, $(\text{CH}_3\text{COO}^-, \text{NH}_4^+)$	1 unit
2 L, CH_3COOH	$[\text{CH}_3\text{COONH}_4] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = \frac{1}{3} \text{ M}$	0.67 unit

Matching this data to the diagrams shown, we find:

Diagram (a): Reactions (2) and (4)

Diagram (c): Reaction (3)

Diagram (b): Reaction (5)

Diagram (d): Reaction (1)

CHAPTER 6

ENERGY RELATIONSHIPS IN CHEMICAL REACTIONS

- 6.1** The system is the specific part of the universe that is of interest to us. The surroundings are the rest of the universe outside the system. An open system can exchange mass and energy, usually in the form of heat with its surroundings. A closed system allows the transfer of energy (heat) but not mass. An isolated system does not allow the transfer of either mass or energy. Thermal energy is the energy associated with the random motion of atoms and molecules. Chemical energy is stored within the structural units of chemical substances. Potential energy is energy available by virtue of an object's position. Kinetic energy is the energy produced by a moving object. The law of conservation of energy states that the total quantity of energy in the universe is assumed constant.
- 6.2** Heat is the transfer of thermal energy between two bodies that are at different temperatures. Thermal energy is the energy associated with the random motion of atoms and molecules.
- 6.3** The units of energy commonly employed in chemistry are the Joule (J) and the kilojoule (kJ).
- 6.4** No, the kinetic energy of motion is converted to heat through the friction between the brakes, wheels, tires, and the road.
- 6.5** Turning on a flashlight converts chemical energy to electrical energy to electromagnetic energy, which includes visible light and infrared (heat) radiation.
- 6.6**
- (a) Mechanical energy to potential energy to kinetic energy.
 - (b) Chemical energy to electrical energy to electromagnetic energy.
 - (c) Mechanical energy to potential energy to kinetic energy.
 - (d) Chemical energy to thermal energy
- 6.7** Thermochemistry is the study of heat change in chemical reactions. An exothermic process is any process that gives off heat—that is, transfers thermal energy to the surroundings. In an endothermic process, heat has to be supplied to the system by the surroundings.
- 6.8** The law of conservation of energy.
- 6.9** The combustion of methane and the freezing of water are exothermic processes. The decomposition of limestone (CaCO_3) and the vaporization of water are endothermic processes.
- 6.10** To decompose a substance, bonds must be broken (an endothermic process). In combination reactions, bonds are formed (an exothermic process).
- 6.11** The first law of thermodynamics is based on the law of conservation of energy. The sign conventions for q and w are as follows: q is positive for an endothermic process and negative for an exothermic process, and w is positive for work done on the system by the surroundings and negative for work done by the system on the surroundings.

- 6.12** State functions are properties that are determined by the state of the system, regardless of how that condition was achieved. Energy and temperature are state functions. Work and heat are not state functions.
- 6.13** (a) Yes. (b) $q > 0$. Heat absorbed by the gas from the surroundings enables the gas to expand at constant temperature. (c) $\Delta U = 0$. Note that the internal energy of an ideal gas depends only on temperature. Because there is no change in temperature, there is no change in internal energy of the gas.
- 6.14** In (a) and (c), work is done by the system on the surroundings. In (b), work is done by the surroundings on the system. In (d), no work is done.
- 6.15** Recall that the work in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

(a) $w = -P\Delta V$

$$w = -(0)(5.4 - 1.6)\text{L} = 0$$

(b) $w = -P\Delta V$

$$w = -(0.80\text{ atm})(5.4 - 1.6)\text{L} = -3.0\text{ L}\cdot\text{atm}$$

To convert the answer to joules, we write

$$w = -3.0\cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\text{ J}}{1\cancel{\text{L}}\cdot\cancel{\text{atm}}} = -3.0 \times 10^2\text{ J}$$

(c) $w = -P\Delta V$

$$w = -(3.7\text{ atm})(5.4 - 1.6)\text{L} = -14\text{ L}\cdot\text{atm}$$

To convert the answer to joules, we write

$$w = -14\cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\text{ J}}{1\cancel{\text{L}}\cdot\cancel{\text{atm}}} = -1.4 \times 10^3\text{ J}$$

- 6.16** (a) Because the external pressure is zero, no work is done in the expansion.

$$w = -P\Delta V = -(0)(89.3 - 26.7)\text{mL}$$

$$w = 0$$

- (b) The external, opposing pressure is 1.5 atm, so

$$w = -P\Delta V = -(1.5\text{ atm})(89.3 - 26.7)\text{mL}$$

$$w = -94\cancel{\text{mL}}\cdot\cancel{\text{atm}} \times \frac{0.001\text{ L}}{1\cancel{\text{mL}}} = -0.094\text{ L}\cdot\text{atm}$$

To convert the answer to joules, we write:

$$w = -0.094\cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\text{ J}}{1\cancel{\text{L}}\cdot\cancel{\text{atm}}} = -9.5\text{ J}$$

(c) The external, opposing pressure is 2.8 atm, so

$$w = -P\Delta V = -(2.8 \text{ atm})(89.3 - 26.7)\text{mL}$$

$$w = (-1.8 \times 10^2 \cancel{\text{mL}} \cdot \text{atm}) \times \frac{0.001 \text{ L}}{1 \cancel{\text{mL}}} = -0.18 \text{ L} \cdot \text{atm}$$

To convert the answer to joules, we write:

$$w = -0.18 \cancel{\text{L}} \cdot \cancel{\text{atm}} \times \frac{101.3 \text{ J}}{1 \cancel{\text{L}} \cdot \cancel{\text{atm}}} = -18 \text{ J}$$

6.17 An expansion implies an increase in volume, therefore w must be -325 J (see the defining equation for pressure-volume work.) If the system absorbs heat, q must be $+127 \text{ J}$. The change in energy (internal energy) is:

$$\Delta U = q + w = 127 \text{ J} - 325 \text{ J} = -198 \text{ J}$$

6.18 Strategy: Compression is work done on the gas, so what is the sign for w ? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q ?

Solution: To calculate the energy change of the gas (ΔU), we need Equation (6.1) of the text. Work of compression is positive and because heat is given off by the gas, q is negative. Therefore, we have:

$$\Delta U = q + w = -26 \text{ J} + 74 \text{ J} = 48 \text{ J}$$

As a result, the energy of the gas increases by 48 J.

6.19 We first find the number of moles of hydrogen gas formed in the reaction:

$$50.0 \cancel{\text{g}} \text{ Sn} \times \frac{1 \cancel{\text{mol}} \text{ Sn}}{118.7 \cancel{\text{g}} \text{ Sn}} \times \frac{1 \text{ mol H}_2}{1 \cancel{\text{mol}} \text{ Sn}} = 0.421 \text{ mol H}_2$$

The next step is to find the volume occupied by the hydrogen gas under the given conditions. This is the change in volume.

$$V = \frac{nRT}{P} = \frac{(0.421 \cancel{\text{mol}})(0.0821 \text{ L} \cdot \cancel{\text{atm}} / \cancel{\text{K}} \cdot \cancel{\text{mol}})(298 \cancel{\text{K}})}{1.00 \cancel{\text{atm}}} = 10.3 \text{ L H}_2$$

The pressure-volume work done is then:

$$w = -P\Delta V = -(1.00 \text{ atm})(10.3 \text{ L}) = -10.3 \cancel{\text{L}} \cdot \cancel{\text{atm}} \times \frac{101.3 \text{ J}}{1 \cancel{\text{L}} \cdot \cancel{\text{atm}}} = -1.04 \times 10^3 \text{ J}$$

6.20 Strategy: The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

$$w = -P\Delta V$$

We assume that the volume of liquid water is zero compared to that of steam. How do we calculate the volume of the steam? What is the conversion factor between $\text{L} \cdot \text{atm}$ and J ?

Solution: First, we need to calculate the volume that the water vapor will occupy (V_f).

Using the ideal gas equation:

$$V_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{P} = \frac{(1 \cancel{\text{mol}}) \left(0.0821 \frac{\text{L} \cdot \cancel{\text{atm}}}{\cancel{\text{mol}} \cdot \text{K}} \right) (373 \cancel{\text{K}})}{(1.0 \text{ atm})} = 31 \text{ L}$$

It is given that the volume occupied by liquid water is negligible. Therefore,

$$\Delta V = V_f - V_i = 31 \text{ L} - 0 \text{ L} = 31 \text{ L}$$

Now, we substitute P and ΔV into Equation (6.3) of the text to solve for w .

$$w = -P\Delta V = -(1.0 \text{ atm})(31 \text{ L}) = -31 \text{ L} \cdot \text{atm}$$

The problem asks for the work done in units of joules. The following conversion factor can be obtained from Appendix 1 of the text.

$$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$$

Thus, we can write:

$$w = -31 \cancel{\text{L} \cdot \text{atm}} \times \frac{101.3 \text{ J}}{1 \cancel{\text{L} \cdot \text{atm}}} = -3.1 \times 10^3 \text{ J}$$

Check: Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

- 6.21** Enthalpy is a thermodynamic quantity used to describe heat changes taking place at constant pressure. The enthalpy of reaction, ΔH , is the difference between the enthalpies of the products and the enthalpies of the reactants. At constant pressure, the heat of reaction is equal to the enthalpy change of the same reaction.
- 6.22** The amount of heat absorbed or released in a reaction will depend on the physical states of each substance.
- 6.23** This is an exothermic process. When four moles of $\text{NH}_3(\text{g})$ react with 5 moles of $\text{O}_2(\text{g})$ to produce four moles of $\text{NO}(\text{g})$ and six moles of $\text{H}_2\text{O}(\text{g})$, 904 kJ of thermal energy is released.
- 6.24** (a) -2905.6 kJ (b) +1452.8 kJ (c) -1276.8 kJ
- 6.25** The equation as written shows that 805.6 kJ of heat is released when two moles of CuS react. We want to calculate the amount of heat released when 1 g of CuS reacts.

The heat evolved per gram of CuS roasted is:

$$\text{heat evolved} = \frac{805.6 \text{ kJ}}{2 \cancel{\text{mol}} \text{ CuS}} \times \frac{1 \cancel{\text{mol}} \text{ CuS}}{95.62 \text{ g CuS}} = 4.213 \text{ kJ/g CuS}$$

- 6.26 Strategy:** The thermochemical equation shows that for every 2 moles of NO_2 produced, 114.6 kJ of heat are given off (note the negative sign). We can write a conversion factor from this information.

$$\frac{-114.6 \text{ kJ}}{2 \text{ mol NO}_2}$$

How many moles of NO_2 are in $1.26 \times 10^4 \text{ g}$ of NO_2 ? What conversion factor is needed to convert between grams and moles?

Solution: We need to first calculate the number of moles of NO_2 in 1.26×10^4 g of the compound. Then, we can convert to the number of kilojoules produced from the exothermic reaction. The sequence of conversions is:

grams of $\text{NO}_2 \rightarrow$ moles of $\text{NO}_2 \rightarrow$ kilojoules of heat generated

Therefore, the heat change is:

$$(1.26 \times 10^4 \cancel{\text{g NO}_2}) \times \frac{1 \cancel{\text{mol NO}_2}}{46.01 \cancel{\text{g NO}_2}} \times \frac{-114.6 \text{ kJ}}{2 \cancel{\text{mol NO}_2}} = -1.57 \times 10^4 \text{ kJ}$$

This is an exothermic reaction. The amount of heat given off is 1.57×10^4 kJ.

6.27 We can calculate ΔU using Equation (6.10) of the text.

$$\Delta U = \Delta H - RT\Delta n$$

We initially have 2.0 moles of gas. Since our products are 2.0 moles of H_2 and 1.0 mole of O_2 , there is a net gain of 1 mole of gas (2 reactant \rightarrow 3 product). Thus, $\Delta n = +1$. Looking at the equation given in the problem, it requires 483.6 kJ to decompose 2.0 moles of water ($\Delta H = 483.6$ kJ). Substituting into the above equation:

$$\Delta U = 483.6 \times 10^3 \text{ J/mol} - (8.314 \text{ J/mol}\cdot\text{K})(398 \text{ K})(+1)$$

$$\Delta U = 4.80 \times 10^5 \text{ J/mol} = 4.80 \times 10^2 \text{ kJ/mol}$$

6.28 We initially have 6 moles of gas (3 moles of chlorine and 3 moles of hydrogen). Since our product is 6 moles of hydrogen chloride, there is no change in the number of moles of gas. Therefore there is no volume change; $\Delta V = 0$.

$$w = -P\Delta V = -(1 \text{ atm})(0 \text{ L}) = 0$$

$$\Delta U^\circ = \Delta H^\circ - P\Delta V$$

$-P\Delta V = 0$, so

$$\Delta U = \Delta H$$

$$\Delta H = 3\Delta H_{\text{rxn}}^\circ = 3(-184.6 \text{ kJ/mol}) = -553.8 \text{ kJ/mol}$$

We need to multiply $\Delta H_{\text{rxn}}^\circ$ by three, because the question involves the formation of 6 moles of HCl ; whereas, the equation as written only produces 2 moles of HCl .

$$\Delta U^\circ = \Delta H^\circ = -553.8 \text{ kJ/mol}$$

6.29 The specific heat (s) of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius. The heat capacity (C) of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. Units of specific heat are $\text{J/g}\cdot^\circ\text{C}$, and units of heat capacity are $\text{J}/^\circ\text{C}$. Specific heat is an intensive property; whereas, heat capacity is an extensive property.

6.30 Calorimetry is the measurement of heat changes. Constant-volume and constant-pressure are two types of calorimetry. We need to know the amount of heat absorbed per degree Celsius change (heat capacity) of the calorimeter so that the heat change of the reaction can be determined. The heat capacity of the calorimeter is determined by calibrating it by burning a substance with an accurately known heat of combustion.

6.31 Choice **(d)** will take place when the two metals are brought into contact. Heat will flow from Cu to Al because Cu is at a higher temperature. The definition of heat is the transfer of thermal energy between two bodies that are at different temperatures.

6.32 Specific heat of a substance is the amount of heat required to raise the temperature of one gram of the substance one degree Celsius. Comparing two substances of equal mass, the substance with a larger specific heat will require that more heat be applied to raise its temperature a given amount. Therefore, under the same heating conditions, it will take longer for **metal A** to reach a temperature of 21°C.

6.33
$$\text{Specific heat} = \frac{C}{m} = \frac{85.7 \text{ J/}^\circ\text{C}}{362 \text{ g}} = \mathbf{0.237 \text{ J/g}\cdot^\circ\text{C}}$$

6.34
$$q = m_{\text{Cu}} s_{\text{Cu}} \Delta t = (6.22 \times 10^3 \text{ g})(0.385 \text{ J/g}\cdot^\circ\text{C})(324.3^\circ\text{C} - 20.5^\circ\text{C}) = 7.28 \times 10^5 \text{ J} = \mathbf{728 \text{ kJ}}$$

6.35 See Table 6.2 of the text for the specific heat of Hg.

$$q = ms\Delta t = (366 \text{ g})(0.139 \text{ J/g}\cdot^\circ\text{C})(12.0 - 77.0)^\circ\text{C} = -3.31 \times 10^3 \text{ J} = \mathbf{-3.31 \text{ kJ}}$$

6.36 **Strategy:** We know the masses of gold and iron as well as the initial temperatures of each. We can look up the specific heats of gold and iron in Table 6.2 of the text. Assuming no heat is lost to the surroundings, we can equate the heat lost by the iron sheet to the heat gained by the gold sheet. With this information, we can solve for the final temperature of the combined metals.

Solution: Treating the calorimeter as an isolated system (no heat lost to the surroundings), we can write:

$$q_{\text{Au}} + q_{\text{Fe}} = 0$$

or

$$q_{\text{Au}} = -q_{\text{Fe}}$$

The heat gained by the gold sheet is given by:

$$q_{\text{Au}} = m_{\text{Au}} s_{\text{Au}} \Delta t = (10.0 \text{ g})(0.129 \text{ J/g}\cdot^\circ\text{C})(t_{\text{f}} - 18.0)^\circ\text{C}$$

where m and s are the mass and specific heat, and $\Delta t = t_{\text{final}} - t_{\text{initial}}$.

The heat lost by the iron sheet is given by:

$$q_{\text{Fe}} = m_{\text{Fe}} s_{\text{Fe}} \Delta t = (20.0 \text{ g})(0.444 \text{ J/g}\cdot^\circ\text{C})(t_{\text{f}} - 55.6)^\circ\text{C}$$

Substituting into the equation derived above, we can solve for t_{f} .

$$q_{\text{Au}} = -q_{\text{Fe}}$$

$$(10.0 \text{ g})(0.129 \text{ J/g}\cdot^\circ\text{C})(t_{\text{f}} - 18.0)^\circ\text{C} = -(20.0 \text{ g})(0.444 \text{ J/g}\cdot^\circ\text{C})(t_{\text{f}} - 55.6)^\circ\text{C}$$

$$1.29 t_{\text{f}} - 23.2 = -8.88 t_{\text{f}} + 494$$

$$10.2 t_{\text{f}} = 517$$

$$t_{\text{f}} = \mathbf{50.7^\circ\text{C}}$$

Check: Must the final temperature be between the two starting values?

6.37 The heat gained by the calorimeter is:

$$q = C_p \Delta t$$

$$q = (3024 \text{ J/}^\circ\text{C})(1.126^\circ\text{C}) = 3.405 \times 10^3 \text{ J}$$

The amount of heat given off by burning Mg in kJ/g is:

$$(3.405 \times 10^3 \text{ J}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{1}{0.1375 \text{ g Mg}} = \mathbf{24.76 \text{ kJ/g Mg}}$$

The amount of heat given off by burning Mg in kJ/mol is:

$$\frac{24.76 \text{ kJ}}{1 \text{ g Mg}} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = \mathbf{601.9 \text{ kJ/mol Mg}}$$

If the reaction were endothermic, what would happen to the temperature of the calorimeter and the water?

6.38 Strategy: The neutralization reaction is exothermic. 56.2 kJ of heat are released when 1 mole of H^+ reacts with 1 mole of OH^- . Assuming no heat is lost to the surroundings, we can equate the heat lost by the reaction to the heat gained by the combined solution. How do we calculate the heat released during the reaction? Are we reacting 1 mole of H^+ with 1 mole of OH^- ? How do we calculate the heat absorbed by the combined solution?

Solution: Assuming no heat is lost to the surroundings, we can write:

$$q_{\text{soln}} + q_{\text{rxn}} = 0$$

or

$$q_{\text{soln}} = -q_{\text{rxn}}$$

First, let's set up how we would calculate the heat gained by the solution,

$$q_{\text{soln}} = m_{\text{soln}} s_{\text{soln}} \Delta t$$

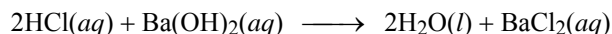
where m and s are the mass and specific heat of the solution and $\Delta t = t_f - t_i$.

We assume that the specific heat of the solution is the same as the specific heat of water, and we assume that the density of the solution is the same as the density of water (1.00 g/mL). Since the density is 1.00 g/mL, the mass of 400 mL of solution (200 mL + 200 mL) is 400 g.

Substituting into the equation above, the heat gained by the solution can be represented as:

$$q_{\text{soln}} = (4.00 \times 10^2 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(t_f - 20.48^\circ\text{C})$$

Next, let's calculate q_{rxn} , the heat released when 200 mL of 0.862 M HCl are mixed with 200 mL of 0.431 M $\text{Ba}(\text{OH})_2$. The equation for the neutralization is:



There is exactly enough $\text{Ba}(\text{OH})_2$ to neutralize all the HCl. Note that 2 mole HCl f 1 mole $\text{Ba}(\text{OH})_2$, and that the concentration of HCl is double the concentration of $\text{Ba}(\text{OH})_2$. The number of moles of HCl is:

$$(2.00 \times 10^2 \text{ mL}) \times \frac{0.862 \text{ mol HCl}}{1000 \text{ mL}} = 0.172 \text{ mol HCl}$$

The amount of heat released when 1 mole of H^+ is reacted is given in the problem (-56.2 kJ/mol). The amount of heat liberated when 0.172 mole of H^+ is reacted is:

$$q_{\text{rxn}} = 0.172 \cancel{\text{mol}} \times \frac{-56.2 \times 10^3 \text{ J}}{1 \cancel{\text{mol}}} = -9.67 \times 10^3 \text{ J}$$

Finally, knowing that the heat lost by the reaction equals the heat gained by the solution, we can solve for the final temperature of the mixed solution.

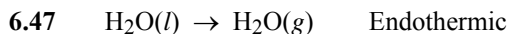
$$q_{\text{soln}} = -q_{\text{rxn}}$$

$$(4.00 \times 10^2 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(t_f - 20.48^\circ\text{C}) = -(-9.67 \times 10^3 \text{ J})$$

$$(1.67 \times 10^3)t_f - (3.43 \times 10^4) = 9.67 \times 10^3 \text{ J}$$

$$t_f = 26.3^\circ\text{C}$$

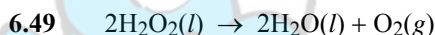
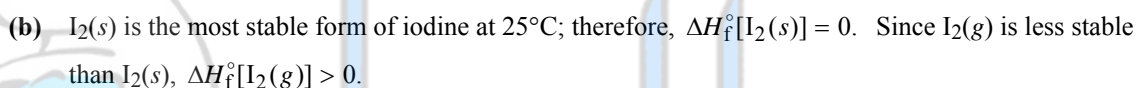
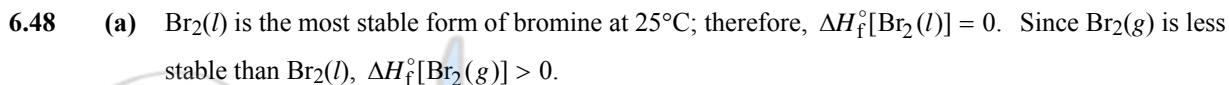
- 6.39** Substances are said to be in the standard state at 1 atmosphere of pressure.
- 6.40** By convention, the standard enthalpy of formation of any element in its most stable form is zero. The standard enthalpy of formation of a compound is the heat change when 1 mole of the compound is formed from its elements at a pressure of 1 atm.
- 6.41** The standard enthalpy of reaction, $\Delta H_{\text{rxn}}^\circ$, is defined as the enthalpy of a reaction carried out at 1 atmosphere pressure.
- 6.42** $\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$, where m and n denote the stoichiometric coefficients (in moles) for the reactants and products, ΔH_f° is the standard enthalpy of formation, and Σ (sigma) means “the sum of.”
- 6.43** Hess’s law can be stated as follows: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. The law enables us to determine the standard enthalpy of formation of a compound from its elements by an indirect route when direct combination of the elements is not feasible. Using Hess’s law, the standard enthalpy change for the reaction of interest can be easily calculated.
- 6.44** See the example for CH_4 given in Section 6.6 of the text. To determine the standard enthalpy of formation of methane, the heat of combustion of methane along with the heats of combustion of carbon and hydrogen are used.
- 6.45** $\text{CH}_4(\text{g})$ and $\text{H}(\text{g})$. All the other choices are elements in their most stable form ($\Delta H_f^\circ = 0$). The most stable form of hydrogen is $\text{H}_2(\text{g})$.
- 6.46** The standard enthalpy of formation of any element in its most stable form is zero. Therefore, since $\Delta H_f^\circ(\text{O}_2) = 0$, O_2 is the more stable form of the element oxygen at this temperature.



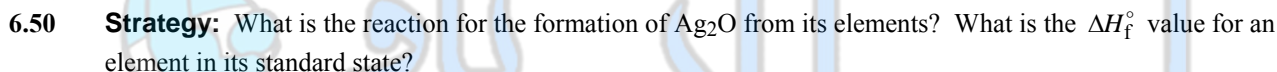
$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(g)] - \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)] > 0$$

$\Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)]$ is more negative since $\Delta H_{\text{rxn}}^{\circ} > 0$.

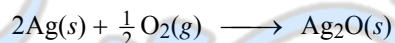
You could also solve the problem by realizing that $\text{H}_2\text{O}(l)$ is the stable form of water at 25°C , and therefore will have the more negative $\Delta H_{\text{f}}^{\circ}$ value.



$\text{H}_2\text{O}_2(l)$ has a tendency to decompose because $\text{H}_2\text{O}(l)$ has a more negative $\Delta H_{\text{f}}^{\circ}$ than $\text{H}_2\text{O}_2(l)$.



Solution: The balanced equation showing the formation of $\text{Ag}_2\text{O}(s)$ from its elements is:



Knowing that the standard enthalpy of formation of any element in its most stable form is zero, and using Equation (6.18) of the text, we write:

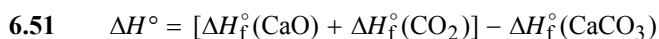
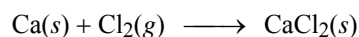
$$\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_{\text{f}}^{\circ}(\text{products}) - \sum m\Delta H_{\text{f}}^{\circ}(\text{reactants})$$

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(\text{Ag}_2\text{O})] - [2\Delta H_{\text{f}}^{\circ}(\text{Ag}) + \frac{1}{2}\Delta H_{\text{f}}^{\circ}(\text{O}_2)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(\text{Ag}_2\text{O})] - [0 + 0]$$

$$\Delta H_{\text{f}}^{\circ}(\text{Ag}_2\text{O}) = \Delta H_{\text{rxn}}^{\circ}$$

In a similar manner, you should be able to show that $\Delta H_{\text{f}}^{\circ}(\text{CaCl}_2) = \Delta H_{\text{rxn}}^{\circ}$ for the reaction

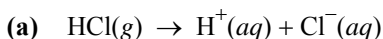


$$\Delta H^{\circ} = [(1)(-635.6 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol})] - (1)(-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}$$

- 6.52 Strategy:** The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation, ΔH_f° , of the species.

Solution: We use the ΔH_f° values in Appendix 2 and Equation (6.18) of the text.

$$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

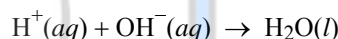


$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{Cl}^-) - \Delta H_f^\circ(\text{HCl})$$

$$-74.9 \text{ kJ/mol} = 0 + \Delta H_f^\circ(\text{Cl}^-) - (1)(-92.3 \text{ kJ/mol})$$

$$\Delta H_f^\circ(\text{Cl}^-) = -167.2 \text{ kJ/mol}$$

- (b) The neutralization reaction is:



and,

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ[\text{H}_2\text{O}(l)] - [\Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{OH}^-)]$$

$$\Delta H_f^\circ[\text{H}_2\text{O}(l)] = -285.8 \text{ kJ/mol} \quad (\text{See Appendix 2 of the text.})$$

$$\Delta H_{\text{rxn}}^\circ = (1)(-285.8 \text{ kJ/mol}) - [(1)(0 \text{ kJ/mol}) + (1)(-229.6 \text{ kJ/mol})] = -56.2 \text{ kJ/mol}$$

- 6.53 (a)** $\Delta H^\circ = 2\Delta H_f^\circ(\text{H}_2\text{O}) - 2\Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(\text{O}_2)$

$$\Delta H^\circ = (2)(-285.8 \text{ kJ/mol}) - (2)(0) - (1)(0) = -571.6 \text{ kJ/mol}$$

- (b) $\Delta H^\circ = 4\Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O}) - 2\Delta H_f^\circ(\text{C}_2\text{H}_2) - 5\Delta H_f^\circ(\text{O}_2)$

$$\Delta H^\circ = (4)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol}) - (2)(226.6 \text{ kJ/mol}) - (5)(0) = -2599 \text{ kJ/mol}$$

- 6.54 (a)** $\Delta H^\circ = [2\Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{C}_2\text{H}_4) + 3\Delta H_f^\circ(\text{O}_2)]$

$$\Delta H^\circ = [(2)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol})] - [(1)(52.3 \text{ kJ/mol}) + (3)(0)]$$

$$\Delta H^\circ = -1410.9 \text{ kJ/mol}$$

- (b) $\Delta H^\circ = [2\Delta H_f^\circ(\text{H}_2\text{O}) + 2\Delta H_f^\circ(\text{SO}_2)] - [2\Delta H_f^\circ(\text{H}_2\text{S}) + 3\Delta H_f^\circ(\text{O}_2)]$

$$\Delta H^\circ = [(2)(-285.8 \text{ kJ/mol}) + (2)(-296.1 \text{ kJ/mol})] - [(2)(-20.15 \text{ kJ/mol}) + (3)(0)]$$

$$\Delta H^\circ = -1123.5 \text{ kJ/mol}$$

- 6.55** The given enthalpies are in units of kJ/g. We must convert them to units of kJ/mol.

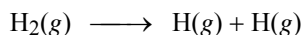
(a) $\frac{-22.6 \text{ kJ}}{1 \text{ g}} \times \frac{32.04 \text{ g}}{1 \text{ mol}} = -724 \text{ kJ/mol}$

(b) $\frac{-29.7 \text{ kJ}}{1 \text{ g}} \times \frac{46.07 \text{ g}}{1 \text{ mol}} = -1.37 \times 10^3 \text{ kJ/mol}$

$$(c) \quad \frac{-33.4 \text{ kJ}}{1 \text{ g}} \times \frac{60.09 \text{ g}}{1 \text{ mol}} = -2.01 \times 10^3 \text{ kJ/mol}$$

$$6.56 \quad \Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_f^{\circ}(\text{products}) - \sum m \Delta H_f^{\circ}(\text{reactants})$$

The reaction is:



and,

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_f^{\circ}(\text{H}) + \Delta H_f^{\circ}(\text{H})] - \Delta H_f^{\circ}(\text{H}_2)$$

$$\Delta H_f^{\circ}(\text{H}_2) = 0$$

$$\Delta H_{\text{rxn}}^{\circ} = 436.4 \text{ kJ/mol} = 2\Delta H_f^{\circ}(\text{H}) - (1)(0)$$

$$\Delta H_f^{\circ}(\text{H}) = \frac{436.4 \text{ kJ/mol}}{2} = 218.2 \text{ kJ/mol}$$

$$6.57 \quad \Delta H^{\circ} = 6\Delta H_f^{\circ}(\text{CO}_2) + 6\Delta H_f^{\circ}(\text{H}_2\text{O}) - [\Delta H_f^{\circ}(\text{C}_6\text{H}_{12}) + 9\Delta H_f^{\circ}(\text{O}_2)]$$

$$\begin{aligned} \Delta H^{\circ} &= (6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - (1)(-151.9 \text{ kJ/mol}) - (1)(0) \\ &= -3924 \text{ kJ/mol} \end{aligned}$$

Why is the standard heat of formation of oxygen zero?

6.58 The equation as written shows that 879 kJ of heat is released when two moles of ZnS react. We want to calculate the amount of heat released when 1 g of ZnS reacts.

Let ΔH° be the heat change per gram of ZnS roasted. We write:

$$\Delta H^{\circ} = \frac{-879 \text{ kJ}}{2 \text{ mol ZnS}} \times \frac{1 \text{ mol ZnS}}{97.46 \text{ g ZnS}} = -4.51 \text{ kJ/g ZnS}$$

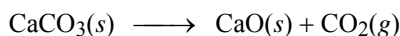
This is an exothermic reaction. The amount of heat evolved per gram of ZnS roasted is **4.51 kJ/g ZnS**.

6.59 This is an exothermic reaction. The amount of heat given off when 1.26×10^4 g of NH_3 are produced is:

$$(1.26 \times 10^4 \text{ g NH}_3) \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{92.6 \text{ kJ}}{2 \text{ mol NH}_3} = 3.43 \times 10^4 \text{ kJ}$$

$$6.60 \quad \Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_f^{\circ}(\text{products}) - \sum m \Delta H_f^{\circ}(\text{reactants})$$

The balanced equation for the reaction is:



$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_f^{\circ}(\text{CaO}) + \Delta H_f^{\circ}(\text{CO}_2)] - \Delta H_f^{\circ}(\text{CaCO}_3)$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1)(-635.6 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol})] - (1)(-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}$$

The enthalpy change calculated above is the enthalpy change if 1 mole of CO_2 is produced. The problem asks for the enthalpy change if 66.8 g of CO_2 are produced. We need to use the molar mass of CO_2 as a conversion factor.

$$\Delta H^\circ = 66.8 \cancel{\text{g CO}_2} \times \frac{1 \cancel{\text{mol CO}_2}}{44.01 \cancel{\text{g CO}_2}} \times \frac{177.8 \text{ kJ}}{1 \cancel{\text{mol CO}_2}} = 2.70 \times 10^2 \text{ kJ}$$

6.61	Reaction	ΔH° (kJ/mol)
	$\text{S}(\text{rhombic}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	-296.06
	$\text{SO}_2(\text{g}) \rightarrow \text{S}(\text{monoclinic}) + \text{O}_2(\text{g})$	296.36
	$\text{S}(\text{rhombic}) \rightarrow \text{S}(\text{monoclinic})$	$\Delta H_{\text{rxn}}^\circ = 0.30 \text{ kJ/mol}$

Which is the more stable allotropic form of sulfur?

- 6.62 Strategy:** Our goal is to calculate the enthalpy change for the formation of C_2H_6 from its elements C and H_2 . This reaction does not occur directly, however, so we must use an indirect route using the information given in the three equations, which we will call equations (a), (b), and (c).

Solution: Here is the equation for the formation of C_2H_6 from its elements.



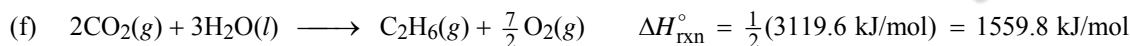
Looking at this reaction, we need two moles of graphite as a reactant. So, we multiply Equation (a) by two to obtain:



Next, we need three moles of H_2 as a reactant. So, we multiply Equation (b) by three to obtain:



Last, we need one mole of C_2H_6 as a product. Equation (c) has two moles of C_2H_6 as a reactant, so we need to reverse the equation and divide it by 2.



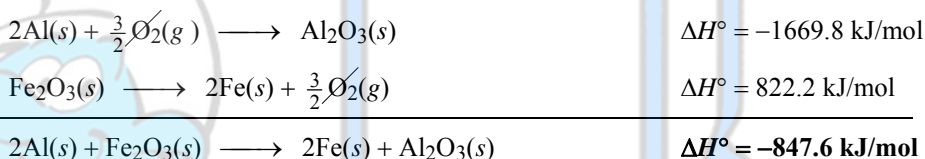
Adding Equations (d), (e), and (f) together, we have:

Reaction	ΔH° (kJ/mol)
(d) $2\text{C}(\text{graphite}) + 2\cancel{\text{O}_2(\text{g})} \longrightarrow 2\cancel{\text{CO}_2(\text{g})}$	-787.0
(e) $3\text{H}_2(\text{g}) + \frac{3}{2}\cancel{\text{O}_2(\text{g})} \longrightarrow 3\text{H}_2\text{O}(\text{l})$	-857.4
(f) $2\cancel{\text{CO}_2(\text{g})} + 3\text{H}_2\text{O}(\text{l}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \frac{7}{2}\cancel{\text{O}_2(\text{g})}$	1559.8
$2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$	$\Delta H^\circ = -84.6 \text{ kJ/mol}$

6.63	Reaction	ΔH° (kJ/mol)
	$\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{OH}(l) + \frac{3}{2}\text{O}_2(g)$	726.4
	$\text{C}(\text{graphite}) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	-393.5
	$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)$	$2(-285.8)$
	$\text{C}(\text{graphite}) + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$	$\Delta H^\circ_{\text{rxn}} = -238.7 \text{ kJ/mol}$

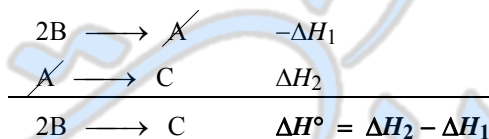
We have just calculated an enthalpy at standard conditions, which we abbreviate $\Delta H^\circ_{\text{rxn}}$. In this case, the reaction in question was for the formation of *one* mole of CH_3OH from its elements in their standard state. Therefore, the $\Delta H^\circ_{\text{rxn}}$ that we calculated is also, by definition, the standard heat of formation ΔH°_f of CH_3OH (-238.7 kJ/mol).

6.64 The second and third equations can be combined to give the first equation.

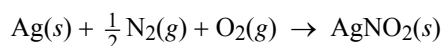


6.65 In a chemical reaction the same elements and the same numbers of atoms are always on both sides of the equation. This provides a consistent reference which allows the energy change in the reaction to be interpreted in terms of the chemical or physical changes that have occurred. In a nuclear reaction the same elements are not always on both sides of the equation and no common reference point exists.

6.66 Rearrange the equations as necessary so they can be added to yield the desired equation.



6.67 The reaction corresponding to standard enthalpy of formation, ΔH°_f , of $\text{AgNO}_2(s)$ is:



Rather than measuring the enthalpy directly, we can use the enthalpy of formation of $\text{AgNO}_3(s)$ and the $\Delta H^\circ_{\text{rxn}}$ provided.



$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_f(\text{AgNO}_2) + \frac{1}{2}\Delta H^\circ_f(\text{O}_2) - \Delta H^\circ_f(\text{AgNO}_3)$$

$$78.67 \text{ kJ/mol} = \Delta H^\circ_f(\text{AgNO}_2) + 0 - (-123.02 \text{ kJ/mol})$$

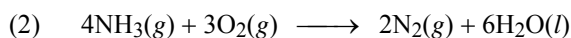
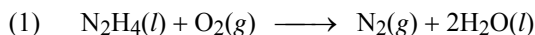
$$\Delta H^\circ_f(\text{AgNO}_2) = -44.35 \text{ kJ/mol}$$

6.68 (a) $\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum m\Delta H_f^{\circ}(\text{reactants})$

$$\Delta H_{\text{rxn}}^{\circ} = [4\Delta H_f^{\circ}(\text{NH}_3) + \Delta H_f^{\circ}(\text{N}_2)] - 3\Delta H_f^{\circ}(\text{N}_2\text{H}_4)$$

$$\Delta H_{\text{rxn}}^{\circ} = [(4)(-46.3 \text{ kJ/mol}) + (0)] - (3)(50.42 \text{ kJ/mol}) = \mathbf{-336.5 \text{ kJ/mol}}$$

(b) The balanced equations are:



The standard enthalpy change for equation (1) is:

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ}(\text{N}_2) + 2\Delta H_f^{\circ}[\text{H}_2\text{O}(l)] - \{\Delta H_f^{\circ}[\text{N}_2\text{H}_4(l)] + \Delta H_f^{\circ}(\text{O}_2)\}$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1)(0) + (2)(-285.8 \text{ kJ/mol})] - [(1)(50.42 \text{ kJ/mol}) + (1)(0)] = \mathbf{-622.0 \text{ kJ/mol}}$$

The standard enthalpy change for equation (2) is:

$$\Delta H_{\text{rxn}}^{\circ} = [2\Delta H_f^{\circ}(\text{N}_2) + 6\Delta H_f^{\circ}(\text{H}_2\text{O})] - [4\Delta H_f^{\circ}(\text{NH}_3) + 3\Delta H_f^{\circ}(\text{O}_2)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(2)(0) + (6)(-285.8 \text{ kJ/mol})] - [(4)(-46.3 \text{ kJ/mol}) + (3)(0)] = \mathbf{-1529.6 \text{ kJ/mol}}$$

We can now calculate the enthalpy change per kilogram of each substance. $\Delta H_{\text{rxn}}^{\circ}$ above is in units of kJ/mol. We need to convert to kJ/kg.

$$\text{N}_2\text{H}_4(l): \Delta H_{\text{rxn}}^{\circ} = \frac{-622.0 \text{ kJ}}{1 \text{ mol N}_2\text{H}_4} \times \frac{1 \text{ mol N}_2\text{H}_4}{32.05 \text{ g N}_2\text{H}_4} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -1.941 \times 10^4 \text{ kJ/kg N}_2\text{H}_4$$

$$\text{NH}_3(g): \Delta H_{\text{rxn}}^{\circ} = \frac{-1529.6 \text{ kJ}}{4 \text{ mol NH}_3} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -2.245 \times 10^4 \text{ kJ/kg NH}_3$$

Since **ammonia**, NH_3 , releases more energy per kilogram of substance, it would be a better fuel.

6.69 We initially have 8 moles of gas (2 of nitrogen and 6 of hydrogen). Since our product is 4 moles of ammonia, there is a net loss of 4 moles of gas (8 reactant \rightarrow 4 product). The corresponding volume loss is

$$V = \frac{nRT}{P} = \frac{(4.0 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1 \text{ atm}} = 98 \text{ L}$$

$$w = -P\Delta V = -(1 \text{ atm})(-98 \text{ L}) = 98 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = \mathbf{9.9 \times 10^3 \text{ J} = 9.9 \text{ kJ}}$$

$$\Delta H = \Delta U + P\Delta V \quad \text{or} \quad \Delta U = \Delta H - P\Delta V$$

Using ΔH as $-185.2 \text{ kJ} = (2 \times -92.6 \text{ kJ})$, (because the question involves the formation of 4 moles of ammonia, not 2 moles of ammonia for which the standard enthalpy is given in the question), and $-P\Delta V$ as 9.9 kJ (for which we just solved):

$$\Delta U = -185.2 \text{ kJ} + 9.9 \text{ kJ} = \mathbf{-175.3 \text{ kJ}}$$

- 6.70** The reaction is, $2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s)$. First, let's calculate ΔH° for this reaction using ΔH_f° values in Appendix 2.

$$\Delta H_{\text{rxn}}^\circ = 2\Delta H_f^\circ(\text{NaCl}) - [2\Delta H_f^\circ(\text{Na}) + \Delta H_f^\circ(\text{Cl}_2)]$$

$$\Delta H_{\text{rxn}}^\circ = 2(-411.0 \text{ kJ/mol}) - [2(0) + 0] = -822.0 \text{ kJ/mol}$$

This is the amount of heat released when 1 mole of Cl_2 reacts (see balanced equation). We are not reacting 1 mole of Cl_2 , however. From the volume and density of Cl_2 , we can calculate grams of Cl_2 . Then, using the molar mass of Cl_2 as a conversion factor, we can calculate moles of Cl_2 . Combining these two calculations into one step, we find moles of Cl_2 to be:

$$2.00 \cancel{\text{L Cl}_2} \times \frac{1.88 \cancel{\text{g Cl}_2}}{1 \cancel{\text{L Cl}_2}} \times \frac{1 \text{ mol Cl}_2}{70.90 \cancel{\text{g Cl}_2}} = 0.0530 \text{ mol Cl}_2$$

Finally, we can use the $\Delta H_{\text{rxn}}^\circ$ calculated above to find the heat change when 0.0530 mole of Cl_2 reacts.

$$0.0530 \cancel{\text{mol Cl}_2} \times \frac{-822.0 \text{ kJ}}{1 \cancel{\text{mol Cl}_2}} = -43.6 \text{ kJ}$$

This reaction is exothermic. The amount of heat released is **43.6 kJ**.

- 6.71 (a)** Although we cannot measure $\Delta H_{\text{rxn}}^\circ$ for this reaction, the reverse process, is the combustion of glucose. We could easily measure $\Delta H_{\text{rxn}}^\circ$ for this combustion in a bomb calorimeter.



- (b)** We can calculate $\Delta H_{\text{rxn}}^\circ$ using standard enthalpies of formation.

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6(s)] + 6\Delta H_f^\circ[\text{O}_2(g)] - \{6\Delta H_f^\circ[\text{CO}_2(g)] + 6\Delta H_f^\circ[\text{H}_2\text{O}(l)]\}$$

$$\Delta H_{\text{rxn}}^\circ = [(1)(-1274.5 \text{ kJ/mol}) + 0] - [(6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol})] = 2801.3 \text{ kJ/mol}$$

$\Delta H_{\text{rxn}}^\circ$ has units of kJ/1 mol glucose. We want the ΔH° change for 7.0×10^{14} kg glucose. We need to calculate how many moles of glucose are in 7.0×10^{14} kg glucose. You should come up with the following strategy to solve the problem.

kg glucose \rightarrow g glucose \rightarrow mol glucose \rightarrow kJ (ΔH°)

$$\Delta H^\circ = (7.0 \times 10^{14} \cancel{\text{kg}}) \times \frac{1000 \cancel{\text{g}}}{1 \cancel{\text{kg}}} \times \frac{1 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6}}{180.16 \cancel{\text{g C}_6\text{H}_{12}\text{O}_6}} \times \frac{2801.3 \text{ kJ}}{1 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6}} = 1.1 \times 10^{19} \text{ kJ}$$

- 6.72** The initial and final states of this system are identical. Since enthalpy is a state function, its value depends only upon the state of the system. The enthalpy change is **zero**.

- 6.73** From the balanced equation we see that there is a 1:2 mole ratio between hydrogen and sodium. The number of moles of hydrogen produced is:

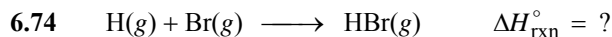
$$0.34 \cancel{\text{g Na}} \times \frac{1 \cancel{\text{mol Na}}}{22.99 \cancel{\text{g Na}}} \times \frac{1 \text{ mol H}_2}{2 \cancel{\text{mol Na}}} = 7.4 \times 10^{-3} \text{ mol H}_2$$

Using the ideal gas equation, we write:

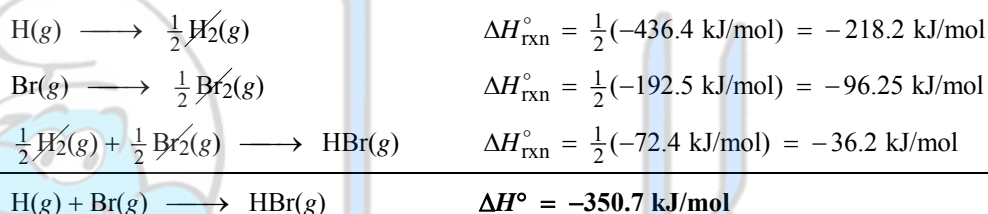
$$V = \frac{nRT}{P} = \frac{(7.4 \times 10^{-3} \text{ mol})(0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})(273 \text{ K})}{(1 \text{ atm})} = 0.17 \text{ L H}_2$$

$$\Delta V = 0.17 \text{ L}$$

$$w = -P\Delta V = -(1.0 \text{ atm})(0.17 \text{ L}) = -0.17 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -17 \text{ J}$$



Rearrange the equations as necessary so they can be added to yield the desired equation.



6.75 Using the balanced equation, we can write:

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= [2\Delta H_f^\circ(\text{CO}_2) + 4\Delta H_f^\circ(\text{H}_2\text{O})] - [2\Delta H_f^\circ(\text{CH}_3\text{OH}) + 3\Delta H_f^\circ(\text{O}_2)] \\ -1452.8 \text{ kJ/mol} &= (2)(-393.5 \text{ kJ/mol}) + (4)(-285.8 \text{ kJ/mol}) - (2)\Delta H_f^\circ(\text{CH}_3\text{OH}) - (3)(0 \text{ kJ/mol}) \\ 477.4 \text{ kJ/mol} &= -(2)\Delta H_f^\circ(\text{CH}_3\text{OH}) \\ \Delta H_f^\circ(\text{CH}_3\text{OH}) &= \mathbf{-238.7 \text{ kJ/mol}} \end{aligned}$$

6.76 $q_{\text{system}} = 0 = q_{\text{metal}} + q_{\text{water}} + q_{\text{calorimeter}}$

$$q_{\text{metal}} + q_{\text{water}} + q_{\text{calorimeter}} = 0$$

$$m_{\text{metal}}s_{\text{metal}}(t_{\text{final}} - t_{\text{initial}}) + m_{\text{water}}s_{\text{water}}(t_{\text{final}} - t_{\text{initial}}) + C_{\text{calorimeter}}(t_{\text{final}} - t_{\text{initial}}) = 0$$

All the needed values are given in the problem. All you need to do is plug in the values and solve for s_{metal} .

$$\begin{aligned} (44.0 \text{ g})(s_{\text{metal}})(28.4 - 99.0)^\circ\text{C} + (80.0 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(28.4 - 24.0)^\circ\text{C} + (12.4 \text{ J/}^\circ\text{C})(28.4 - 24.0)^\circ\text{C} &= 0 \\ (-3.11 \times 10^3)s_{\text{metal}} (\text{g} \cdot ^\circ\text{C}) &= -1.53 \times 10^3 \text{ J} \\ s_{\text{metal}} &= \mathbf{0.492 \text{ J/g} \cdot ^\circ\text{C}} \end{aligned}$$

6.77 The original volume of ammonia is:

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})(298 \text{ K})}{14.0 \text{ atm}} = 1.75 \text{ L NH}_3$$

(a) $T_2 = \frac{P_2V_2T_1}{P_1V_1} = \frac{(1 \text{ atm})(23.5 \text{ L})(298 \text{ K})}{(14.0 \text{ atm})(1.75 \text{ L})} = \mathbf{286 \text{ K}}$

(b) $\Delta t = (286 - 298)^{\circ}\text{C} = -12^{\circ}\text{C}$

$$q = ms\Delta t = (17.03 \text{ g})(0.0258 \text{ J/g}\cdot^{\circ}\text{C})(-12^{\circ}\text{C}) = -5.27 \text{ J}$$

$$w = -P\Delta V = -(1 \text{ atm})(23.5 - 1.75)\text{L} = -21.75 \text{ L}\cdot\text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} = -2.20 \times 10^3 \text{ J}$$

$$\Delta U = q + w = -5.27 \text{ J} - (2.20 \times 10^3 \text{ J}) = -2.21 \times 10^3 \text{ J} = -2.21 \text{ kJ}$$

6.78 A good starting point would be to calculate the standard enthalpy for both reactions.

Calculate the standard enthalpy for the reaction: $\text{C}(s) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{CO}(g)$

This reaction corresponds to the standard enthalpy of formation of CO, so we use the value of -110.5 kJ/mol (see Appendix 2 of the text).

Calculate the standard enthalpy for the reaction: $\text{C}(s) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + \text{H}_2(g)$

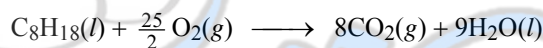
$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(\text{CO}) + \Delta H_{\text{f}}^{\circ}(\text{H}_2)] - [\Delta H_{\text{f}}^{\circ}(\text{C}) + \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O})]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1)(-110.5 \text{ kJ/mol}) + (1)(0)] - [(1)(0) + (1)(-241.8 \text{ kJ/mol})] = 131.3 \text{ kJ/mol}$$

The first reaction, which is exothermic, can be used to promote the second reaction, which is endothermic. Thus, the two gases are produced alternately.

6.79 As energy consumers, we are interested in the availability of **usable** energy.

6.80 First, calculate the energy produced by 1 mole of octane, C_8H_{18} .



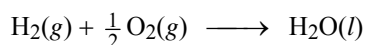
$$\Delta H_{\text{rxn}}^{\circ} = 8\Delta H_{\text{f}}^{\circ}(\text{CO}_2) + 9\Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)] - [\Delta H_{\text{f}}^{\circ}(\text{C}_8\text{H}_{18}) + \frac{25}{2}\Delta H_{\text{f}}^{\circ}(\text{O}_2)]$$

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= [(8)(-393.5 \text{ kJ/mol}) + (9)(-285.8 \text{ kJ/mol})] - [(1)(-249.9 \text{ kJ/mol}) + (\frac{25}{2})(0)] \\ &= -5470 \text{ kJ/mol} \end{aligned}$$

The problem asks for the energy produced by the combustion of 1 gallon of octane. $\Delta H_{\text{rxn}}^{\circ}$ above has units of kJ/mol octane. We need to convert from kJ/mol octane to kJ/gallon octane. The heat of combustion for 1 gallon of octane is:

$$\Delta H^{\circ} = \frac{-5470 \text{ kJ}}{1 \text{ mol octane}} \times \frac{1 \text{ mol octane}}{114.22 \text{ g octane}} \times \frac{2660 \text{ g}}{1 \text{ gal}} = -1.274 \times 10^5 \text{ kJ/gal}$$

The combustion of hydrogen corresponds to the standard heat of formation of water:



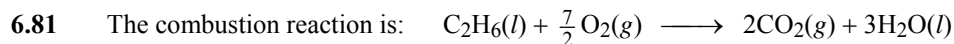
Thus, $\Delta H_{\text{rxn}}^{\circ}$ is the same as $\Delta H_{\text{f}}^{\circ}$ for $\text{H}_2\text{O}(l)$, which has a value of -285.8 kJ/mol . The number of moles of hydrogen required to produce $1.274 \times 10^5 \text{ kJ}$ of heat is:

$$n_{\text{H}_2} = (1.274 \times 10^5 \text{ kJ}) \times \frac{1 \text{ mol H}_2}{285.8 \text{ kJ}} = 445.8 \text{ mol H}_2$$

Finally, use the ideal gas law to calculate the volume of gas corresponding to 445.8 moles of H_2 at 25°C and 1 atm.

$$V_{\text{H}_2} = \frac{n_{\text{H}_2}RT}{P} = \frac{(445.8 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})}{(1 \text{ atm})} = 1.09 \times 10^4 \text{ L}$$

That is, the volume of hydrogen that is energy-equivalent to 1 gallon of gasoline is over **10,000 liters** at 1 atm and 25°C !



The heat released during the combustion of 1 mole of ethane is:

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= [2\Delta H_f^\circ(\text{CO}_2) + 3\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{C}_2\text{H}_6) + \frac{7}{2}\Delta H_f^\circ(\text{O}_2)] \\ \Delta H_{\text{rxn}}^\circ &= [(2)(-393.5 \text{ kJ/mol}) + (3)(-285.8 \text{ kJ/mol})] - [(1)(-84.7 \text{ kJ/mol}) + (\frac{7}{2})(0)] \\ &= -1559.7 \text{ kJ/mol} \end{aligned}$$

The heat required to raise the temperature of the water to 98°C is:

$$q = m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \Delta t = (855 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(98.0 - 25.0)^\circ\text{C} = 2.61 \times 10^5 \text{ J} = 261 \text{ kJ}$$

The combustion of 1 mole of ethane produces 1559.7 kJ; the number of moles required to produce 261 kJ is:

$$261 \text{ kJ} \times \frac{1 \text{ mol ethane}}{1559.7 \text{ kJ}} = 0.167 \text{ mol ethane}$$

The volume of ethane is:

$$V_{\text{ethane}} = \frac{nRT}{P} = \frac{(0.167 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (296 \text{ K})}{\left(752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right)} = 4.10 \text{ L}$$



$$q_{\text{N}_2} = -q_{\text{H}_2\text{O}}$$

If we can calculate the heat lost by the water, we can calculate the heat gained by 60.0 g of the nitrogen.

$$\text{Heat lost by the water} = q_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \Delta t$$

$$q_{\text{H}_2\text{O}} = (2.00 \times 10^2 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(41.0 - 55.3)^\circ\text{C} = -1.20 \times 10^4 \text{ J}$$

The heat gained by 60.0 g nitrogen is the opposite sign of the heat lost by the water.

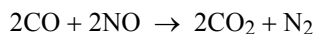
$$q_{\text{N}_2} = -q_{\text{H}_2\text{O}}$$

$$q_{\text{N}_2} = 1.20 \times 10^4 \text{ J}$$

The problem asks for the molar heat of vaporization of liquid nitrogen. Above, we calculated the amount of heat necessary to vaporize 60.0 g of liquid nitrogen. We need to convert from J/60.0 g N_2 to J/mol N_2 .

$$\Delta H_{\text{vap}} = \frac{1.20 \times 10^4 \text{ J}}{60.0 \text{ g N}_2} \times \frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} = 5.60 \times 10^3 \text{ J/mol} = 5.60 \text{ kJ/mol}$$

6.83 The reaction is:



The limiting reagent is CO (NO is in excess).

$$\Delta H^\circ = [2\Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{N}_2)] - [2\Delta H_f^\circ(\text{CO}) + 2\Delta H_f^\circ(\text{NO})]$$

$$\Delta H^\circ = [(2)(-393.5 \text{ kJ/mol}) + (1)(0)] - [(2)(-110.5 \text{ kJ/mol}) + (2)(90.4 \text{ kJ/mol})] = \mathbf{-747 \text{ kJ/mol}}$$

6.84 Recall that the standard enthalpy of formation (ΔH_f°) is defined as the heat change that results when 1 mole of a compound is formed from its elements at a pressure of 1 atm. Only in choice (a) does $\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ$. In choice (b), C(diamond) is *not* the most stable form of elemental carbon under standard conditions; C(graphite) is the most stable form.

6.85 (a) No work is done by a gas expanding in a vacuum, because the pressure exerted on the gas is zero.

(b) $w = -P\Delta V$

$$w = -(0.20 \text{ atm})(0.50 - 0.050)\text{L} = -0.090 \text{ L}\cdot\text{atm}$$

Converting to units of joules:

$$w = -0.090 \cancel{\text{L}\cdot\text{atm}} \times \frac{101.3 \text{ J}}{\cancel{\text{L}\cdot\text{atm}}} = \mathbf{-9.1 \text{ J}}$$

(c) The gas will expand until the pressure is the same as the applied pressure of 0.20 atm. We can calculate its final volume using the ideal gas equation.

$$V = \frac{nRT}{P} = \frac{(0.020 \text{ mol}) \left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (273 + 20)\text{K}}{0.20 \text{ atm}} = \mathbf{2.4 \text{ L}}$$

The amount of work done is:

$$w = -P\Delta V = (0.20 \text{ atm})(2.4 - 0.050)\text{L} = -0.47 \text{ L}\cdot\text{atm}$$

Converting to units of joules:

$$w = -0.47 \cancel{\text{L}\cdot\text{atm}} \times \frac{101.3 \text{ J}}{\cancel{\text{L}\cdot\text{atm}}} = \mathbf{-48 \text{ J}}$$

6.86 (a) The more closely packed, the greater the mass of food. Heat capacity depends on both the mass and specific heat.

$$C = ms$$

The heat capacity of the food is greater than the heat capacity of air; hence, the cold in the freezer will be retained longer.

(b) Tea and coffee are mostly water; whereas, soup might contain vegetables and meat. Water has a higher heat capacity than the other ingredients in soup; therefore, coffee and tea retain heat longer than soup.

6.87 The balanced equation is:



$$\Delta H_{\text{rxn}}^\circ = [2\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}) + 2\Delta H_f^\circ(\text{CO}_2)] - \Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6)$$

$$\Delta H_{\text{rxn}}^\circ = [(2)(-276.98 \text{ kJ/mol}) + (2)(-393.5 \text{ kJ/mol})] - (1)(-1274.5 \text{ kJ/mol}) = \mathbf{-66.5 \text{ kJ/mol}}$$

6.88 $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$. This equation represents twice the standard enthalpy of formation of Fe_2O_3 . From Appendix 2, the standard enthalpy of formation of $\text{Fe}_2\text{O}_3 = -822.2 \text{ kJ/mol}$. So, ΔH° for the given reaction is:

$$\Delta H_{\text{rxn}}^\circ = (2)(-822.2 \text{ kJ/mol}) = -1644 \text{ kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released when four moles of Fe react. But, we are reacting 250 g of Fe, not 4 moles. We can convert from grams of Fe to moles of Fe, then use ΔH° as a conversion factor to convert to kJ.

$$250 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \times \frac{-1644 \text{ kJ}}{4 \text{ mol Fe}} = -1.84 \times 10^3 \text{ kJ}$$

The amount of heat *produced* by this reaction is $\mathbf{1.84 \times 10^3 \text{ kJ}}$.

6.89 One conversion factor needed to solve this problem is the molar mass of water. The other conversion factor is given in the problem. It takes 44.0 kJ of energy to vaporize 1 mole of water.

$$\frac{1 \text{ mol H}_2\text{O}}{44.0 \text{ kJ}}$$

You should come up with the following strategy to solve the problem.

$$4000 \text{ kJ} \rightarrow \text{mol H}_2\text{O} \rightarrow \text{g H}_2\text{O}$$

$$? \text{ g H}_2\text{O} = 4000 \text{ kJ} \times \frac{1 \text{ mol H}_2\text{O}}{44.0 \text{ kJ}} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = \mathbf{1.64 \times 10^3 \text{ g H}_2\text{O}}$$

6.90 The heat required to raise the temperature of 1 liter of water by 1°C is:

$$4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \times \frac{1 \text{ g}}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times 1^\circ\text{C} = 4184 \text{ J/L}$$

Next, convert the volume of the Pacific Ocean to liters.

$$(7.2 \times 10^8 \text{ km}^3) \times \left(\frac{1000 \text{ m}}{1 \text{ km}}\right)^3 \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 7.2 \times 10^{20} \text{ L}$$

The amount of heat needed to raise the temperature of $7.2 \times 10^{20} \text{ L}$ of water is:

$$(7.2 \times 10^{20} \text{ L}) \times \frac{4184 \text{ J}}{1 \text{ L}} = 3.0 \times 10^{24} \text{ J}$$

Finally, we can calculate the number of atomic bombs needed to produce this much heat.

$$(3.0 \times 10^{24} \cancel{\text{J}}) \times \frac{1 \text{ atomic bomb}}{1.0 \times 10^{15} \cancel{\text{J}}} = 3.0 \times 10^9 \text{ atomic bombs} = 3.0 \text{ billion atomic bombs}$$

6.91 First calculate the final volume of CO₂ gas:

$$V = \frac{nRT}{P} = \frac{\left(19.2 \cancel{\text{g}} \times \frac{1 \cancel{\text{mol}}}{44.01 \cancel{\text{g}}}\right)(0.0821 \text{ L} \cdot \cancel{\text{atm}} / \cancel{\text{K}} \cdot \cancel{\text{mol}})(295 \cancel{\text{K}})}{0.995 \cancel{\text{atm}}} = 10.6 \text{ L}$$

$$w = -P\Delta V = -(0.995 \text{ atm})(10.6 \text{ L}) = -10.5 \text{ L} \cdot \text{atm}$$

$$w = -10.5 \cancel{\text{L} \cdot \text{atm}} \times \frac{101.3 \text{ J}}{1 \cancel{\text{L} \cdot \text{atm}}} = -1.06 \times 10^3 \text{ J} = -1.06 \text{ kJ}$$

The expansion work done is 1.06 kJ.

6.92 Strategy: The heat released during the reaction is absorbed by both the water and the calorimeter. How do we calculate the heat absorbed by the water? How do we calculate the heat absorbed by the calorimeter? How much heat is released when 1.9862 g of benzoic acid are reacted? The problem gives the amount of heat that is released when 1 mole of benzoic acid is reacted (−3226.7 kJ/mol).

Solution: The heat of the reaction (combustion) is absorbed by both the water and the calorimeter.

$$q_{\text{rxn}} = -(q_{\text{water}} + q_{\text{cal}})$$

If we can calculate both q_{water} and q_{rxn} , then we can calculate q_{cal} . First, let's calculate the heat absorbed by the water.

$$q_{\text{water}} = m_{\text{water}} s_{\text{water}} \Delta t$$

$$q_{\text{water}} = (2000 \cancel{\text{g}})(4.184 \text{ J} / \cancel{\text{g}} \cdot \cancel{\text{°C}})(25.67 - 21.84) \cancel{\text{°C}} = 3.20 \times 10^4 \text{ J} = 32.0 \text{ kJ}$$

Next, let's calculate the heat released (q_{rxn}) when 1.9862 g of benzoic acid are burned. ΔH_{rxn} is given in units of kJ/mol. Let's convert to q_{rxn} in kJ.

$$q_{\text{rxn}} = 1.9862 \cancel{\text{g benzoic acid}} \times \frac{1 \cancel{\text{mol benzoic acid}}}{122.12 \cancel{\text{g benzoic acid}}} \times \frac{-3226.7 \text{ kJ}}{1 \cancel{\text{mol benzoic acid}}} = -52.48 \text{ kJ}$$

And,

$$q_{\text{cal}} = -q_{\text{rxn}} - q_{\text{water}}$$

$$q_{\text{cal}} = 52.48 \text{ kJ} - 32.0 \text{ kJ} = 20.5 \text{ kJ}$$

To calculate the heat capacity of the bomb calorimeter, we can use the following equation:

$$q_{\text{cal}} = C_{\text{cal}} \Delta t$$

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta t} = \frac{20.5 \text{ kJ}}{(25.67 - 21.84) \text{ °C}} = 5.35 \text{ kJ/°C}$$

6.93 (a) We carry an extra significant figure throughout this calculation to avoid rounding errors. The number of moles of water present in 500 g of water is:

$$\text{moles of H}_2\text{O} = 500 \cancel{\text{g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \cancel{\text{g H}_2\text{O}}} = 27.75 \text{ mol H}_2\text{O}$$

From the equation for the production of Ca(OH)_2 , we have 1 mol H_2O *f* 1 mol CaO *f* 1 mol Ca(OH)_2 . Therefore, the heat generated by the reaction is:

$$27.75 \cancel{\text{mol Ca(OH)}_2} \times \frac{-65.2 \text{ kJ}}{1 \cancel{\text{mol Ca(OH)}_2}} = -1.809 \times 10^3 \text{ kJ}$$

Knowing the specific heat and the number of moles of Ca(OH)_2 produced, we can calculate the temperature rise using Equation (6.12) of the text. First, we need to find the mass of Ca(OH)_2 in 27.75 moles.

$$27.75 \cancel{\text{mol Ca(OH)}_2} \times \frac{74.10 \text{ g Ca(OH)}_2}{1 \cancel{\text{mol Ca(OH)}_2}} = 2.056 \times 10^3 \text{ g Ca(OH)}_2$$

From Equation (6.12) of the text, we write:

$$q = ms\Delta t$$

Rearranging, we get

$$\Delta t = \frac{q}{ms}$$

$$\Delta t = \frac{1.809 \times 10^6 \cancel{\text{J}}}{(2.056 \times 10^3 \cancel{\text{g}})(1.20 \cancel{\text{J/g}\cdot^\circ\text{C}})} = 733^\circ\text{C}$$

and the final temperature is

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

$$t_{\text{final}} = 733^\circ\text{C} + 25^\circ\text{C} = \mathbf{758^\circ\text{C}}$$

A temperature of 758°C is high enough to ignite wood.

(b) The reaction is:



$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ[\text{Ca(OH)}_2] - [\Delta H_f^\circ(\text{CaO}) + \Delta H_f^\circ(\text{H}_2\text{O})]$$

$\Delta H_{\text{rxn}}^\circ$ is given in the problem (-65.2 kJ/mol). Also, the ΔH_f° values of CaO and H_2O are given.

Thus, we can solve for ΔH_f° of Ca(OH)_2 .

$$-65.2 \text{ kJ/mol} = \Delta H_f^\circ[\text{Ca(OH)}_2] - [(1)(-635.6 \text{ kJ/mol}) + (1)(-285.8 \text{ kJ/mol})]$$

$$\Delta H_f^\circ[\text{Ca(OH)}_2] = \mathbf{-986.6 \text{ kJ/mol}}$$

6.94 First, let's calculate the standard enthalpy of reaction.

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 2\Delta H_f^\circ(\text{CaSO}_4) - [2\Delta H_f^\circ(\text{CaO}) + 2\Delta H_f^\circ(\text{SO}_2) + \Delta H_f^\circ(\text{O}_2)] \\ &= (2)(-1432.69 \text{ kJ/mol}) - [(2)(-635.6 \text{ kJ/mol}) + (2)(-296.1 \text{ kJ/mol}) + 0] \\ &= \mathbf{-1002 \text{ kJ/mol}} \end{aligned}$$

This is the enthalpy change for every 2 moles of SO_2 that are removed. The problem asks to calculate the enthalpy change for this process if $6.6 \times 10^5 \text{ g}$ of SO_2 are removed.

$$(6.6 \times 10^5 \cancel{\text{g SO}_2}) \times \frac{1 \cancel{\text{mol SO}_2}}{64.07 \cancel{\text{g SO}_2}} \times \frac{-1002 \text{ kJ}}{2 \cancel{\text{mol SO}_2}} = -5.2 \times 10^6 \text{ kJ}$$

6.95 First, we need to calculate the volume of the balloon.

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(8 \text{ m})^3 = (2.1 \times 10^3 \cancel{\text{m}^3}) \times \frac{1000 \text{ L}}{1 \cancel{\text{m}^3}} = 2.1 \times 10^6 \text{ L}$$

(a) We can calculate the mass of He in the balloon using the ideal gas equation.

$$n_{\text{He}} = \frac{PV}{RT} = \frac{\left(98.7 \cancel{\text{kPa}} \times \frac{1 \cancel{\text{atm}}}{1.01325 \times 10^2 \cancel{\text{kPa}}}\right)(2.1 \times 10^6 \cancel{\text{L}})}{\left(0.0821 \frac{\cancel{\text{L} \cdot \text{atm}}}{\cancel{\text{mol} \cdot \text{K}}}\right)(273 + 18) \cancel{\text{K}}} = 8.6 \times 10^4 \text{ mol He}$$

$$\text{mass He} = (8.6 \times 10^4 \cancel{\text{mol He}}) \times \frac{4.003 \text{ g He}}{1 \cancel{\text{mol He}}} = 3.4 \times 10^5 \text{ g He}$$

(b) Work done = $-P\Delta V$

$$\begin{aligned} &= -\left(98.7 \cancel{\text{kPa}} \times \frac{1 \cancel{\text{atm}}}{1.01325 \times 10^2 \cancel{\text{kPa}}}\right)(2.1 \times 10^6 \text{ L}) \\ &= (-2.0 \times 10^6 \cancel{\text{L} \cdot \text{atm}}) \times \frac{101.3 \text{ J}}{1 \cancel{\text{L} \cdot \text{atm}}} \end{aligned}$$

$$\text{Work done} = -2.0 \times 10^8 \text{ J}$$

6.96 (a) The heat needed to raise the temperature of the water from 3°C to 37°C can be calculated using the equation:

$$q = ms\Delta t$$

First, we need to calculate the mass of the water.

$$4 \cancel{\text{glasses of water}} \times \frac{2.5 \times 10^2 \cancel{\text{mL}}}{1 \cancel{\text{glass}}} \times \frac{1 \text{ g water}}{1 \cancel{\text{mL water}}} = 1.0 \times 10^3 \text{ g water}$$

The heat needed to raise the temperature of $1.0 \times 10^3 \text{ g}$ of water is:

$$q = ms\Delta t = (1.0 \times 10^3 \cancel{\text{g}})(4.184 \cancel{\text{J/g} \cdot ^\circ\text{C}})(37 - 3)^\circ\text{C} = 1.4 \times 10^5 \text{ J} = 1.4 \times 10^2 \text{ kJ}$$

(b) We need to calculate both the heat needed to melt the snow and also the heat needed to heat liquid water from 0°C to 37°C (normal body temperature).

The heat needed to melt the snow is:

$$(8.0 \times 10^2 \cancel{\text{g}}) \times \frac{1 \cancel{\text{mol}}}{18.02 \cancel{\text{g}}} \times \frac{6.01 \text{ kJ}}{1 \cancel{\text{mol}}} = 2.7 \times 10^2 \text{ kJ}$$

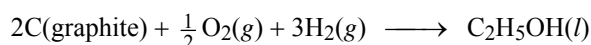
The heat needed to raise the temperature of the water from 0°C to 37°C is:

$$q = ms\Delta t = (8.0 \times 10^2 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(37 - 0)^\circ\text{C} = 1.2 \times 10^5 \text{ J} = 1.2 \times 10^2 \text{ kJ}$$

The total heat lost by your body is:

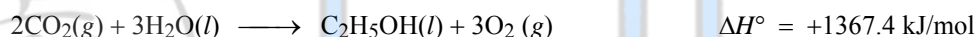
$$(2.7 \times 10^2 \text{ kJ}) + (1.2 \times 10^2 \text{ kJ}) = \mathbf{3.9 \times 10^2 \text{ kJ}}$$

6.97 The reaction we are interested in is the formation of ethanol from its elements.

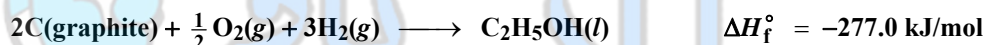
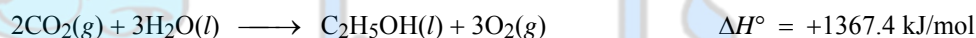


Along with the reaction for the combustion of ethanol, we can add other reactions together to end up with the above reaction.

Reversing the reaction representing the combustion of ethanol gives:



We need to add equations to add C (graphite) and remove CO₂ and H₂O from the reactants side of the equation. We write:



6.98 Heat gained by ice = Heat lost by the soft drink

$$m_{\text{ice}} \times 334 \text{ J/g} = -m_{\text{sd}} s_{\text{sd}} \Delta t$$

$$m_{\text{ice}} \times 334 \text{ J/g} = -(361 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(0 - 23)^\circ\text{C}$$

$$m_{\text{ice}} = \mathbf{104 \text{ g}}$$

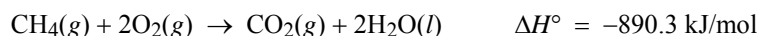
6.99 The heat required to heat 200 g of water (assume $d = 1 \text{ g/mL}$) from 20°C to 100°C is:

$$q = ms\Delta t$$

$$q = (200 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(100 - 20)^\circ\text{C} = 6.7 \times 10^4 \text{ J}$$

Since 50% of the heat from the combustion of methane is lost to the surroundings, twice the amount of heat needed must be produced during the combustion: $2(6.7 \times 10^4 \text{ J}) = 1.3 \times 10^5 \text{ J} = 1.3 \times 10^2 \text{ kJ}$.

Use standard enthalpies of formation (see Appendix 2) to calculate the heat of combustion of methane.



The number of moles of methane needed to produce $1.3 \times 10^2 \text{ kJ}$ of heat is:

$$(1.3 \times 10^2 \text{ kJ}) \times \frac{1 \text{ mol CH}_4}{890.3 \text{ kJ}} = 0.15 \text{ mol CH}_4$$

The volume of 0.15 mole CH₄ at 1 atm and 20°C is:

$$V = \frac{nRT}{P} = \frac{(0.15 \text{ mol})(0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})(293 \text{ K})}{1.0 \text{ atm}} = 3.6 \text{ L}$$

Since we have the volume of methane needed in units of liters, let's convert the cost of natural gas per 15 ft³ to the cost per liter.

$$\frac{\$1.30}{15 \text{ ft}^3} \times \left(\frac{1 \text{ ft}}{12 \text{ in}} \right)^3 \times \left(\frac{1 \text{ in}}{2.54 \text{ cm}} \right)^3 \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = \frac{\$3.1 \times 10^{-3}}{1 \text{ L CH}_4}$$

The cost for 3.6 L of methane is:

$$3.6 \cancel{\text{L}} / \text{CH}_4 \times \frac{\$3.1 \times 10^{-3}}{1 \cancel{\text{L}} / \text{CH}_4} = \text{\$0.011} \text{ or about } \text{1.1¢}$$

6.100 From Chapter 5, we saw that the kinetic energy (or internal energy) of 1 mole of a gas is $\frac{3}{2}RT$. For 1 mole of an ideal gas, $PV = RT$. We can write:

$$\begin{aligned} \text{internal energy} &= \frac{3}{2}RT = \frac{3}{2}PV \\ &= \frac{3}{2}(1.2 \times 10^5 \text{ Pa})(5.5 \times 10^{-3} \text{ m}^3) \\ &= 9.9 \times 10^8 \text{ Pa} \cdot \text{m}^3 \end{aligned}$$

$$1 \text{ Pa} \cdot \text{m}^3 = 1 \frac{\text{N}}{\text{m}^2} \text{m}^3 = 1 \text{ N} \cdot \text{m} = 1 \text{ J}$$

Therefore, the internal energy is $9.9 \times 10^8 \text{ J}$.

The final temperature of the copper metal can be calculated. (10 tons = $9.072 \times 10^6 \text{ g}$)

$$q = m_{\text{Cu}} s_{\text{Cu}} \Delta t$$

$$9.9 \times 10^8 \text{ J} = (9.072 \times 10^6 \text{ g})(0.385 \text{ J/g}^\circ\text{C})(t_f - 21^\circ\text{C})$$

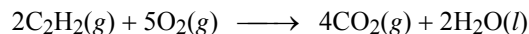
$$(3.49 \times 10^6)t_f = 1.06 \times 10^9$$

$$t_f = \text{304}^\circ\text{C}$$

6.101 Energy must be supplied to break a chemical bond. By the same token, energy is released when a bond is formed.

6.102 (a) $\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \longrightarrow \text{Ca}(\text{OH})_2(s) + \text{C}_2\text{H}_2(g)$

(b) The reaction for the combustion of acetylene is:



We can calculate the enthalpy change for this reaction from standard enthalpy of formation values given in Appendix 2 of the text.

$$\Delta H_{\text{rxn}}^{\circ} = [4\Delta H_{\text{f}}^{\circ}(\text{CO}_2) + 2\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O})] - [2\Delta H_{\text{f}}^{\circ}(\text{C}_2\text{H}_2) + 5\Delta H_{\text{f}}^{\circ}(\text{O}_2)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(4)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol})] - [(2)(226.6 \text{ kJ/mol}) + (5)(0)]$$

$$\Delta H_{\text{rxn}}^{\circ} = -2599 \text{ kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released when two moles of C_2H_2 are reacted. The problem asks for the amount of heat that can be obtained starting with 74.6 g of CaC_2 . From this amount of CaC_2 , we can calculate the moles of C_2H_2 produced.

$$74.6 \cancel{\text{g CaC}_2} \times \frac{1 \cancel{\text{mol CaC}_2}}{64.10 \cancel{\text{g CaC}_2}} \times \frac{1 \text{ mol C}_2\text{H}_2}{1 \cancel{\text{mol CaC}_2}} = 1.16 \text{ mol C}_2\text{H}_2$$

Now, we can use the $\Delta H_{\text{rxn}}^{\circ}$ calculated above as a conversion factor to determine the amount of heat obtained when 1.16 moles of C_2H_2 are burned.

$$1.16 \cancel{\text{mol C}_2\text{H}_2} \times \frac{2599 \text{ kJ}}{2 \cancel{\text{mol C}_2\text{H}_2}} = 1.51 \times 10^3 \text{ kJ}$$

6.103 When 1.034 g of naphthalene are burned, 41.56 kJ of heat are evolved. Let's convert this to the amount of heat evolved on a molar basis. The molar mass of naphthalene is 128.2 g/mol.

$$q = \frac{-41.56 \text{ kJ}}{1.034 \cancel{\text{g C}_{10}\text{H}_8}} \times \frac{128.2 \cancel{\text{g C}_{10}\text{H}_8}}{1 \text{ mol C}_{10}\text{H}_8} = -5153 \text{ kJ/mol}$$

q has a negative sign because this is an exothermic reaction.

This reaction is run at constant volume ($\Delta V = 0$); therefore, no work will result from the change.

$$w = -P\Delta V = 0$$

From Equation (6.4) of the text, it follows that the change in energy is equal to the heat change.

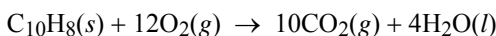
$$\Delta U = q + w = q_v = -5153 \text{ kJ/mol}$$

To calculate ΔH , we rearrange Equation (6.10) of the text.

$$\Delta U = \Delta H - RT\Delta n$$

$$\Delta H = \Delta U + RT\Delta n$$

To calculate ΔH , Δn must be determined, which is the difference in moles of *gas* products and moles of *gas* reactants. Looking at the balanced equation for the combustion of naphthalene:



$$\Delta n = 10 - 12 = -2$$

$$\Delta H = \Delta U + RT\Delta n$$

$$\Delta H = -5153 \text{ kJ/mol} + (8.314 \cancel{\text{J/mol}\cdot\text{K}})(298 \cancel{\text{K}})(-2) \times \frac{1 \text{ kJ}}{1000 \cancel{\text{J}}}$$

$$\Delta H = -5158 \text{ kJ/mol}$$

Is ΔH equal to q_p in this case?

- 6.104 (a)** If no heat exchange occurs between the system and surroundings, then $q = 0$ (called an adiabatic process).

$$\Delta U = q + w = w$$

Because the system does work on the surroundings, w is a negative quantity, and there is a decrease in the system's energy. In Section 5.6 of the text, we saw that the average kinetic energy of a gas is directly proportional to the absolute temperature [Equation (5.15) of the text]. It follows that as the energy of the system decreases, the temperature also decreases. It is this cooling effect (or the decrease in the kinetic energy of the water molecules) that is responsible for the formation of snow.

- (b)** This process is approximately adiabatic, so that $q = 0$ and $\Delta U = w$. Because work is done on the gas (system), w is positive, and there is an increase in the system's energy. As discussed in part (a) above, the kinetic energy of a gas is directly proportional to the absolute temperature. Thus, the temperature of the system increases, which we notice as a warming effect at the valve stem.

- (c)** We assume that when the car is stopped, its kinetic energy is completely converted into heat (friction of the brakes and friction between the tires and the road). Thus,

$$q = \frac{1}{2}mu^2$$

Thus the amount of heat generated must be proportional to the braking distance, d :

$$d \propto q$$

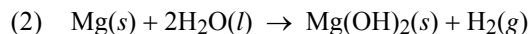
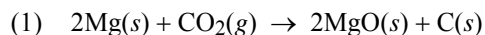
$$d \propto u^2$$

Therefore, as u increases to $2u$, d increases to $(2u)^2 = 4u^2$ which is proportional to $4d$.

- 6.105** Water has a larger specific heat than air. Thus cold, damp air can extract more heat from the body than cold, dry air. By the same token, hot, humid air can deliver more heat to the body.

- 6.106** Since the humidity is very low in deserts, there is little water vapor in the air to trap and hold the heat radiated back from the ground during the day. Once the sun goes down, the temperature drops dramatically. 40°F temperature drops between day and night are common in desert climates. Coastal regions have much higher humidity levels compared to deserts. The water vapor in the air retains heat, which keeps the temperature at a more constant level during the night. In addition, sand and rocks in the desert have small specific heats compared with water in the ocean. The water absorbs much more heat during the day compared to sand and rocks, which keeps the temperature warmer at night.

- 6.107** Let's write balanced equations for the reactions between Mg and CO₂, and Mg and H₂O. Then, we can calculate $\Delta H_{\text{rxn}}^\circ$ for each reaction from ΔH_f° values.



For reaction (1), $\Delta H_{\text{rxn}}^\circ$ is:

$$\Delta H_{\text{rxn}}^\circ = 2\Delta H_f^\circ[\text{MgO}(s)] + \Delta H_f^\circ[\text{C}(s)] - \{2\Delta H_f^\circ[\text{Mg}(s)] + \Delta H_f^\circ[\text{CO}_2(g)]\}$$

$$\Delta H_{\text{rxn}}^\circ = (2)(-601.8 \text{ kJ/mol}) + (1)(0) - [(2)(0) + (1)(-393.5 \text{ kJ/mol})] = -8.10 \times 10^2 \text{ kJ/mol}$$

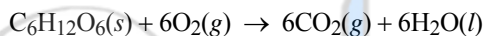
For reaction (2), $\Delta H_{\text{rxn}}^{\circ}$ is:

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ}[\text{Mg}(\text{OH})_2(s)] + \Delta H_f^{\circ}[\text{H}_2(g)] - \{\Delta H_f^{\circ}[\text{Mg}(s)] + 2\Delta H_f^{\circ}[\text{H}_2\text{O}(l)]\}$$

$$\Delta H_{\text{rxn}}^{\circ} = (1)(-924.66 \text{ kJ/mol}) + (1)(0) - [(1)(0) + (2)(-285.8 \text{ kJ/mol})] = -353.1 \text{ kJ/mol}$$

Both of these reactions are highly exothermic, which will promote the fire rather than extinguishing it.

- 6.108** First, we calculate ΔH for the combustion of 1 mole of glucose using data in Appendix 2 of the text. We can then calculate the heat produced in the calorimeter. Using the heat produced along with ΔH for the combustion of 1 mole of glucose will allow us to calculate the mass of glucose in the sample. Finally, the mass % of glucose in the sample can be calculated.



$$\Delta H_{\text{rxn}}^{\circ} = (6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - (1)(-1274.5 \text{ kJ/mol}) = -2801 \text{ kJ/mol}$$

The heat produced in the calorimeter is:

$$(3.134^{\circ}\text{C})(19.65 \text{ kJ}/^{\circ}\text{C}) = 61.58 \text{ kJ}$$

Let x equal the mass of glucose in the sample:

$$x \cancel{\text{g glucose}} \times \frac{1 \cancel{\text{mol glucose}}}{180.16 \cancel{\text{g glucose}}} \times \frac{2801 \text{ kJ}}{1 \cancel{\text{mol glucose}}} = 61.58 \text{ kJ}$$

$$x = 3.961 \text{ g}$$

$$\% \text{ glucose} = \frac{3.961 \text{ g}}{4.117 \text{ g}} \times 100\% = \mathbf{96.21\%}$$

6.109	q	w	ΔU	ΔH
(a)	—	—	—	—
(b)	—	+	0	0
(c)	—	—	—	—
(d)	+	—	+	+
(e)	+	0	+	+
(f)	+	+	+	+

In (b), the internal energy of an ideal gas depends only on temperature. Since temperature is held constant, $\Delta U = 0$. Also, $\Delta H = 0$ because $\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0$.

- 6.110 (a)** From the mass of CO_2 produced, we can calculate the moles of carbon in the compound. From the mass of H_2O produced, we can calculate the moles of hydrogen in the compound.

$$1.419 \cancel{\text{g CO}_2} \times \frac{1 \cancel{\text{mol CO}_2}}{44.01 \cancel{\text{g CO}_2}} \times \frac{1 \text{ mol C}}{1 \cancel{\text{mol CO}_2}} = 0.03224 \text{ mol C}$$

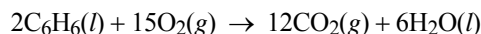
$$0.290 \cancel{\text{g H}_2\text{O}} \times \frac{1 \cancel{\text{mol H}_2\text{O}}}{18.02 \cancel{\text{g H}_2\text{O}}} \times \frac{2 \text{ mol H}}{1 \cancel{\text{mol H}_2\text{O}}} = 0.03219 \text{ mol H}$$

The mole ratio between C and H is 1:1, so the empirical formula is **CH**.

- (b) The empirical molar mass of CH is 13.02 g/mol.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{76 \text{ g}}{13.02 \text{ g}} = 5.8 \approx 6$$

Therefore, the molecular formula is C₆H₆, and the hydrocarbon is benzene. The combustion reaction is:



17.55 kJ of heat is released when 0.4196 g of the hydrocarbon undergoes combustion. We can now calculate the enthalpy of combustion ($\Delta H_{\text{rxn}}^\circ$) for the above reaction in units of kJ/mol. Then, from the enthalpy of combustion, we can calculate the enthalpy of formation of C₆H₆.

$$\frac{-17.55 \text{ kJ}}{0.4196 \text{ g C}_6\text{H}_6} \times \frac{78.11 \text{ g C}_6\text{H}_6}{1 \text{ mol C}_6\text{H}_6} \times 2 \text{ mol C}_6\text{H}_6 = -6534 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}}^\circ = (12)\Delta H_f^\circ(\text{CO}_2) + (6)\Delta H_f^\circ(\text{H}_2\text{O}) - (2)\Delta H_f^\circ(\text{C}_6\text{H}_6)$$

$$-6534 \text{ kJ/mol} = (12)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - (2)\Delta H_f^\circ(\text{C}_6\text{H}_6)$$

$$\Delta H_f^\circ(\text{C}_6\text{H}_6) = \mathbf{49 \text{ kJ/mol}}$$

- 6.111** If the body absorbs all the heat released and is an isolated system, the temperature rise, Δt , is:

$$q = ms\Delta t$$

$$\Delta t = \frac{q}{ms} = \frac{1.0 \times 10^7 \text{ J}}{(50,000 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})} = \mathbf{48^\circ\text{C}}$$

If the body temperature is to remain constant, the heat released by metabolic activity must be used for the evaporation of water as perspiration, that is,

$$\frac{1 \text{ g H}_2\text{O}}{2.41 \text{ kJ}} \times (1.0 \times 10^4 \text{ kJ}) = \mathbf{4.1 \times 10^3 \text{ g H}_2\text{O}}$$

Assuming that the density of perspiration is 1 g/mL, this mass corresponds to a volume of 4.1 L. The actual amount of perspiration is less than this because part of the body heat is lost to the surroundings by convection and radiation.

- 6.112**
- | | |
|-------|----------------------------------------------------------------------------------|
| A → B | $w = 0$, because $\Delta V = 0$ |
| B → C | $w = -P\Delta V = -(2 \text{ atm})(2 - 1)\text{L} = -2 \text{ L}\cdot\text{atm}$ |
| C → D | $w = 0$, because $\Delta V = 0$ |
| D → A | $w = -P\Delta V = -(1 \text{ atm})(1 - 2)\text{L} = +1 \text{ L}\cdot\text{atm}$ |

The total work done = $(-2 \text{ L}\cdot\text{atm}) + (1 \text{ L}\cdot\text{atm}) = \mathbf{-1 \text{ L}\cdot\text{atm}}$

Converting to units of joules,

$$-1 \cancel{\text{L}\cdot\text{atm}} \times \frac{101.3 \text{ J}}{1 \cancel{\text{L}\cdot\text{atm}}} = \mathbf{-101.3 \text{ J}}$$

In a cyclic process, the change in a state function must be zero. We therefore conclude that work is not a state function. Note that the total work done equals the area of the enclosure.

- 6.113** (a) Heating water at room temperature to its boiling point.
 (b) Heating water at its boiling point.
 (c) A chemical reaction taking place in a bomb calorimeter (an isolated system) where there is no heat exchange with the surroundings.

6.114 C (graphite) \rightarrow C (diamond)

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H - \Delta U = P\Delta V$$

The pressure is 50,000 atm. From the given densities, we can calculate the volume in liters occupied by one mole of graphite and one mole of diamond. Taking the difference will give ΔV . We carry additional significant figures throughout the calculations to avoid rounding errors.

$$\frac{1 \text{ cm}^3}{2.25 \text{ g/graphite}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{12.01 \text{ g/graphite}}{1 \text{ mol graphite}} = 0.0053378 \text{ L/mol graphite}$$

$$\frac{1 \text{ cm}^3}{3.52 \text{ g/diamond}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{12.01 \text{ g/diamond}}{1 \text{ mol diamond}} = 0.0034119 \text{ L/mol diamond}$$

$$\Delta H - \Delta U = P\Delta V = (50,000 \text{ atm})(0.0034119 \text{ L/mol} - 0.0053378 \text{ L/mol})$$

$$\Delta H - \Delta U = -96.295 \frac{\text{L} \cdot \text{atm}}{\text{mol}} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -9.75 \times 10^3 \text{ J/mol}$$

CHAPTER 7

THE ELECTRONIC STRUCTURE OF ATOMS

7.1 A wave can be thought of as a vibrating disturbance by which energy is transmitted. The distance between identical points on successive waves is called the wavelength (λ). The frequency (ν) of the wave is the number of waves that pass through a particular point in one second. The amplitude is the vertical distance from the midline of a wave to the peak or trough.

7.2 The unit for wavelength is the meter, and the unit for frequency is s^{-1} (or Hz). The speed of light is $3.00 \times 10^8 \text{ m/s}$ which is equal to $1.86 \times 10^5 \text{ mph}$.

7.3 From longest wavelength to shortest, the types of electromagnetic radiation are: radiowaves, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays.

7.4 The visible region of the electromagnetic spectrum has wavelength values from 400-700 nm.

7.5 Planck said that atoms and molecules could emit (or absorb) energy only in discrete quantities, like small packages or bundles. Planck gave the name quantum to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy (E) of a single quantum of energy is given by, $E = h\nu$. The units for Planck's constant (h) are J-s.

7.6 Everyday examples include the number of people voting in an election, and the number of goals scored in a soccer match (The number is an integral number. You cannot score $\frac{1}{2}$ a goal.).

7.7 (a)
$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{8.6 \times 10^{13} / \text{s}} = 3.5 \times 10^{-6} \text{ m} = \mathbf{3.5 \times 10^3 \text{ nm}}$$

(b)
$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{566 \times 10^{-9} \text{ m}} = 5.30 \times 10^{14} / \text{s} = \mathbf{5.30 \times 10^{14} \text{ Hz}}$$

7.8 (a)

Strategy: We are given the wavelength of an electromagnetic wave and asked to calculate the frequency. Rearranging Equation (7.1) of the text and replacing u with c (the speed of light) gives:

$$\nu = \frac{c}{\lambda}$$

Solution: Because the speed of light is given in meters per second, it is convenient to first convert wavelength to units of meters. Recall that $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ (see Table 1.3 of the text). We write:

$$456 \text{ nm} \times \frac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}} = 456 \times 10^{-9} \text{ m} = 4.56 \times 10^{-7} \text{ m}$$

Substituting in the wavelength and the speed of light ($3.00 \times 10^8 \text{ m/s}$), the frequency is:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{4.56 \times 10^{-7} \text{ m}} = \mathbf{6.58 \times 10^{14} \text{ s}^{-1} \text{ or } 6.58 \times 10^{14} \text{ Hz}}$$

Check: The answer shows that 6.58×10^{14} waves pass a fixed point every second. This very high frequency is in accordance with the very high speed of light.

(b)

Strategy: We are given the frequency of an electromagnetic wave and asked to calculate the wavelength. Rearranging Equation (7.1) of the text and replacing u with c (the speed of light) gives:

$$\lambda = \frac{c}{\nu}$$

Solution: Substituting in the frequency and the speed of light (3.00×10^8 m/s) into the above equation, the wavelength is:

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \frac{\text{m}}{\cancel{\text{s}}}}{2.45 \times 10^9 \frac{1}{\cancel{\text{s}}}} = 0.122 \text{ m}$$

The problem asks for the wavelength in units of nanometers. Recall that $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$.

$$\lambda = 0.122 \cancel{\text{m}} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \cancel{\text{m}}} = 1.22 \times 10^8 \text{ nm}$$

7.9 Since the speed of light is 3.00×10^8 m/s, we can write

$$(1.3 \times 10^8 \cancel{\text{mi}}) \times \frac{1.61 \cancel{\text{km}}}{1 \cancel{\text{mi}}} \times \frac{1000 \cancel{\text{m}}}{1 \cancel{\text{km}}} \times \frac{1 \text{ s}}{3.00 \times 10^8 \cancel{\text{m}}} = 7.0 \times 10^2 \text{ s}$$

Would the time be different for other types of electromagnetic radiation?

7.10 A radio wave is an electromagnetic wave, which travels at the speed of light. The speed of light is in units of m/s, so let's convert distance from units of miles to meters. ($28 \text{ million mi} = 2.8 \times 10^7 \text{ mi}$)

$$? \text{ distance (m)} = (2.8 \times 10^7 \cancel{\text{mi}}) \times \frac{1.61 \cancel{\text{km}}}{1 \cancel{\text{mi}}} \times \frac{1000 \text{ m}}{1 \cancel{\text{km}}} = 4.5 \times 10^{10} \text{ m}$$

Now, we can use the speed of light as a conversion factor to convert from meters to seconds ($c = 3.00 \times 10^8$ m/s).

$$? \text{ min} = (4.5 \times 10^{10} \cancel{\text{m}}) \times \frac{1 \text{ s}}{3.00 \times 10^8 \cancel{\text{m}}} = 1.5 \times 10^2 \text{ s} = 2.5 \text{ min}$$

$$\text{7.11} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \cancel{\text{m/s}}}{9192631770 \cancel{\text{s}^{-1}}} = 3.26 \times 10^{-2} \text{ m} = 3.26 \times 10^7 \text{ nm}$$

This radiation falls in the **microwave** region of the spectrum. (See Figure 7.3 of the text.)

7.12 The wavelength is:

$$\lambda = \frac{1 \text{ m}}{1,650,763.73 \text{ wavelengths}} = 6.05780211 \times 10^{-7} \text{ m}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{6.05780211 \times 10^{-7} \text{ m}} = 4.95 \times 10^{14} \text{ s}^{-1}$$

7.13 The photoelectric effect is a phenomenon in which electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency, called the threshold frequency.

7.14 Photons are particles of light. Einstein's explanation of the photoelectric effect proved that light can have particle-like properties. Depending on the experiment, light behaves as a wave or a stream of particles.

$$\text{7.15} \quad E = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{624 \times 10^{-9} \text{ m}} = 3.19 \times 10^{-19} \text{ J}$$

7.16 (a)

Strategy: We are given the frequency of an electromagnetic wave and asked to calculate the wavelength. Rearranging Equation (7.1) of the text and replacing u with c (the speed of light) gives:

$$\lambda = \frac{c}{\nu}$$

Solution: Substituting in the frequency and the speed of light ($3.00 \times 10^8 \text{ m/s}$) into the above equation, the wavelength is:

$$\lambda = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}}}{7.5 \times 10^{14} \frac{1}{\text{s}}} = 4.0 \times 10^{-7} \text{ m} = 4.0 \times 10^2 \text{ nm}$$

Check: The wavelength of 400 nm calculated is in the blue region of the visible spectrum as expected.

(b)

Strategy: We are given the frequency of an electromagnetic wave and asked to calculate its energy. Equation (7.2) of the text relates the energy and frequency of an electromagnetic wave.

$$E = h\nu$$

Solution: Substituting in the frequency and Planck's constant ($6.63 \times 10^{-34} \text{ J}\cdot\text{s}$) into the above equation, the energy of a single photon associated with this frequency is:

$$E = h\nu = (6.63 \times 10^{-34} \text{ J}\cdot\text{s}) \left(7.5 \times 10^{14} \frac{1}{\text{s}} \right) = 5.0 \times 10^{-19} \text{ J}$$

Check: We expect the energy of a single photon to be a very small energy as calculated above, $5.0 \times 10^{-19} \text{ J}$.

$$\text{7.17 (a)} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{6.0 \times 10^{14} \text{ /s}} = 5.0 \times 10^{-7} \text{ m} = 5.0 \times 10^2 \text{ nm}$$

Yes, this radiation does fall in the visible region. (See Figure 7.3 of the text.)

$$\text{(b)} \quad E = h\nu = (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(6.0 \times 10^{14} \text{ /s}) = 4.0 \times 10^{-19} \text{ J}$$

$$\text{(c)} \quad \text{Converting to J/mol: } E = \frac{4.0 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} = 2.4 \times 10^5 \text{ J/mol}$$

- 7.18** The energy given in this problem is for *1 mole* of photons. To apply $E = h\nu$, we must divide the energy by Avogadro's number. The energy of one photon is:

$$E = \frac{1.0 \times 10^3 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1.7 \times 10^{-18} \text{ J/photon}$$

The wavelength of this photon can be found using the relationship, $E = \frac{hc}{\lambda}$.

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s}) \left(3.00 \times 10^8 \frac{\text{m}}{\text{s}} \right)}{1.7 \times 10^{-18} \text{ J}} = 1.2 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = \mathbf{1.2 \times 10^2 \text{ nm}}$$

The radiation is in the **ultraviolet** region (see Figure 7.3 of the text).

7.19 $E = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s}) \left(3.00 \times 10^8 \frac{\text{m}}{\text{s}} \right)}{(0.154 \times 10^{-9} \text{ m})} = \mathbf{1.29 \times 10^{-15} \text{ J}}$

7.20 (a) $\lambda = \frac{c}{\nu}$

$$\lambda = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}}}{8.11 \times 10^{14} \frac{1}{\text{s}}} = \mathbf{3.70 \times 10^{-7} \text{ m} = 3.70 \times 10^2 \text{ nm}}$$

(b) Checking Figure 7.3 of the text, you should find that the visible region of the spectrum runs from 400 to 700 nm. 370 nm is in the **ultraviolet** region of the spectrum.

(c) $E = h\nu$. Substitute the frequency (ν) into this equation to solve for the energy of one quantum associated with this frequency.

$$E = h\nu = (6.63 \times 10^{-34} \text{ J}\cdot\text{s}) \left(8.11 \times 10^{14} \frac{1}{\text{s}} \right) = \mathbf{5.38 \times 10^{-19} \text{ J}}$$

- 7.21 (a)** The mathematical equation for studying the photoelectric effect is

$$h\nu = W + \text{KE}$$

where ν is the frequency of light shining on the metal, W is the work function, and KE is the kinetic energy of the ejected electron. To calculate the minimum frequency of light needed to eject electrons, we assume that the kinetic energy of the ejected electron is zero.

We solve for frequency (ν).

$$h\nu = W + \text{KE}$$

$$(6.63 \times 10^{-34} \text{ J}\cdot\text{s})\nu = 3.68 \times 10^{-19} \text{ J} + 0$$

$$\nu = \mathbf{5.55 \times 10^{14} \text{ s}^{-1}}$$

- (b)** We use the same equation as in part (a) and solve for the kinetic energy (KE).

$$h\nu = W + \text{KE}$$

$$(6.63 \times 10^{-34} \text{ J}\cdot\text{s}) (8.62 \times 10^{14} \text{ s}^{-1}) = 3.68 \times 10^{-19} \text{ J} + \text{KE}$$

$$\mathbf{\text{KE} = 2.04 \times 10^{-19} \text{ J}}$$

- 7.22 The mathematical equation for studying the photoelectric effect is

$$h\nu = W + \text{KE}$$

where ν is the frequency of light shining on the metal, W is the work function, and KE is the kinetic energy of the ejected electron. We substitute h , ν , and KE into the equation to solve for the work function, W .

$$h\nu = W + \text{KE}$$

$$(6.63 \times 10^{-34} \text{ J}\cdot\cancel{\text{s}})(2.11 \times 10^{15} \cancel{\text{s}}^{-1}) = W + (5.83 \times 10^{-19} \text{ J})$$

$$W = 8.16 \times 10^{-19} \text{ J}$$

- 7.23 According to Niels Bohr, the electron is allowed to occupy only certain orbits of specific energies (energy levels, n). In other words, the energies of the electron are quantized. The most stable energy state is called the ground state, which refers to the lowest energy state of an atom. The stability of the electron diminishes for increasing n values. Each of these levels is called an excited state, which is higher in energy than the ground state.

- 7.24 Bohr postulated that the electron is allowed to occupy only certain orbits of specific energies. In other words, the energies of the electron are quantized. Energy is released (emitted) during electron transitions from higher energy orbits to lower energy orbits. According to the laws of classical physics, an electron moving in an orbit of a hydrogen atom would experience an acceleration toward the nucleus by radiating away energy in the form of electromagnetic waves. Thus, such an electron would quickly spiral into the nucleus and annihilate itself with the proton.

- 7.25 The arrangement of energy levels for each element is unique. The frequencies of light emitted by an element are characteristic of that element. Even the frequencies emitted by isotopes of the same element are very slightly different.

- 7.26 The emitted light could be analyzed by passing it through a prism.

- 7.27 Light emitted by fluorescent materials always has lower energy than the light striking the fluorescent substance. Absorption of visible light could not give rise to emitted ultraviolet light because the latter has higher energy.

The reverse process, ultraviolet light producing visible light by fluorescence, is very common. Certain brands of laundry detergents contain materials called “optical brighteners” which, for example, can make a white shirt look much whiter and brighter than a similar shirt washed in ordinary detergent.

- 7.28 Excited atoms of the chemical elements emit the same characteristic frequencies or lines in a terrestrial laboratory, in the sun, or in a star many light-years distant from earth.

- 7.29 (a) The energy difference between states E_1 and E_4 is:

$$E_4 - E_1 = (-1.0 \times 10^{-19} \text{ J}) - (-15 \times 10^{-19} \text{ J}) = 14 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{14 \times 10^{-19} \cancel{\text{J}}} = 1.4 \times 10^{-7} \text{ m} = 1.4 \times 10^2 \text{ nm}$$

- (b) The energy difference between the states E_2 and E_3 is:

$$E_3 - E_2 = (-5.0 \times 10^{-19} \text{ J}) - (-10.0 \times 10^{-19} \text{ J}) = 5 \times 10^{-19} \text{ J}$$

(c) The energy difference between the states E_1 and E_3 is:

$$E_1 - E_3 = (-15 \times 10^{-19} \text{ J}) - (-5.0 \times 10^{-19} \text{ J}) = -10 \times 10^{-19} \text{ J}$$

Ignoring the negative sign of ΔE , the wavelength is found as in part (a).

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{10 \times 10^{-19} \text{ J}} = 2.0 \times 10^{-7} \text{ m} = 2.0 \times 10^2 \text{ nm}$$

7.30 We use more accurate values of h and c for this problem.

$$E = \frac{hc}{\lambda} = \frac{(6.6256 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{656.3 \times 10^{-9} \text{ m}} = 3.027 \times 10^{-19} \text{ J}$$

7.31 In this problem $n_i = 5$ and $n_f = 3$.

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{5^2} - \frac{1}{3^2} \right) = -1.55 \times 10^{-19} \text{ J}$$

The sign of ΔE means that this is energy associated with an emission process.

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.55 \times 10^{-19} \text{ J}} = 1.28 \times 10^{-6} \text{ m} = 1.28 \times 10^3 \text{ nm}$$

Is the sign of the energy change consistent with the sign conventions for exo- and endothermic processes?

7.32 Strategy: We are given the initial and final states in the emission process. We can calculate the energy of the emitted photon using Equation (7.6) of the text. Then, from this energy, we can solve for the frequency of the photon, and from the frequency we can solve for the wavelength. The value of Rydberg's constant is $2.18 \times 10^{-18} \text{ J}$.

Solution: From Equation (7.6) we write:

$$\begin{aligned} \Delta E &= R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ \Delta E &= (2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{4^2} - \frac{1}{2^2} \right) \\ \Delta E &= -4.09 \times 10^{-19} \text{ J} \end{aligned}$$

The negative sign for ΔE indicates that this is energy associated with an emission process. To calculate the frequency, we will omit the minus sign for ΔE because the frequency of the photon must be positive. We know that

$$\Delta E = h\nu$$

Rearranging the equation and substituting in the known values,

$$\nu = \frac{\Delta E}{h} = \frac{(4.09 \times 10^{-19} \text{ J})}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})} = 6.17 \times 10^{14} \text{ s}^{-1} = 6.17 \times 10^{14} \text{ Hz}$$

We also know that $\lambda = \frac{c}{\nu}$. Substituting the frequency calculated above into this equation gives:

$$\lambda = \frac{3.00 \times 10^8 \frac{\text{m}}{\text{s}}}{\left(6.17 \times 10^{14} \frac{1}{\text{s}}\right)} = 4.86 \times 10^{-7} \text{ m} = \mathbf{486 \text{ nm}}$$

Check: This wavelength is in the visible region of the electromagnetic region (see Figure 7.3 of the text). This is consistent with the fact that because $n_i = 4$ and $n_f = 2$, this transition gives rise to a spectral line in the Balmer series (see Figure 7.9 of the text).

7.33 This problem must be worked to four significant figure accuracy. We use $6.6256 \times 10^{-34} \text{ J}\cdot\text{s}$ for Planck's constant and $2.998 \times 10^8 \text{ m/s}$ for the speed of light. First calculate the energy of each of the photons.

$$E = \frac{hc}{\lambda} = \frac{(6.6256 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{589.0 \times 10^{-9} \text{ m}} = 3.372 \times 10^{-19} \text{ J}$$

$$E = \frac{hc}{\lambda} = \frac{(6.6256 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{589.6 \times 10^{-9} \text{ m}} = 3.369 \times 10^{-19} \text{ J}$$

For *one* photon the energy difference is:

$$\Delta E = (3.372 \times 10^{-19} \text{ J}) - (3.369 \times 10^{-19} \text{ J}) = \mathbf{3 \times 10^{-22} \text{ J}}$$

7.34
$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

n_f is given in the problem and R_H is a constant, but we need to calculate ΔE . The photon energy is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{434 \times 10^{-9} \text{ m}} = 4.58 \times 10^{-19} \text{ J}$$

Since this is an emission process, the energy change ΔE must be negative, or $-4.58 \times 10^{-19} \text{ J}$.

Substitute ΔE into the following equation, and solve for n_i .

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$-4.58 \times 10^{-19} \text{ J} = (2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n_i^2} - \frac{1}{2^2} \right)$$

$$\frac{1}{n_i^2} = \left(\frac{-4.58 \times 10^{-19} \text{ J}}{2.18 \times 10^{-18} \text{ J}} \right) + \frac{1}{2^2} = -0.210 + 0.250 = 0.040$$

$$n_i = \frac{1}{\sqrt{0.040}} = \mathbf{5}$$

7.35 Matter and radiation possess both particlelike and wavelike properties. Depending on the experiment, matter or radiation behaves either as a wave or as a stream of particles.

7.36 De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles such as electrons can possess wave properties. If an electron does behave like a standing wave in the hydrogen atom, the length of the wave must fit the circumference of the orbit exactly (see Figure 7.11 of the text). The equation relating the circumference of the orbit to the electron wavelength is: $2\pi r = n\lambda$, where n is an integer. Because n is an integer, it follows that r (radius of orbit) can have only certain allowed values. Because the energy of an electron depends on the size of the orbit (or the value of r), its value must be quantized.

7.37 Wave properties become observable only for submicroscopic objects because h is a very small quantity.

7.38 Yes, but the wave properties are too small to be detected.

$$\mathbf{7.39} \quad \lambda = \frac{h}{mu} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{(1.675 \times 10^{-27} \text{ kg})(7.00 \times 10^2 \text{ m/s})} = 5.65 \times 10^{-10} \text{ m} = \mathbf{0.565 \text{ nm}}$$

7.40 Strategy: We are given the mass and the speed of the proton and asked to calculate the wavelength. We need the de Broglie equation, which is Equation (7.8) of the text. Note that because the units of Planck's constant are J·s, m must be in kg and u must be in m/s (1 J = 1 kg·m²/s²).

Solution: Using Equation (7.8) we write:

$$\lambda = \frac{h}{mu}$$

$$\lambda = \frac{h}{mu} = \frac{\left(6.63 \times 10^{-34} \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}\cdot\text{s}\right)}{(1.673 \times 10^{-27} \text{ kg})(2.90 \times 10^8 \text{ m/s})} = 1.37 \times 10^{-15} \text{ m}$$

The problem asks to express the wavelength in nanometers.

$$\lambda = (1.37 \times 10^{-15} \text{ m}) \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = \mathbf{1.37 \times 10^{-6} \text{ nm}}$$

7.41 Converting the velocity to units of m/s:

$$\frac{1.20 \times 10^2 \text{ mi}}{1 \text{ h}} \times \frac{1.61 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 53.7 \text{ m/s}$$

$$\lambda = \frac{h}{mu} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{(0.0124 \text{ kg})(53.7 \text{ m/s})} = 9.96 \times 10^{-34} \text{ m} = \mathbf{9.96 \times 10^{-32} \text{ cm}}$$

7.42 First, we convert mph to m/s.

$$\frac{35 \text{ mi}}{1 \text{ h}} \times \frac{1.61 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 16 \text{ m/s}$$

$$\lambda = \frac{h}{mu} = \frac{\left(6.63 \times 10^{-34} \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}\cdot\text{s}\right)}{(2.5 \times 10^{-3} \text{ kg})(16 \text{ m/s})} = 1.7 \times 10^{-32} \text{ m} = \mathbf{1.7 \times 10^{-23} \text{ nm}}$$

- 7.43** Bohr's approach could not account for the emission spectra of atoms containing more than one electron, such as atoms of helium and lithium. Nor did it explain why extra lines appear in the hydrogen emission spectrum when a magnetic field is applied. Another problem arose with the discovery that electrons are wavelike: How can the "position" of a wave be specified? We cannot define the precise location of a wave because a wave extends in space.
- 7.44** The Heisenberg uncertainty principle states that it is impossible to know simultaneously both the momentum (mass times velocity) and the position of a particle with certainty. The Schrodinger equation is an equation that describes the behavior and energies of submicroscopic particles.
- 7.45** The wave function (ψ) itself has no direct physical meaning. However, the probability of finding the electron in a certain region in space is proportional to the square of the wave function, ψ^2 .
- 7.46** Electron density falls off rapidly as distance from the nucleus increases (see Figure 7.15 of the text). We draw a boundary surface diagram that encloses about 90 percent of the total electron density in an orbital. The exact position of the electron is not known, but 90% of the time, the electron should be in the region of space represented by the shape of the orbital.
- 7.47** An atomic orbital can be thought of as the wave function of an electron in an atom. When we say that an electron is in a certain orbital, we mean that the distribution of the electron density or the probability of locating the electron in space is described by the square of the wave function associated with that orbital. An orbit is a circular path of the electron around the nucleus of an atom.
- 7.48** All s orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases. The boundary surface diagrams of p orbitals (see Figure 7.17 of the text) show that each p orbital can be thought of as two lobes of electron density on opposite sides of the nucleus. Like s orbitals, p orbitals increase in size from $2p$ to $3p$ to $4p$ orbitals and so on. The boundary surface diagrams of d orbitals (see Figure 7.18 of the text) show that four of the d orbitals have four lobes of electron density. Although the $3d_{z^2}$ orbital looks different, it is equivalent to the other four d orbitals in all other respects. $1p$, $2d$, $3f$, and $4g$ orbitals do not exist.
- 7.49** A typical boundary surface diagram encloses about 90 percent of the total electron density in an orbital. This is the region of space where the electron is most likely to be found. It is also easy to draw.
- 7.50** The principal quantum number (n) can have integral values 1, 2, 3, and so forth; it corresponds to the quantum number in Equation (7.5) of the text. In a hydrogen atom, the value of n determines the energy of an orbital. The angular momentum quantum number (l) tells us the "shape" of the orbitals. The magnetic quantum number (m_l) describes the orientation of the orbital in space. The electron spin quantum number (m_s) accounts for the spin of the electron.
- 7.51** The principal quantum number (n) defines a shell. The angular momentum quantum number (l) defines a subshell.
- 7.52** (a) In a hydrogen atom (n), but in a many-electron atom both n and l (b) Both n and l
(c) l (d) m_l

- 7.53** The angular momentum quantum number l can have integral (i.e. whole number) values from 0 to $n - 1$. In this case $n = 2$, so the allowed values of the angular momentum quantum number, l , are **0** and **1**.

Each allowed value of the angular momentum quantum number labels a subshell. Within a given subshell (label l) there are $2l + 1$ allowed energy states (orbitals) each labeled by a different value of the magnetic quantum number. The allowed values run from $-l$ through 0 to $+l$ (whole numbers only). For the subshell labeled by the angular momentum quantum number $l = 1$, the allowed values of the magnetic quantum number, m_l , are **-1, 0, and 1**. For the other subshell in this problem labeled by the angular momentum quantum number $l = 0$, the allowed value of the magnetic quantum number is **0**.

If the allowed whole number values run from $-l$ to $+l$, are there always $2l + 1$ values? Why?

- 7.54 Strategy:** What are the relationships among n , l , and m_l ?

Solution: We are given the principal quantum number, $n = 3$. The possible l values range from 0 to $(n - 1)$. Thus, there are three possible values of l : 0, 1, and 2, corresponding to the s , p , and d orbitals, respectively. The values of m_l can vary from $-l$ to l . The values of m_l for each l value are:

$$l = 0: \quad m_l = 0 \qquad l = 1: \quad m_l = -1, 0, 1 \qquad l = 2: \quad m_l = -2, -1, 0, 1, 2$$

- 7.55** (a) $2p$: $n = 2$, $l = 1$, $m_l = 1, 0$, or -1
 (b) $3s$: $n = 3$, $l = 0$, $m_l = 0$ (only allowed value)
 (c) $5d$: $n = 5$, $l = 2$, $m_l = 2, 1, 0, -1$, or -2

An orbital in a subshell can have any of the allowed values of the magnetic quantum number for that subshell. All the orbitals in a subshell have exactly the same energy.

- 7.56** (a) The number given in the designation of the subshell is the principal quantum number, so in this case $n = 3$. For s orbitals, $l = 0$. m_l can have integer values from $-l$ to $+l$, therefore, $m_l = 0$. The electron spin quantum number, m_s , can be either $+1/2$ or $-1/2$.

Following the same reasoning as part (a)

- (b) $4p$: $n = 4$; $l = 1$; $m_l = -1, 0, 1$; $m_s = +1/2, -1/2$
 (c) $3d$: $n = 3$; $l = 2$; $m_l = -2, -1, 0, 1, 2$; $m_s = +1/2, -1/2$

- 7.57** A $2s$ orbital is larger than a $1s$ orbital. Both have the same spherical shape. The $1s$ orbital is lower in energy than the $2s$.

- 7.58** The two orbitals are identical in size, shape, and energy. They differ only in their orientation with respect to each other.

Can you assign a specific value of the magnetic quantum number to these orbitals? What are the allowed values of the magnetic quantum number for the $2p$ subshell?

- 7.59** The allowed values of l are 0, 1, 2, 3, and 4. These correspond to the **5s**, **5p**, **5d**, **5f**, and **5g** subshells. These subshells each have **one**, **three**, **five**, **seven**, and **nine** orbitals, respectively.

- 7.60** For $n = 6$, the allowed values of l are 0, 1, 2, 3, 4, and 5 [$l = 0$ to $(n - 1)$, integer values]. These l values correspond to the **6s**, **6p**, **6d**, **6f**, **6g**, and **6h** subshells. These subshells each have **1**, **3**, **5**, **7**, **9**, and **11** orbitals, respectively (number of orbitals = $2l + 1$).

7.61 There can be a maximum of two electrons occupying one orbital.

- (a) two (b) six (c) ten (d) fourteen

What rule of nature demands a maximum of two electrons per orbital? Do they have the same energy? How are they different? Would five $4d$ orbitals hold as many electrons as five $3d$ orbitals? In other words, does the principal quantum number n affect the number of electrons in a given subshell?

7.62	<u>n value</u>	<u>orbital sum</u>	<u>total number of electrons</u>
	1	1	2
	2	$1 + 3 = 4$	8
	3	$1 + 3 + 5 = 9$	18
	4	$1 + 3 + 5 + 7 = 16$	32
	5	$1 + 3 + 5 + 7 + 9 = 25$	50
	6	$1 + 3 + 5 + 7 + 9 + 11 = 36$	72

In each case the total number of orbitals is just the square of the n value (n^2). The total number of electrons is $2n^2$.

7.63 $3s$: two $3d$: ten $4p$: six $4f$: fourteen $5f$: fourteen

7.64 The electron configurations for the elements are

- (a) N: $1s^2 2s^2 2p^3$ There are three p -type electrons.
 (b) Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ There are six s -type electrons.
 (c) S: $1s^2 2s^2 2p^6 3s^2 3p^4$ There are no d -type electrons.

7.65 See Figure 7.19 in your textbook.

7.66 In the many-electron atom, the $3p$ orbital electrons are more effectively shielded by the inner electrons of the atom (that is, the $1s$, $2s$, and $2p$ electrons) than the $3s$ electrons. The $3s$ orbital is said to be more “penetrating” than the $3p$ and $3d$ orbitals. In the hydrogen atom there is only one electron, so the $3s$, $3p$, and $3d$ orbitals have the same energy.

7.67 Equation (7.5) of the text gives the orbital energy in terms of the principal quantum number, n , alone (for the hydrogen atom). The energy does not depend on any of the other quantum numbers. If two orbitals in the hydrogen atom have the same value of n , they have equal energy.

- (a) $2s > 1s$ (b) $3p > 2p$ (c) equal (d) equal (e) $5s > 4f$

7.68 (a) $2s < 2p$ (b) $3p < 3d$ (c) $3s < 4s$ (d) $4d < 5f$

7.69 The shapes of the s , p , and d orbitals are shown in Section 7.7 of the text. Values of 0, 1, and 2 for the angular momentum quantum number (l) represent the s , p , and d orbitals, respectively.

7.70 See Figure 7.19 of the text. $1s < 2s$, $2p < 3s$, $3p$, $3d < 4s$, $4p$, $4d$, $4f$, and so on.

- 7.71** The electron configuration of an atom represents how the electrons are distributed among the various atomic orbitals. The Pauli exclusion principle states that no two electrons in an atom can have the same four quantum numbers. If two electrons in an atom should have the same n , l , and m_l values (that is, these two electrons are in the same atomic orbital), then they must have different values of m_s . In other words, only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins. Hund's rule states that the most stable arrangement of electrons in a subshell is the one that has the greatest number of parallel spins.
- 7.72** This symbol means that there are 6 electrons in the $4d$ orbitals ($n = 4$ and $l = 2$).
- 7.73** Paramagnetic substances are those that contain net unpaired spins and are attracted by a magnet. Diamagnetic substances do not contain net unpaired spins and are slightly repelled by a magnet. A sodium (Na) atom is paramagnetic and a magnesium (Mg) atom is diamagnetic. When two electrons in an orbital have anti-parallel spins, we say that the electrons are paired.
- 7.74** Electrons that are further from the nucleus are partially "shielded" from the nuclear charge by electrons that are closer to the nucleus. In the Li atom, the $2s^1$ electron is shielded by the inner $1s^2$ electrons. The $2s$ electron is higher in energy than a $1s$ electron.
- 7.75** Transition metals either have incompletely filled d subshells or readily give rise to cations that have incompletely filled d subshells. Titanium (Ti) is an example. The lanthanides, or rare earth metals, have incompletely filled $4f$ subshells or readily give rise to cations that have incompletely filled $4f$ subshells. Europium (Eu) is an example. The last row of elements on the periodic table is the actinide series, which starts at thorium ($Z = 90$). Most of these elements are not found in nature but have been synthesized. Neptunium (Np) is an example.
- 7.76** The electron configuration of chromium is $[\text{Ar}]4s^13d^5$ and not $[\text{Ar}]4s^23d^4$, as we might expect. A similar break in the pattern is observed for copper, whose electron configuration is $[\text{Ar}]4s^13d^{10}$ rather than $[\text{Ar}]4s^23d^9$. The reason for these irregularities is that a slightly greater stability is associated with the half-filled ($3d^5$) and completely filled ($3d^{10}$) subshells.
- 7.77** A noble gas core is used when writing electron configurations. The noble gas element that most nearly precedes the element being considered is shown in square brackets in the electron configuration. The electron configuration of a Xe core is: $[\text{Kr}]5s^24d^{10}5p^6$.
- 7.78** This statement is correct. The Pauli Exclusion Principle states that no two electrons in the same atom can have the same four quantum numbers.
- 7.79** (a) is wrong because the magnetic quantum number m_l can have only whole number values.
(c) is wrong because the maximum value of the angular momentum quantum number l is $n - 1$.
(e) is wrong because the electron spin quantum number m_s can have only have the values $\pm 1/2$.
- 7.80** For aluminum, there are not enough electrons in the $2p$ subshell. (The $2p$ subshell holds six electrons.) The number of electrons (13) is correct. The electron configuration should be $1s^22s^22p^63s^23p^1$. The configuration shown might be an excited state of an aluminum atom.

For boron, there are too many electrons. (Boron only has five electrons.) The electron configuration should be $1s^22s^22p^1$. What would be the electric charge of a boron ion with the electron arrangement given in the problem?

For fluorine, there are also too many electrons. (Fluorine only has nine electrons.) The configuration shown is that of the F^- ion. The correct electron configuration is $1s^2 2s^2 2p^5$.

7.81 Since the atomic number is odd, it is mathematically impossible for all the electrons to be paired. There must be at least one that is unpaired. The element would be **paramagnetic**.

7.82 You should write the electron configurations for each of these elements to answer this question. In some cases, an orbital diagram may be helpful.

B: $[He]2s^2 2p^1$ (1 unpaired electron)

P: $[Ne]3s^2 3p^3$ (3 unpaired electrons)

Mn: $[Ar]4s^2 3d^5$ (5 unpaired electrons)

Kr: (0 unpaired electrons)

Cd: $[Kr]5s^2 4d^{10}$ (0 unpaired electrons)

Pb: $[Xe]6s^2 4f^{14} 5d^{10} 6p^2$ (2 unpaired electrons)

Ne: (0 unpaired electrons, Why?)

Sc: $[Ar]4s^2 3d^1$ (1 unpaired electron)

Se: $[Ar]4s^2 3d^{10} 4p^4$ (2 unpaired electrons)

Fe: $[Ar]4s^2 3d^6$ (4 unpaired electrons)

I: $[Kr]5s^2 4d^{10} 5p^5$ (1 unpaired electron)

7.83 B: $1s^2 2s^2 2p^1$

As: $[Ar]4s^2 3d^{10} 4p^3$

V: $[Ar]4s^2 3d^3$

I: $[Kr]5s^2 4d^{10} 5p^5$

Ni: $[Ar]4s^2 3d^8$

Au: $[Xe]6s^1 4f^{14} 5d^{10}$

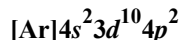
What is the meaning of “[Ar]”? of “[Kr]”? of “[Xe]”?

7.84 Strategy: How many electrons are in the Ge atom ($Z = 32$)? We start with $n = 1$ and proceed to fill orbitals in the order shown in Figure 7.20 of the text. Remember that any given orbital can hold at most 2 electrons. However, don't forget about degenerate orbitals. Starting with $n = 2$, there are three p orbitals of equal energy, corresponding to $m_l = -1, 0, 1$. Starting with $n = 3$, there are five d orbitals of equal energy, corresponding to $m_l = -2, -1, 0, 1, 2$. We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule. The task is simplified if we use the noble gas core preceding Ge for the inner electrons.

Solution: Germanium has 32 electrons. The noble gas core in this case is [Ar]. (Ar is the noble gas in the period preceding germanium.) [Ar] represents $1s^2 2s^2 2p^6 3s^2 3p^6$. This core accounts for 18 electrons, which leaves 14 electrons to place.

See Figure 7.20 of your text to check the order of filling subshells past the Ar noble gas core. You should find that the order of filling is $4s, 3d, 4p$. There are 14 remaining electrons to distribute among these orbitals. The $4s$ orbital can hold two electrons. Each of the five $3d$ orbitals can hold two electrons for a total of 10 electrons. This leaves two electrons to place in the $4p$ orbitals.

The electrons configuration for Ge is:



You should follow the same reasoning for the remaining atoms.

Fe: $[Ar]4s^2 3d^6$
W: $[Xe]6s^2 4f^{14} 5d^4$

Zn: $[Ar]4s^2 3d^{10}$
Tl: $[Xe]6s^2 4f^{14} 5d^{10} 6p^1$

Ni: $[Ar]4s^2 3d^8$

7.85 There are a total of twelve electrons:

Orbital	n	l	m_l	m_s
1s	1	0	0	$+\frac{1}{2}$
1s	1	0	0	$-\frac{1}{2}$
2s	2	0	0	$+\frac{1}{2}$
2s	2	0	0	$-\frac{1}{2}$
2p	2	1	1	$+\frac{1}{2}$
2p	2	1	1	$-\frac{1}{2}$
2p	2	1	0	$+\frac{1}{2}$
2p	2	1	0	$-\frac{1}{2}$
2p	2	1	-1	$+\frac{1}{2}$
2p	2	1	-1	$-\frac{1}{2}$
3s	3	0	0	$+\frac{1}{2}$
3s	3	0	0	$-\frac{1}{2}$

The element is **magnesium**.

7.86

$\uparrow\downarrow$
 $3s^2$
 \uparrow
 $3p^3$
 S^+ (5 valence electrons)
 3 unpaired electrons

$\uparrow\downarrow$
 $3s^2$
 $\uparrow\downarrow$
 $3p^4$
 S (6 valence electrons)
 2 unpaired electrons

$\uparrow\downarrow$
 $3s^2$
 $\uparrow\downarrow$
 $3p^5$
 S^- (7 valence electrons)
 1 unpaired electron

S^+ has the most unpaired electrons

7.87 The Aufbau principle dictates that as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to the atomic orbitals. Through this process we gain a detailed knowledge of the ground-state electron configurations of the elements. Knowledge of electron configurations helps us to understand and predict the properties of the elements.

7.88 Transition metals either have incompletely filled d subshells or readily give rise to cations that have incompletely filled d subshells. Lanthanides, or rare earth series [cerium ($Z = 58$) to lutetium ($Z = 71$)], have incompletely filled $4f$ subshells or readily give rise to cations that have incompletely filled $4f$ subshells. The last row of elements is the actinide series, which starts at thorium ($Z = 90$). Most of these elements are not found in nature but have been synthesized.

7.89 A noble gas core is used when writing electron configurations. The noble gas element that most nearly precedes the element being considered is shown in square brackets in the electron configuration. By using the noble gas core for the inner electrons, writing of electron configurations is simplified.

7.90 Osmium is in Group 8B and in Period 6.

7.91 $[Ar]4s^2 3d^{10} 4p^4$

7.92 The ground state electron configuration of Tc is: $[Kr]5s^2 4d^5$.

7.93 We first calculate the wavelength, then we find the color using Figure 7.3 of the text.

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{4.30 \times 10^{-19} \text{ J}} = 4.63 \times 10^{-7} \text{ m} = 463 \text{ nm, which is blue.}$$

7.94 (a) With $n = 2$, there are n^2 orbitals $= 2^2 = 4$. $m_s = +1/2$, specifies 1 electron per orbital, for a total of **4 electrons**.

(b) $n = 4$ and $m_l = +1$, specifies one orbital in each subshell with $l = 1, 2$, or 3 (i.e., a $4p$, $4d$, and $4f$ orbital). Each of the three orbitals holds 2 electrons for a total of **6 electrons**.

(c) If $n = 3$ and $l = 2$, m_l has the values $2, 1, 0, -1$, or -2 . Each of the five orbitals can hold 2 electrons for a total of **10 electrons** ($2e^-$ in each of the five $3d$ orbitals).

(d) If $n = 2$ and $l = 0$, then m_l can only be zero. $m_s = -1/2$ specifies 1 electron in this orbital for a total of **1 electron** (one e^- in the $2s$ orbital).

(e) $n = 4$, $l = 3$ and $m_l = -2$, specifies one $4f$ orbital. This orbital can hold **2 electrons**.

7.95 See the appropriate sections of the textbook in Chapter 7.

7.96 The wave properties of electrons are used in the operation of an electron microscope.

7.97 It takes:

$$(5.0 \times 10^2 \text{ g ice}) \times \frac{334 \text{ J}}{1 \text{ g ice}} = 1.67 \times 10^5 \text{ J to melt } 5.0 \times 10^2 \text{ g of ice.}$$

Energy of a photon with a wavelength of 660 nm:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{660 \times 10^{-9} \text{ m}} = 3.01 \times 10^{-19} \text{ J}$$

Number of photons needed to melt 5.0×10^2 g of ice:

$$(1.67 \times 10^5 \text{ J}) \times \frac{1 \text{ photon}}{3.01 \times 10^{-19} \text{ J}} = \mathbf{5.5 \times 10^{23} \text{ photons}}$$

The number of water molecules is:

$$(5.0 \times 10^2 \text{ g H}_2\text{O}) \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{6.022 \times 10^{23} \text{ H}_2\text{O molecules}}{1 \text{ mol H}_2\text{O}} = 1.7 \times 10^{25} \text{ H}_2\text{O molecules}$$

The number of water molecules converted from ice to water by one photon is:

$$\frac{1.7 \times 10^{25} \text{ H}_2\text{O molecules}}{5.5 \times 10^{23} \text{ photons}} = \mathbf{31 \text{ H}_2\text{O molecules/photon}}$$

- 7.98 (a)** First convert 100 mph to units of m/s.

$$\frac{100 \cancel{\text{mi}}}{1 \cancel{\text{h}}} \times \frac{1 \cancel{\text{h}}}{3600 \text{ s}} \times \frac{1.609 \cancel{\text{km}}}{1 \cancel{\text{mi}}} \times \frac{1000 \text{ m}}{1 \cancel{\text{km}}} = 44.7 \text{ m/s}$$

Using the de Broglie equation:

$$\lambda = \frac{h}{mu} = \frac{\left(6.63 \times 10^{-34} \frac{\cancel{\text{kg}} \cdot \cancel{\text{m}^2}}{\cancel{\text{s}^2}} \cdot \cancel{\text{s}} \right)}{(0.141 \cancel{\text{kg}})(44.7 \cancel{\text{m/s}})} = 1.05 \times 10^{-34} \text{ m} = \mathbf{1.05 \times 10^{-25} \text{ nm}}$$

- (b)** The average mass of a hydrogen atom is:

$$\frac{1.008 \cancel{\text{g}}}{1 \cancel{\text{mol}}} \times \frac{1 \cancel{\text{mol}}}{6.022 \times 10^{23} \text{ atoms}} = 1.674 \times 10^{-24} \text{ g/H atom} = 1.674 \times 10^{-27} \text{ kg}$$

$$\lambda = \frac{h}{mu} = \frac{\left(6.63 \times 10^{-34} \frac{\cancel{\text{kg}} \cdot \cancel{\text{m}^2}}{\cancel{\text{s}^2}} \cdot \cancel{\text{s}} \right)}{(1.674 \times 10^{-27} \cancel{\text{kg}})(44.7 \cancel{\text{m/s}})} = 8.86 \times 10^{-9} \text{ m} = \mathbf{8.86 \text{ nm}}$$

- 7.99** There are many more **paramagnetic** elements than diamagnetic elements because of Hund's rule.

- 7.100 (a)** First, we can calculate the energy of a single photon with a wavelength of 633 nm.

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}} \cdot \cancel{\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{633 \times 10^{-9} \cancel{\text{m}}} = 3.14 \times 10^{-19} \text{ J}$$

The number of photons produced in a 0.376 J pulse is:

$$0.376 \cancel{\text{J}} \times \frac{1 \text{ photon}}{3.14 \times 10^{-19} \cancel{\text{J}}} = \mathbf{1.20 \times 10^{18} \text{ photons}}$$

- (b)** Since a 1 W = 1 J/s, the power delivered per a 1.00×10^{-9} s pulse is:

$$\frac{0.376 \text{ J}}{1.00 \times 10^{-9} \text{ s}} = 3.76 \times 10^8 \text{ J/s} = \mathbf{3.76 \times 10^8 \text{ W}}$$

Compare this with the power delivered by a 100-W light bulb!

- 7.101** The energy required to heat the water is: $q = ms\Delta t = (368 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(5.00^\circ\text{C}) = 7.70 \times 10^3 \text{ J}$

Energy of a photon with a wavelength = $1.06 \times 10^4 \text{ nm}$:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}} \cdot \cancel{\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{1.06 \times 10^{-5} \cancel{\text{m}}} = 1.88 \times 10^{-20} \text{ J/photon}$$

The number of photons required is:

$$(7.70 \times 10^3 \cancel{\text{J}}) \times \frac{1 \text{ photon}}{1.88 \times 10^{-20} \cancel{\text{J}}} = \mathbf{4.10 \times 10^{23} \text{ photons}}$$

7.102 First, let's find the energy needed to photodissociate one water molecule.

$$\frac{285.8 \text{ kJ}}{1 \cancel{\text{mol}}} \times \frac{1 \cancel{\text{mol}}}{6.022 \times 10^{23} \text{ molecules}} = 4.746 \times 10^{-22} \text{ kJ/molecule} = 4.746 \times 10^{-19} \text{ J/molecule}$$

The maximum wavelength of a photon that would provide the above energy is:

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{4.746 \times 10^{-19} \cancel{\text{J}}} = 4.19 \times 10^{-7} \text{ m} = 419 \text{ nm}$$

This wavelength is in the visible region of the electromagnetic spectrum. Since water is continuously being struck by visible radiation *without* decomposition, it seems unlikely that photodissociation of water by this method is feasible.

7.103 For the Lyman series, we want the longest wavelength (smallest energy), with $n_i = 2$ and $n_f = 1$. Using Equation (7.6) of the text:

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{2^2} - \frac{1}{1^2} \right) = -1.64 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{1.64 \times 10^{-18} \cancel{\text{J}}} = 1.21 \times 10^{-7} \text{ m} = 121 \text{ nm}$$

For the Balmer series, we want the shortest wavelength (highest energy), with $n_i = \infty$ and $n_f = 2$.

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{\infty^2} - \frac{1}{2^2} \right) = -5.45 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{5.45 \times 10^{-19} \text{ J}} = 3.65 \times 10^{-7} \text{ m} = 365 \text{ nm}$$

Therefore the two series do not overlap.

7.104 Since $1 \text{ W} = 1 \text{ J/s}$, the energy output of the light bulb in 1 second is 75 J. The actual energy converted to visible light is 15 percent of this value or 11 J.

First, we need to calculate the energy of one 550 nm photon. Then, we can determine how many photons are needed to provide 11 J of energy.

The energy of one 550 nm photon is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{550 \times 10^{-9} \cancel{\text{m}}} = 3.62 \times 10^{-19} \text{ J/photon}$$

The number of photons needed to produce 11 J of energy is:

$$11 \cancel{\text{J}} \times \frac{1 \text{ photon}}{3.62 \times 10^{-19} \cancel{\text{J}}} = 3.0 \times 10^{19} \text{ photons}$$

- 7.105** The heat needed to raise the temperature of 150 mL of water from 20°C to 100°C is:

$$q = ms\Delta t = (150 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(100 - 20)^\circ\text{C} = 5.0 \times 10^4 \text{ J}$$

The microwave will need to supply more energy than this because only 92.0% of microwave energy is converted to thermal energy of water. The energy that needs to be supplied by the microwave is:

$$\frac{5.0 \times 10^4 \text{ J}}{0.920} = 5.4 \times 10^4 \text{ J}$$

The energy supplied by one photon with a wavelength of $1.22 \times 10^8 \text{ nm}$ (0.122 m) is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(0.122 \text{ m})} = 1.63 \times 10^{-24} \text{ J}$$

The number of photons needed to supply $5.4 \times 10^4 \text{ J}$ of energy is:

$$(5.4 \times 10^4 \text{ J}) \times \frac{1 \text{ photon}}{1.63 \times 10^{-24} \text{ J}} = 3.3 \times 10^{28} \text{ photons}$$

- 7.106** The Balmer series corresponds to transitions to the $n = 2$ level.

For He^+ :

$$\Delta E = R_{\text{He}^+} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{\Delta E}$$

For the transition, $n = 3 \rightarrow 2$

$$\Delta E = (8.72 \times 10^{-18} \text{ J}) \left(\frac{1}{3^2} - \frac{1}{2^2} \right) = -1.21 \times 10^{-18} \text{ J} \quad \lambda = \frac{1.99 \times 10^{-25} \text{ J}\cdot\text{m}}{1.21 \times 10^{-18} \text{ J}} = 1.64 \times 10^{-7} \text{ m} = \mathbf{164 \text{ nm}}$$

For the transition, $n = 4 \rightarrow 2$, $\Delta E = -1.64 \times 10^{-18} \text{ J}$

$$\lambda = \mathbf{121 \text{ nm}}$$

For the transition, $n = 5 \rightarrow 2$, $\Delta E = -1.83 \times 10^{-18} \text{ J}$

$$\lambda = \mathbf{109 \text{ nm}}$$

For the transition, $n = 6 \rightarrow 2$, $\Delta E = -1.94 \times 10^{-18} \text{ J}$

$$\lambda = \mathbf{103 \text{ nm}}$$

For H, the calculations are identical to those above, except the Rydberg constant for H is $2.18 \times 10^{-18} \text{ J}$.

For the transition, $n = 3 \rightarrow 2$, $\Delta E = -3.03 \times 10^{-19} \text{ J}$

$$\lambda = \mathbf{657 \text{ nm}}$$

For the transition, $n = 4 \rightarrow 2$, $\Delta E = -4.09 \times 10^{-19} \text{ J}$

$$\lambda = \mathbf{487 \text{ nm}}$$

For the transition, $n = 5 \rightarrow 2$, $\Delta E = -4.58 \times 10^{-19} \text{ J}$

$$\lambda = \mathbf{434 \text{ nm}}$$

For the transition, $n = 6 \rightarrow 2$, $\Delta E = -4.84 \times 10^{-19} \text{ J}$

$$\lambda = \mathbf{411 \text{ nm}}$$

All the Balmer transitions for He^+ are in the ultraviolet region; whereas, the transitions for H are all in the visible region. Note the negative sign for energy indicating that a photon has been emitted.

7.107 (a) $\Delta H^\circ = \Delta H_f^\circ(\text{O}) + \Delta H_f^\circ(\text{O}_2) - \Delta H_f^\circ(\text{O}_3) = 249.4 \text{ kJ/mol} + (0) - 142.2 \text{ kJ/mol} = \mathbf{107.2 \text{ kJ/mol}}$

(b) The energy in part (a) is for *one mole* of photons. To apply $E = h\nu$ we must divide by Avogadro's number. The energy of one photon is:

$$E = \frac{107.2 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1.780 \times 10^{-19} \text{ J/photon}$$

The wavelength of this photon can be found using the relationship $E = hc/\lambda$.

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.780 \times 10^{-19} \text{ J}} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = \mathbf{1.12 \times 10^3 \text{ nm}}$$

7.108 First, we need to calculate the energy of one 600 nm photon. Then, we can determine how many photons are needed to provide $4.0 \times 10^{-17} \text{ J}$ of energy.

The energy of one 600 nm photon is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{600 \times 10^{-9} \text{ m}} = 3.32 \times 10^{-19} \text{ J/photon}$$

The number of photons needed to produce $4.0 \times 10^{-17} \text{ J}$ of energy is:

$$(4.0 \times 10^{-17} \text{ J}) \times \frac{1 \text{ photon}}{3.32 \times 10^{-19} \text{ J}} = \mathbf{1.2 \times 10^2 \text{ photons}}$$

7.109 Since the energy corresponding to a photon of wavelength λ_1 equals the energy of photon of wavelength λ_2 plus the energy of photon of wavelength λ_3 , then the equation must relate the wavelength to energy.

$$\text{energy of photon 1} = (\text{energy of photon 2} + \text{energy of photon 3})$$

Since $E = \frac{hc}{\lambda}$, then:

$$\frac{hc}{\lambda_1} = \frac{hc}{\lambda_2} + \frac{hc}{\lambda_3}$$

Dividing by hc :

$$\frac{1}{\lambda_1} = \frac{1}{\lambda_2} + \frac{1}{\lambda_3}$$

7.110 A “blue” photon (shorter wavelength) is higher energy than a “yellow” photon. For the same amount of energy delivered to the metal surface, there must be fewer “blue” photons than “yellow” photons. Thus, the **yellow light would eject more electrons** since there are more “yellow” photons. Since the “blue” photons are of higher energy, **blue light will eject electrons with greater kinetic energy**.

7.111 Energy of a photon at 360 nm:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{360 \times 10^{-9} \text{ m}} = 5.53 \times 10^{-19} \text{ J}$$

Area of exposed body in cm^2 :

$$0.45 \cancel{\text{m}^2} \times \left(\frac{1 \cancel{\text{cm}}}{1 \times 10^{-2} \cancel{\text{m}}} \right)^2 = 4.5 \times 10^3 \text{ cm}^2$$

The number of photons absorbed by the body in 2 hours is:

$$0.5 \times \frac{2.0 \times 10^{16} \cancel{\text{photons}}}{\cancel{\text{cm}^2} \cdot \cancel{\text{s}}} \times (4.5 \times 10^3 \cancel{\text{cm}^2}) \times \frac{7200 \cancel{\text{s}}}{2 \text{ hr}} = 3.2 \times 10^{23} \text{ photons/2 hr}$$

The factor of 0.5 is used above because only 50% of the radiation is absorbed.

3.2×10^{23} photons with a wavelength of 360 nm correspond to an energy of:

$$(3.2 \times 10^{23} \cancel{\text{photons}}) \times \frac{5.53 \times 10^{-19} \text{ J}}{1 \cancel{\text{photon}}} = \mathbf{1.8 \times 10^5 \text{ J}}$$

- 7.112** The wavelength of a He atom can be calculated using the de Broglie equation. First, we need to calculate the root-mean-square speed using Equation (5.16) from the text.

$$u_{\text{rms}} = \sqrt{\frac{3 \left(8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) (273 + 20) \text{ K}}{4.003 \times 10^{-3} \text{ kg/mol}}} = 1.35 \times 10^3 \text{ m/s}$$

To calculate the wavelength, we also need the mass of a He atom in kg.

$$\frac{4.003 \times 10^{-3} \text{ kg He}}{1 \cancel{\text{mol He}}} \times \frac{1 \cancel{\text{mol He}}}{6.022 \times 10^{23} \text{ He atoms}} = 6.647 \times 10^{-27} \text{ kg/atom}$$

Finally, the wavelength of a He atom is:

$$\lambda = \frac{h}{mu} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})}{(6.647 \times 10^{-27} \text{ kg})(1.35 \times 10^3 \text{ m/s})} = \mathbf{7.39 \times 10^{-11} \text{ m} = 7.39 \times 10^{-2} \text{ nm}}$$

- 7.113** As an estimate, we can equate the energy for ionization ($\text{Fe}^{13+} \rightarrow \text{Fe}^{14+}$) to the average kinetic energy $\left(\frac{3}{2} RT \right)$ of the ions.

$$\frac{3.5 \times 10^4 \cancel{\text{kJ}}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \cancel{\text{kJ}}} = 3.5 \times 10^7 \text{ J/mol}$$

$$IE = \frac{3}{2} RT$$

$$3.5 \times 10^7 \cancel{\text{J/mol}} = \frac{3}{2} (8.314 \cancel{\text{J/mol} \cdot \text{K}}) T$$

$$\mathbf{T = 2.8 \times 10^6 \text{ K}}$$

The actual temperature can be, and most probably is, higher than this.

- 7.114** The energy given in the problem is the energy of 1 mole of gamma rays. We need to convert this to the energy of one gamma ray, then we can calculate the wavelength and frequency of this gamma ray.

$$\frac{1.29 \times 10^{11} \text{ J}}{1 \cancel{\text{mol}}} \times \frac{1 \cancel{\text{mol}}}{6.022 \times 10^{23} \text{ gamma rays}} = 2.14 \times 10^{-13} \text{ J/gamma ray}$$

Now, we can calculate the wavelength and frequency from this energy.

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

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{2.14 \times 10^{-13} \cancel{\text{J}}} = 9.29 \times 10^{-13} \text{ m} = 0.929 \text{ pm}$$

and

$$E = h\nu$$

$$\nu = \frac{E}{h} = \frac{2.14 \times 10^{-13} \cancel{\text{J}}}{6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}}} = 3.23 \times 10^{20} \text{ s}^{-1}$$

- 7.115** (a) **False.** $n = 2$ is the first excited state.
 (b) **False.** In the $n = 4$ state, the electron is (on average) further from the nucleus and hence easier to remove.
 (c) **True.**
 (d) **False.** The $n = 4$ to $n = 1$ transition is a higher energy transition, which corresponds to a *shorter* wavelength.
 (e) **True.**

- 7.116** Based on the *selection rule*, which states that $\Delta l = \pm 1$, only (b) and (d) are allowed transitions.

- 7.117** (a) Line A corresponds to the longest wavelength or lowest energy transition, which is the $3 \rightarrow 2$ transition. Therefore, **line B** corresponds to the $4 \rightarrow 2$ transition, and **line C** corresponds to the $5 \rightarrow 2$ transition.
 (b) We can derive an equation for the energy change (ΔE) for an electronic transition.

$$E_f = -R_H Z^2 \left(\frac{1}{n_f^2} \right) \quad \text{and} \quad E_i = -R_H Z^2 \left(\frac{1}{n_i^2} \right)$$

$$\Delta E = E_f - E_i = -R_H Z^2 \left(\frac{1}{n_f^2} \right) - \left(-R_H Z^2 \left(\frac{1}{n_i^2} \right) \right)$$

$$\Delta E = R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Line C corresponds to the $5 \rightarrow 2$ transition. The energy change associated with this transition can be calculated from the wavelength (27.1 nm).

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \cancel{\text{J}\cdot\text{s}})(3.00 \times 10^8 \cancel{\text{m/s}})}{(27.1 \times 10^{-9} \cancel{\text{m}})} = 7.34 \times 10^{-18} \text{ J}$$

For the $5 \rightarrow 2$ transition, we now know ΔE , n_i , n_f , and R_H ($R_H = 2.18 \times 10^{-18}$ J). Since this transition corresponds to an emission process, energy is released and ΔE is negative. ($\Delta E = -7.34 \times 10^{-18}$ J). We can now substitute these values into the equation above to solve for Z .

$$\begin{aligned}\Delta E &= R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ -7.34 \times 10^{-18} \text{ J} &= (2.18 \times 10^{-18} \text{ J}) Z^2 \left(\frac{1}{5^2} - \frac{1}{2^2} \right) \\ -7.34 \times 10^{-18} \text{ J} &= (-4.58 \times 10^{-19}) Z^2 \\ Z^2 &= 16.0 \\ Z &= 4\end{aligned}$$

Z must be an integer because it represents the atomic number of the parent atom.

Now, knowing the value of Z , we can substitute in n_i and n_f for the $3 \rightarrow 2$ (Line A) and the $4 \rightarrow 2$ (Line B) transitions to solve for ΔE . We can then calculate the wavelength from the energy.

For Line A ($3 \rightarrow 2$)

$$\begin{aligned}\Delta E &= R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J})(4)^2 \left(\frac{1}{3^2} - \frac{1}{2^2} \right) \\ \Delta E &= -4.84 \times 10^{-18} \text{ J} \\ \lambda &= \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(4.84 \times 10^{-18} \text{ J})} = 4.11 \times 10^{-8} \text{ m} = 41.1 \text{ nm}\end{aligned}$$

For Line B ($4 \rightarrow 2$)

$$\begin{aligned}\Delta E &= R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J})(4)^2 \left(\frac{1}{4^2} - \frac{1}{2^2} \right) \\ \Delta E &= -6.54 \times 10^{-18} \text{ J} \\ \lambda &= \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(6.54 \times 10^{-18} \text{ J})} = 3.04 \times 10^{-8} \text{ m} = 30.4 \text{ nm}\end{aligned}$$

- (c) The value of the final energy state is $n_f = \infty$. Use the equation derived in part (b) to solve for ΔE .

$$\begin{aligned}\Delta E &= R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J})(4)^2 \left(\frac{1}{4^2} - \frac{1}{\infty^2} \right) \\ \Delta E &= 2.18 \times 10^{-18} \text{ J}\end{aligned}$$

- (d) As we move to higher energy levels in an atom or ion, the energy levels get closer together. See Figure 7.9 of the text, which represents the energy levels for the hydrogen atom. Transitions from higher energy levels to the $n = 2$ level will be very close in energy and hence will have similar wavelengths. The lines are so close together that they overlap, forming a continuum. The continuum shows that the electron has been removed from the ion, and we no longer have quantized energy levels associated with the electron. In other words, the energy of the electron can now vary continuously.

- 7.118** To calculate the energy to remove an electron from the $n = 1$ state and the $n = 5$ state in the Li^{2+} ion, we use the equation derived in Problem 7.117 (b).

$$\Delta E = R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

For $n_i = 1$, $n_f = \infty$, and $Z = 3$, we have:

$$\Delta E = (2.18 \times 10^{-18} \text{ J})(3)^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = \mathbf{1.96 \times 10^{-17} \text{ J}}$$

For $n_i = 5$, $n_f = \infty$, and $Z = 3$, we have:

$$\Delta E = (2.18 \times 10^{-18} \text{ J})(3)^2 \left(\frac{1}{5^2} - \frac{1}{\infty^2} \right) = \mathbf{7.85 \times 10^{-19} \text{ J}}$$

To calculate the wavelength of the emitted photon in the electronic transition from $n = 5$ to $n = 1$, we first calculate ΔE and then calculate the wavelength.

$$\Delta E = R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (2.18 \times 10^{-18} \text{ J})(3)^2 \left(\frac{1}{5^2} - \frac{1}{1^2} \right) = -1.88 \times 10^{-17} \text{ J}$$

We ignore the minus sign for ΔE in calculating λ .

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.88 \times 10^{-17} \text{ J}}$$

$$\lambda = 1.06 \times 10^{-8} \text{ m} = \mathbf{10.6 \text{ nm}}$$

- 7.119 (a)** First, we need to calculate the moving mass of the proton, and then we can calculate its wavelength using the de Broglie equation.

$$m_{\text{moving}} = \frac{m_{\text{rest}}}{\sqrt{1 - \left(\frac{u}{c}\right)^2}} = \frac{1.673 \times 10^{-27} \text{ kg}}{\sqrt{1 - \left(\frac{(0.50)(3.00 \times 10^8 \text{ m/s})}{3.00 \times 10^8 \text{ m/s}}\right)^2}} = 1.93 \times 10^{-27} \text{ kg}$$

$$\lambda = \frac{h}{mu} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{(1.93 \times 10^{-27} \text{ kg})[(0.50)(3.00 \times 10^8 \text{ m/s})]}$$

$$\lambda = 2.29 \times 10^{-15} \text{ m} = \mathbf{2.29 \times 10^{-6} \text{ nm}}$$

$$(b) \quad m_{\text{moving}} = \frac{m_{\text{rest}}}{\sqrt{1 - \left(\frac{u}{c}\right)^2}} = \frac{6.0 \times 10^{-2} \text{ kg}}{\sqrt{1 - \left(\frac{63 \text{ m/s}}{3.00 \times 10^8 \text{ m/s}}\right)^2}} \approx \mathbf{6.0 \times 10^{-2} \text{ kg}}$$

The equation is only important for speeds close to that of light. Note that photons have a rest mass of zero; otherwise, their moving mass would be infinite!

- 7.120** We calculate W (the energy needed to remove an electron from the metal) at a wavelength of 351 nm. Once W is known, we can then calculate the velocity of an ejected electron using light with a wavelength of 313 nm.

First, we convert wavelength to frequency.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \cancel{\text{m/s}}}{351 \times 10^{-9} \cancel{\text{m}}} = 8.55 \times 10^{14} \text{ s}^{-1}$$

$$h\nu = W + \frac{1}{2}m_e u^2$$

$$(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(8.55 \times 10^{14} \text{ s}^{-1}) = W + \frac{1}{2}(9.1094 \times 10^{-31} \text{ kg})(0 \text{ m/s})^2$$

$$W = 5.67 \times 10^{-19} \text{ J}$$

Next, we convert a wavelength of 313 nm to frequency, and then calculate the velocity of the ejected electron.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \cancel{\text{m/s}}}{313 \times 10^{-9} \cancel{\text{m}}} = 9.58 \times 10^{14} \text{ s}^{-1}$$

$$h\nu = W + \frac{1}{2}m_e u^2$$

$$(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(9.58 \times 10^{14} \text{ s}^{-1}) = (5.67 \times 10^{-19} \text{ J}) + \frac{1}{2}(9.1094 \times 10^{-31} \text{ kg})u^2$$

$$6.82 \times 10^{-20} = (4.5547 \times 10^{-31})u^2$$

$$u = 3.87 \times 10^5 \text{ m/s}$$

- 7.121** We note that the maximum solar radiation centers around 500 nm. Thus, over billions of years, organisms have adjusted their development to capture energy at or near this wavelength. The two most notable cases are photosynthesis and vision.

7.122 (a)

$$\begin{array}{l} \text{_____ } n = 2, E_2 = \frac{5}{2} h\nu \\ \text{_____ } n = 1, E_1 = \frac{3}{2} h\nu \\ \text{_____ } n = 0, E_0 = \frac{1}{2} h\nu \end{array}$$

(b) $\Delta E = E_1 - E_0 = \frac{3}{2} h\nu - \frac{1}{2} h\nu = h\nu$

$$\Delta E = h\nu = (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(8.66 \times 10^{13} \text{ s}^{-1}) = 5.74 \times 10^{-20} \text{ J}$$

- (c) The Heisenberg uncertainty principle stated mathematically is

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

where Δx and Δp are the uncertainties in the position and momentum, respectively. For a nonvibrating molecule, both Δu and Δp are zero, where Δu is the uncertainty in the velocity. Therefore, Δx must approach infinity. However, the maximum uncertainty in determining the positions of the H and Cl atoms cannot exceed the bond length of HCl. Therefore, it follows that

$\Delta u \neq 0$, which means that the molecule is constantly vibrating, even at the absolute zero.

- 7.123 (a)** From Problem 7.121, we note that the maximum solar radiation centers at a wavelength of approximately 500 nm. We substitute into Wien's law to solve for the temperature.

$$\lambda_{\max} = \frac{b}{T}$$

$$500 \text{ nm} = \frac{2.898 \times 10^6 \text{ nm} \cdot \text{K}}{T}$$

$$T = 6 \times 10^3 \text{ K}$$

- (b) Measure the radiation from the star. Plot radiant energy versus wavelength and determine λ_{\max} . Use Wien's law to estimate the surface temperature.

- 7.124** At a node, the wave function is zero. This indicates that there is zero probability of finding an electron at this distance from the nucleus.

$$\psi_{2s} = \frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{\rho}{2} \right) e^{-\rho/2}$$

$$0 = \frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{\rho}{2} \right) e^{-\rho/2}$$

The right hand side of the equation will equal zero when $\frac{\rho}{2} = 1$. This is the location of the node.

$$\frac{\rho}{2} = 1$$

$$\rho = 2 = Z \left(\frac{r}{a_0} \right)$$

For a hydrogen atom, the atomic number, Z , is 1. The location of the node as a distance from the nucleus, r , is:

$$2 = \frac{r}{a_0}$$

$$r = 2a_0$$

$$r = (2)(0.529 \text{ nm}) = 1.06 \text{ nm}$$

CHAPTER 8

THE PERIODIC TABLE

- 8.1** Mendeleev's periodic table was a great improvement over previous efforts for two reasons. First, it grouped the elements together more accurately, according to their properties. Equally important, it made possible the prediction of the properties of several elements that had not yet been discovered.
- 8.2** Henry Moseley discovered a correlation between atomic number and the frequency of X rays generated by the bombardment of the element under study with high-energy electrons. Initially, it was thought that the periodic table should be arranged by atomic mass. This led to some discrepancies (see Ar and K). Moseley's determination of atomic numbers led to arranging the periodic table by atomic number rather than atomic mass.
- 8.3** A modern periodic table is arranged by atomic number and usually shows the atomic number along with the element symbol. The importance and usefulness of the periodic table lie in the fact that we can use our understanding of the general properties and trends within a group or a period to predict with considerable accuracy the properties of any element, even though that element may be unfamiliar to us.
- 8.4** We can use the general properties and trends within a group to predict with considerable accuracy the properties of any element in that group, even though that element may be unfamiliar to us.
- 8.5** Metals: Fe, Li, Ba. Nonmetals: Xe, Cl, P, I. Metalloids: As, B, Si.
- 8.6** Metals are good conductors of heat and electricity, while nonmetals are usually poor conductors of heat and electricity. Metals, excluding mercury, are solids, whereas many nonmetals are gases. Metals tend to have low ionization energies and low electron affinities. Nonmetals tend to have high ionization energies and high electron affinities.
- 8.7** Please see Figure 2.9 of the text.
- 8.8** The representative elements (also called main group elements) are the elements in Groups 1A through 7A of the periodic table, all of which have incompletely filled *s* or *p* subshells of the highest principal quantum number.
- 8.9** 1A: potassium (K), 2A: barium (Ba), 3A: aluminum (Al), 4A: silicon (Si), 5A: nitrogen (N), 6A: tellurium (Te), 7A: bromine (Br), 8A: krypton (Kr), transition metal: cobalt (Co).
- 8.10** Phosphorus (molecular, P₄), iodine (molecular, I₂), magnesium (three-dimensional structure, Mg), neon (atomic, Ne), arsenic (three-dimensional, As), sulfur (molecular, S₈), carbon (three-dimensional structure, C), selenium (molecular, Se₈), oxygen (molecular, O₂).
- 8.11** Test to see if the substance conducts electricity. Only a metallic element would conduct electricity.
- 8.12** Valence electrons are the outer electrons of an atom, which are those involved in chemical bonding. Al (Group 3A, 3 valence electrons), Sr (Group 2A, 2 valence electrons), K (Group 1A, 1 valence electron), Br (Group 7A, 7 valence electrons), P (Group 5A, 5 valence electrons), S (Group 6A, 6 valence electrons), C (Group 4A, 4 valence electrons).

8.13 (a) ns^1 (b) ns^2 (c) ns^2np^5 (d) ns^2np^6

8.14 Sc ($[\text{Ar}]4s^23d^1$), Ti ($[\text{Ar}]4s^23d^2$), V ($[\text{Ar}]4s^23d^3$), Cr ($[\text{Ar}]4s^13d^5$), Mn ($[\text{Ar}]4s^23d^5$), Fe ($[\text{Ar}]4s^23d^6$), Co ($[\text{Ar}]4s^23d^7$), Ni ($[\text{Ar}]4s^23d^8$), Cu ($[\text{Ar}]4s^13d^{10}$).

8.15 Hydrogen forms the H^+ ion (resembles the alkali metals) and the H^- ion (resembles the halogens).

8.16 **Strategy:** (a) We refer to the building-up principle discussed in Section 7.9 of the text. We start writing the electron configuration with principal quantum number $n = 1$ and continue upward in energy until all electrons are accounted for. (b) What are the electron configuration characteristics of representative elements, transition elements, and noble gases? (c) Examine the pairing scheme of the electrons in the outermost shell. What determines whether an element is diamagnetic or paramagnetic?

Solution:

(a) We know that for $n = 1$, we have a $1s$ orbital (2 electrons). For $n = 2$, we have a $2s$ orbital (2 electrons) and three $2p$ orbitals (6 electrons). For $n = 3$, we have a $3s$ orbital (2 electrons). The number of electrons left to place is $17 - 12 = 5$. These five electrons are placed in the $3p$ orbitals. The electron configuration is $1s^22s^22p^63s^23p^5$ or $[\text{Ne}]3s^23p^5$.

(b) Because the $3p$ subshell is not completely filled, this is a **representative element**. Without consulting a periodic table, you might know that the halogen family has seven valence electrons. You could then further classify this element as a **halogen**. In addition, all halogens are **nonmetals**.

(c) If you were to write an orbital diagram for this electron configuration, you would see that there is *one* unpaired electron in the p subshell. Remember, the three $3p$ orbitals can hold a total of six electrons. Therefore, the atoms of this element are **paramagnetic**.

Check: For (b), note that a transition metal possesses an incompletely filled d subshell, and a noble gas has a completely filled outer-shell. For (c), recall that if the atoms of an element contain an odd number of electrons, the element must be paramagnetic.

8.17 (a) and (d); (b) and (f); (c) and (e).

8.18 Elements that have the same number of valence electrons will have similarities in chemical behavior. Looking at the periodic table, elements with the same number of valence electrons are in the same group. Therefore, the pairs that would represent similar chemical properties of their atoms are:

(a) and (d) (b) and (e) (c) and (f).

8.19 (a) $1s^22s^22p^5$ (halogen) (c) $[\text{Ar}]4s^23d^6$ (transition metal)
(b) $[\text{Ar}]4s^2$ (alkaline earth metal) (d) $[\text{Ar}]4s^23d^{10}4p^3$ (Group 5A)

8.20 (a) Group 1A (b) Group 5A (c) Group 8A (d) Group 8B

Identify the elements.

8.21 There are no electrons in the $4s$ subshell because transition metals lose electrons from the ns valence subshell before they are lost from the $(n - 1)d$ subshell. For the neutral atom there are only six valence electrons. The element can be identified as **Cr (chromium)** simply by counting six across starting with potassium (K, atomic number 19).

What is the electron configuration of neutral chromium?

8.22 You should realize that the metal ion in question is a transition metal ion because it has five electrons in the $3d$ subshell. Remember that in a transition metal ion, the $(n-1)d$ orbitals are more stable than the ns orbital. Hence, when a cation is formed from an atom of a transition metal, electrons are *always* removed first from the ns orbital and then from the $(n-1)d$ orbitals if necessary. Since the metal ion has a +3 charge, three electrons have been removed. Since the $4s$ subshell is less stable than the $3d$, two electrons would have been lost from the $4s$ and one electron from the $3d$. Therefore, the electron configuration of the neutral atom is $[\text{Ar}]4s^2 3d^6$. This is the electron configuration of iron. Thus, the metal is **iron**.

8.23 The stable ions of representative elements have a noble gas electron configuration.

8.24 Ions, or atoms and ions, that have the same number of electrons and hence the same ground-state electron configuration, are said to be isoelectronic.

8.25 It is not possible for atoms of two different elements to be isoelectronic. Isoelectronic means that ions, or atoms and ions, have the same number of electrons, and hence the same ground-state electron configuration.

8.26 Ti^{4+} , Cr^{6+} , and Mn^{7+} .

8.27 Determine the number of electrons, and then “fill in” the electrons as you learned in Chapter 7 (Figure 7.21 and Table 7.3 of the text).

(a) $1s^2$

(g) $[\text{Ar}]4s^2 3d^{10} 4p^6$

(b) $1s^2$

(h) $[\text{Ar}]4s^2 3d^{10} 4p^6$

(c) $1s^2 2s^2 2p^6$

(i) $[\text{Kr}]$

(d) $1s^2 2s^2 2p^6$

(j) $[\text{Kr}]$

(e) $[\text{Ne}]3s^2 3p^6$

(k) $[\text{Kr}]5s^2 4d^{10}$

(f) $[\text{Ne}]$

8.28 Strategy: In the formation of a **cation** from the neutral atom of a representative element, one or more electrons are *removed* from the highest occupied n shell. In the formation of an **anion** from the neutral atom of a representative element, one or more electrons are *added* to the highest partially filled n shell. Representative elements typically gain or lose electrons to achieve a stable noble gas electron configuration. When a cation is formed from an atom of a transition metal, electrons are *always* removed first from the ns orbital and then from the $(n-1)d$ orbitals if necessary.

Solution:

(a) $[\text{Ne}]$

(e) Same as (c)

(b) same as (a). Do you see why?

(f) $[\text{Ar}]3d^6$. Why isn't it $[\text{Ar}]4s^2 3d^4$?

(c) $[\text{Ar}]$

(g) $[\text{Ar}]3d^9$. Why not $[\text{Ar}]4s^2 3d^7$?

(d) Same as (c). Do you see why?

(h) $[\text{Ar}]3d^{10}$. Why not $[\text{Ar}]4s^2 3d^8$?

8.29 This exercise simply depends on determining the total number of electrons and using Figure 7.21 and Table 7.3 of the text.

- | | | |
|-------------------------|--------------------------|-------------------------------------------|
| (a) [Ar] | (f) [Ar]3d ⁶ | (k) [Ar]3d ⁹ |
| (b) [Ar] | (g) [Ar]3d ⁵ | (l) [Kr]4d ¹⁰ |
| (c) [Ar] | (h) [Ar]3d ⁷ | (m) [Xe]4f ¹⁴ 5d ¹⁰ |
| (d) [Ar]3d ³ | (i) [Ar]3d ⁸ | (n) [Xe]4f ¹⁴ 5d ⁸ |
| (e) [Ar]3d ⁵ | (j) [Ar]3d ¹⁰ | (o) [Xe]4f ¹⁴ 5d ⁸ |

8.30 (a) Cr³⁺ (b) Sc³⁺ (c) Rh³⁺ (d) Ir³⁺

8.31 Two species are isoelectronic if they have the same number of electrons. Can two neutral atoms of different elements be isoelectronic?

C and B⁻ are isoelectronic. Mn²⁺ and Fe³⁺ are isoelectronic. Ar and Cl⁻ are isoelectronic. Zn and Ge²⁺ are isoelectronic.

With which neutral atom are the positive ions Mn²⁺ and Fe³⁺ isoelectronic?

8.32 Isoelectronic means that the species have the same number of electrons and the same electron configuration.

Be²⁺ and He (2 e⁻) F⁻ and N³⁻ (10 e⁻) Fe²⁺ and Co³⁺ (24 e⁻) S²⁻ and Ar (18 e⁻)

8.33 Atomic radius is one-half the distance between the nuclei of two adjacent atoms of the same element in a metal. For elements that exist as a diatomic molecule, the atomic radius is one-half the distance between the two nuclei of the atoms in a molecule. Atomic radius does not have a precise meaning because the wave function in theory extends to infinity.

8.34 (a) Decreases (b) Increases

8.35 Ionic radius is the radius of a cation or an anion. (a) The size increases when an atom is converted to an anion. (b) The size decreases when an atom is converted to a cation.

8.36 In the anions, the same number of electrons is attracted by fewer protons in the nucleus. With this decreased attraction, the electrons can spread out further from the nucleus.

8.37 (a) Cs is larger. It is below Na in Group 1A. (d) Br is larger. It is below F in Group 7A.
 (b) Ba is larger. It is below Be in Group 2A. (e) Xe is larger. It is below Ne in Group 8A.
 (c) Sb is larger. It is below N in Group 5A.

8.38 Strategy: What are the trends in atomic radii in a periodic group and in a particular period. Which of the above elements are in the same group and which are in the same period?

Solution: Recall that the general periodic trends in atomic size are:

- (1) Moving from left to right across a row (period) of the periodic table, the atomic radius **decreases** due to an increase in effective nuclear charge.
- (2) Moving down a column (group) of the periodic table, the atomic radius **increases** since the orbital size increases with increasing principal quantum number.

The atoms that we are considering are all in the same period of the periodic table. Hence, the atom furthest to the left in the row will have the largest atomic radius, and the atom furthest to the right in the row will have the smallest atomic radius. Arranged in order of decreasing atomic radius, we have:



Check: See Figure 8.4 of the text to confirm that the above is the correct order of decreasing atomic radius.

8.39 **Pb**, as can be seen in Figure 8.4 of the text.

8.40 **Fluorine** is the smallest atom in Group 7A. Atomic radius increases moving down a group since the orbital size increases with increasing principal quantum number, n .

8.41 The electron configuration of lithium is $1s^2 2s^1$. The two $1s$ electrons shield the $2s$ electron effectively from the nucleus. Consequently, the lithium atom is considerably larger than the hydrogen atom.

8.42 The atomic radius is largely determined by how strongly the outer-shell electrons are held by the nucleus. The larger the effective nuclear charge, the more strongly the electrons are held and the smaller the atomic radius. For the second period, the atomic radius of Li is largest because the $2s$ electron is well shielded by the filled $1s$ shell. The effective nuclear charge that the outermost electrons feel increases across the period as a result of incomplete shielding by electrons in the same shell. Consequently, the orbital containing the electrons is compressed and the atomic radius decreases.

8.43 (a) **Cl** is smaller than Cl^- . An atom gets bigger when more electrons are added.

(b) Na^+ is smaller than **Na**. An atom gets smaller when electrons are removed.

(c) O^{2-} is smaller than S^{2-} . Both elements belong to the same group, and ionic radius increases going down a group.

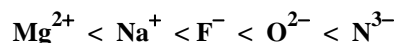
(d) Al^{3+} is smaller than Mg^{2+} . The two ions are isoelectronic (What does that mean? See Section 8.3 of the text) and in such cases the radius gets smaller as the charge becomes more positive.

(e) Au^{3+} is smaller than Au^+ for the same reason as part (b).

In each of the above cases from which atom would it be harder to remove an electron?

8.44 **Strategy:** In comparing ionic radii, it is useful to classify the ions into three categories: (1) isoelectronic ions, (2) ions that carry the same charges and are generated from atoms of the same periodic group, and (3) ions that carry different charges but are generated from the same atom. In case (1), ions carrying a greater negative charge are always larger; in case (2), ions from atoms having a greater atomic number are always larger; in case (3), ions have a smaller positive charge are always larger.

Solution: The ions listed are all isoelectronic. They each have ten electrons. The ion with the fewest protons will have the largest ionic radius, and the ion with the most protons will have the smallest ionic radius. The effective nuclear charge increases with increasing number of protons. The electrons are attracted more strongly by the nucleus, decreasing the ionic radius. N^{3-} has only 7 protons resulting in the smallest attraction exerted by the nucleus on the 10 electrons. N^{3-} is the largest ion of the group. Mg^{2+} has 12 protons resulting in the largest attraction exerted by the nucleus on the 10 electrons. Mg^{2+} is the smallest ion of the group. The order of increasing atomic radius is:



- 8.45 The Cu^+ ion is larger than Cu^{2+} because it has one more electron.
- 8.46 Both selenium and tellurium are Group 6A elements. Since atomic radius increases going down a column in the periodic table, it follows that Te^{2-} must be larger than Se^{2-} .
- 8.47 Bromine is liquid; all the others are solids.
- 8.48 We assume the approximate boiling point of argon is the mean of the boiling points of neon and krypton, based on its position in the periodic table being between Ne and Kr in Group 8A.

$$\text{b.p.} = \frac{-245.9^\circ\text{C} + (-152.9^\circ\text{C})}{2} = -199.4^\circ\text{C}$$

The actual boiling point of argon is -185.7°C .

- 8.49 Ionization energy is the minimum energy (in kJ/mol) required to remove an electron from a gaseous atom in its ground state. Gaseous atoms are specified in this definition because an atom in the gas phase is virtually uninfluenced by its neighbors and so there are no intermolecular forces (that is, forces between molecules) to take into account when measuring ionization energy. When an electron is removed from an atom, the repulsion among the remaining electrons decreases. Because the nuclear charge remains constant, more energy is needed to remove another electron from the positively charged ion.
- 8.50 In general, first ionization energy increases across a row and decreases down a column of the periodic table. Nonmetals tend to have high first-ionization energies, and metals tend to have low first-ionization energies.
- 8.51 Apart from the small irregularities, the ionization energies of elements in a period increase with increasing atomic number. We can explain this trend by referring to the increase in effective nuclear charge from left to right. A larger effective nuclear charge means a more tightly held outer electron, and hence a higher first ionization energy. Thus, in the third period, sodium has the lowest and neon has the highest first ionization energy.
- 8.52 The Group 3A elements (such as Al) all have a single electron in the outermost p subshell, which is well shielded from the nuclear charge by the inner electrons and the ns^2 electrons. Therefore, less energy is needed to remove a single p electron than to remove a paired s electron from the same principal energy level (such as for Mg).
- 8.53 To form the +2 ion of calcium, it is only necessary to remove two valence electrons. For potassium, however, the second electron must come from the atom's noble gas core, which accounts for the much higher second ionization energy. Would you expect a similar effect if you tried to form the +3 ion of calcium?
- 8.54 **Strategy:** Removal of the outermost electron requires less energy if it is shielded by a filled inner shell.

Solution: The lone electron in the $3s$ orbital will be much easier to remove. This lone electron is shielded from the nuclear charge by the filled inner shell. Therefore, the ionization energy of 496 kJ/mol is paired with the electron configuration $1s^2 2s^2 2p^6 3s^1$.

A noble gas electron configuration, such as $1s^2 2s^2 2p^6$, is a very stable configuration, making it extremely difficult to remove an electron. The $2p$ electron is not as effectively shielded by electrons in the same energy level. The high ionization energy of 2080 kJ/mol would be associated with the element having this noble gas electron configuration.

Check: Compare this answer to the data in Table 8.2. The electron configuration of $1s^2 2s^2 2p^6 3s^1$ corresponds to a Na atom, and the electron configuration of $1s^2 2s^2 2p^6$ corresponds to a Ne atom.

- 8.55** The ionization energy is the difference between the $n = \infty$ state (final) and the $n = 1$ state (initial).

$$\Delta E = E_{\infty} - E_1 = (-2.18 \times 10^{-18} \text{ J})(2)^2 \left(\frac{1}{\infty} \right)^2 - (-2.18 \times 10^{-18} \text{ J})(2)^2 \left(\frac{1}{1} \right)^2$$

$$\Delta E = 0 + (2.18 \times 10^{-18} \text{ J})(2)^2 \left(\frac{1}{1} \right)^2 = 8.72 \times 10^{-18} \text{ J/ion}$$

$$\text{In units of kJ/mol: } \frac{8.72 \times 10^{-18} \cancel{\text{J}}}{1 \cancel{\text{ion}}} \times \frac{1 \text{ kJ}}{1000 \cancel{\text{J}}} \times \frac{6.022 \times 10^{23} \cancel{\text{ions}}}{1 \text{ mol}} = \mathbf{5.25 \times 10^3 \text{ kJ/mol}}$$

Should this be larger than the first ionization energy of helium (see Table 8.2 of the text)?

- 8.56** The atomic number of mercury is 80. We carry an extra significant figure throughout this calculation to limit rounding errors.

$$\Delta E = (2.18 \times 10^{-18} \text{ J})(80^2) \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = 1.395 \times 10^{-14} \text{ J/ion}$$

$$\Delta E = \frac{1.395 \times 10^{-14} \cancel{\text{J}}}{1 \cancel{\text{ion}}} \times \frac{6.022 \times 10^{23} \cancel{\text{ions}}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \cancel{\text{J}}} = \mathbf{8.40 \times 10^6 \text{ kJ/mol}}$$

- 8.57** (a) Electron affinity is the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion. Gaseous atoms are specified in this definition because an atom in the gas phase is virtually uninfluenced by its neighbors. (b) Ionization energies are always positive because energy is always required to remove an electron from an atom. Electron affinities are usually positive; however, some elements, like the noble gases, have no affinity to gain an electron and therefore, the electron affinities are zero or negative.

- 8.58** Electron affinities tend to increase across a row of the periodic table. We see this trend from Al to Cl, except that phosphorus is an exception due to the increased stability of a half-filled subshell.

- 8.59** (a) $\text{K} < \text{Na} < \text{Li}$ (b) $\text{I} < \text{Br} < \text{F} < \text{Cl}$

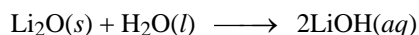
- 8.60** **Strategy:** What are the trends in electron affinity in a periodic group and in a particular period. Which of the above elements are in the same group and which are in the same period?

Solution: One of the general periodic trends for electron affinity is that the tendency to accept electrons increases (that is, electron affinity values become more positive) as we move from left to right across a period. However, this trend does not include the noble gases. We know that noble gases are extremely stable, and they do not want to gain or lose electrons.

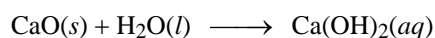
Based on the above periodic trend, **Cl** would be expected to have the highest electron affinity. Addition of an electron to Cl forms Cl^- , which has a stable noble gas electron configuration.

- 8.61** Based on electron affinity values, we would not expect the alkali metals to form anions. A few years ago most chemists would have answered this question with a loud "No"! In the early nineteen seventies a chemist named J.L. Dye at Michigan State University discovered that under very special circumstances alkali metals could be coaxed into accepting an electron to form negative ions! These ions are called alkalide ions.
- 8.62** Alkali metals have a valence electron configuration of ns^1 so they can accept another electron in the ns orbital. On the other hand, alkaline earth metals have a valence electron configuration of ns^2 . Alkaline earth metals have little tendency to accept another electron, as it would have to go into a higher energy p orbital.
- 8.63** Diagonal relationships are similarities between pairs of elements in different groups and periods of the periodic table. Examples are: Li and Mg; and Be and Al.
- 8.64** Nonmetals tend to form acidic oxides, metals tend to form basic oxides, and amphoteric oxides are formed from elements that are intermediate within a period of the table.
- 8.65** Basically, we look for the process that will result in forming a cation of the metal that will be isoelectronic with the noble gas preceding the metal in the periodic table. Since all alkali metals have the ns^1 outer electron configuration, we predict that they will form unipositive ions: M^+ . Similarly, the alkaline earth metals, which have the ns^2 outer electron configuration, will form M^{2+} ions.
- 8.66** Since ionization energies decrease going down a column in the periodic table, francium should have the lowest first ionization energy of all the alkali metals. As a result, Fr should be the most reactive of all the Group 1A elements toward water and oxygen. The reaction with oxygen would probably be similar to that of K, Rb, or Cs.
- What would you expect the formula of the oxide to be? The chloride?
- 8.67** The electron configuration of helium is $1s^2$ and that of the other noble gases is ns^2np^6 . The completely filled subshell represents great stability. Consequently, these elements are chemically unreactive.
- 8.68** The Group 1B elements are much less reactive than the Group 1A elements. The 1B elements are more stable because they have much higher ionization energies resulting from incomplete shielding of the nuclear charge by the inner d electrons. The ns^1 electron of a Group 1A element is shielded from the nucleus more effectively by the completely filled noble gas core. Consequently, the outer s electrons of 1B elements are more strongly attracted by the nucleus.
- 8.69** Across a period, oxides change from basic to amphoteric to acidic. Going down a group, the oxides become more basic.

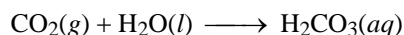
- 8.70** (a) Lithium oxide is a basic oxide. It reacts with water to form the metal hydroxide:



- (b) Calcium oxide is a basic oxide. It reacts with water to form the metal hydroxide:



- (c) Carbon dioxide is an acidic oxide. It reacts with water to form carbonic acid:



- 8.71** LiH (lithium hydride): ionic compound; BeH₂ (beryllium hydride): covalent compound; B₂H₆ (diborane, you aren't expected to know that name): molecular compound; CH₄ (methane, do you know that one?): molecular compound; NH₃ (ammonia, you should know that one): molecular compound; H₂O (water): molecular compound; HF (hydrogen fluoride): molecular compound. LiH and BeH₂ are solids, B₂H₆, CH₄, NH₃, and HF are gases, and H₂O is a liquid.
- 8.72** As we move down a column, the metallic character of the elements increases. Since magnesium and barium are both Group 2A elements, we expect barium to be more metallic than magnesium and **BaO** to be more basic than MgO.
- 8.73** (a) Metallic character decreases moving left to right across a period and increases moving down a column (Group).
 (b) Atomic size decreases moving left to right across a period and increases moving down a column (Group).
 (c) Ionization energy increases (with some exceptions) moving left to right across a period and decreases moving down a column.
 (d) Acidity of oxides increases moving left to right across a period and decreases moving down a column.
- 8.74** (a) bromine (b) nitrogen (c) rubidium (d) magnesium
- 8.75** Both ionization energy and electron affinity are affected by atomic size. The smaller the atom, the greater the attraction between the electrons and the nucleus. If it is difficult to remove an electron from an atom (that is, high ionization energy), then it follows that it would also be favorable to add an electron to the atom (large electron affinity).
- 8.76** This is an isoelectronic series with ten electrons in each species. The nuclear charge interacting with these ten electrons ranges from +8 for oxygen to +12 for magnesium. Therefore the +12 charge in Mg²⁺ will draw in the ten electrons more tightly than the +11 charge in Na⁺, than the +9 charge in F⁻, than the +8 charge in O²⁻. Recall that the largest species will be the *easiest* to ionize.
 (a) increasing ionic radius: Mg²⁺ < Na⁺ < F⁻ < O²⁻
 (b) increasing ionization energy: O²⁻ < F⁻ < Na⁺ < Mg²⁺
- 8.77** Ionic compounds are combinations of a metal and a nonmetal. Molecular compounds are usually nonmetal–nonmetal combinations.
 (a) Na₂O (ionic); MgO (ionic); Al₂O₃ (ionic); SiO₂ (molecular);
 P₄O₆ and P₄O₁₀ (both molecular); SO₂ or SO₃ (molecular);
 Cl₂O and several others (all molecular).
 (b) NaCl (ionic); MgCl₂ (ionic); AlCl₃ (ionic); SiCl₄ (molecular);
 PCl₃ and PCl₅ (both molecular); SCl₂ (molecular).
- 8.78** According to the *Handbook of Chemistry and Physics* (1966-67 edition), potassium metal has a melting point of 63.6°C, bromine is a reddish brown liquid with a melting point of -7.2°C, and potassium bromide (KBr) is a colorless solid with a melting point of 730°C. **M** is **potassium** (K) and **X** is **bromine** (Br).

- 8.79** (a) matches bromine (Br_2), (b) matches hydrogen (H_2), (c) matches calcium (Ca),
 (d) matches gold (Au), (e) matches neon (Ne)

- 8.80** O^+ and N Ar and S^{2-} Ne and N^{3-} Zn and As^{3+} Cs^+ and Xe

- 8.81** Only (b) is listed in order of decreasing radius. Answer (a) is listed in increasing size because the radius increases down a group. Answer (c) is listed in increasing size because the number of electrons is increasing.

- 8.82** (a) and (d)

- 8.83** The equation is: $\text{CO}_2(g) + \text{Ca}(\text{OH})_2(aq) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l)$

The milky white color is due to calcium carbonate. Calcium hydroxide is a base and carbon dioxide is an acidic oxide. The products are a salt and water.

- 8.84** Fluorine is a yellow-green gas that attacks glass; chlorine is a pale yellow gas; bromine is a fuming red liquid; and iodine is a dark, metallic-looking solid.

- 8.85** (a) (i) Both react with water to produce hydrogen;
 (ii) Their oxides are basic;
 (iii) Their halides are ionic.
 (b) (i) Both are strong oxidizing agents;
 (ii) Both react with hydrogen to form HX (where X is Cl or Br);
 (iii) Both form halide ions (Cl^- or Br^-) when combined with electropositive metals (Na, K, Ca, Ba).

- 8.86** Fluorine

- 8.87** Sulfur has a ground state electron configuration of $[\text{Ne}]3s^23p^4$. Therefore, it has a tendency to accept one electron to become S^- . Although adding another electron makes S^{2-} , which is isoelectronic with Ar, the increase in electron repulsion makes the process unfavorable.

- 8.88** H^- and He are isoelectronic species with two electrons. Since H^- has only one proton compared to two protons for He, the nucleus of H^- will attract the two electrons less strongly compared to He. Therefore, H^- is larger.

- 8.89** Na_2O (basic oxide) $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$
 BaO (basic oxide) $\text{BaO} + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2$
 CO_2 (acidic oxide) $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$
 N_2O_5 (acidic oxide) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$
 P_4O_{10} (acidic oxide) $\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$
 SO_3 (acidic oxide) $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

8.90	<u>Oxide</u>	<u>Name</u>	<u>Property</u>
	Li ₂ O	lithium oxide	basic
	BeO	beryllium oxide	amphoteric
	B ₂ O ₃	boron oxide	acidic
	CO ₂	carbon dioxide	acidic
	N ₂ O ₅	dinitrogen pentoxide	acidic

Note that only the highest oxidation states are considered.

8.91	<u>Element</u>	<u>State</u>	<u>Form</u>
	Mg	solid	three dimensional
	Cl	gas	diatomic molecules
	Si	solid	three dimensional
	Kr	gas	monatomic
	O	gas	diatomic molecules
	I	solid	diatomic molecules
	Hg	liquid	liquid (metallic)
	Br	liquid	diatomic molecules

8.92 In its chemistry, hydrogen can behave like an alkali metal (H^+) and like a halogen (H^-). H^+ is a single proton.

8.93 Replacing Z in the equation given in Problem 8.55 with $(Z - \sigma)$ gives:

$$E_n = (2.18 \times 10^{-18} \text{ J})(Z - \sigma)^2 \left(\frac{1}{n^2} \right)$$

For helium, the atomic number (Z) is 2, and in the ground state, its two electrons are in the first energy level, so $n = 1$. Substitute Z , n , and the first ionization energy into the above equation to solve for σ .

$$E_1 = 3.94 \times 10^{-18} \text{ J} = (2.18 \times 10^{-18} \text{ J})(2 - \sigma)^2 \left(\frac{1}{1^2} \right)$$

$$(2 - \sigma)^2 = \frac{3.94 \times 10^{-18} \text{ J}}{2.18 \times 10^{-18} \text{ J}}$$

$$2 - \sigma = \sqrt{1.81}$$

$$\sigma = 2 - 1.35 = \mathbf{0.65}$$

8.94 Rearrange the given equation to solve for ionization energy.

$$IE = h\nu - \frac{1}{2}mu^2$$

or,
$$IE = \frac{hc}{\lambda} - KE$$

The kinetic energy of the ejected electron is given in the problem. Substitute h , c , and λ into the above equation to solve for the ionization energy.

$$IE = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\cancel{s})(3.00 \times 10^8 \cancel{\text{ m/s}})}{162 \times 10^{-9} \cancel{\text{ m}}} - (5.34 \times 10^{-19} \text{ J})$$

$$IE = \mathbf{6.94 \times 10^{-19} \text{ J}}$$

We might also want to express the ionization energy in kJ/mol.

$$\frac{6.94 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \mathbf{418 \text{ kJ/mol}}$$

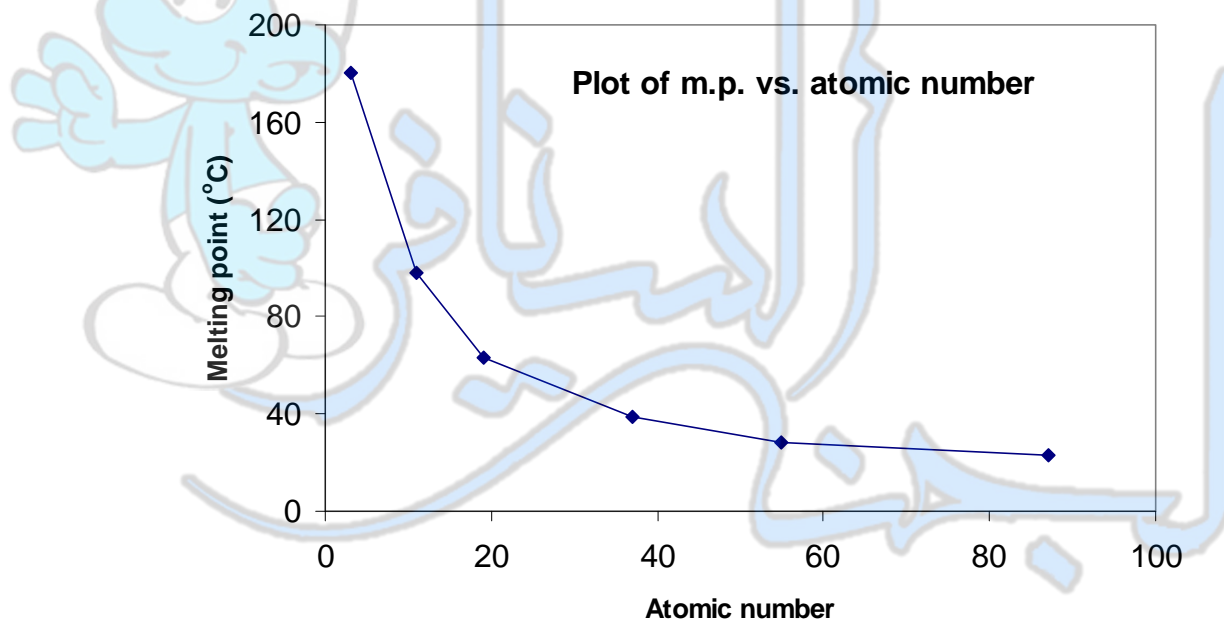
To ensure that the ejected electron is the valence electron, UV light of the *longest* wavelength (lowest energy) should be used that can still eject electrons.

- 8.95** X must belong to Group 4A; it is probably Sn or Pb because it is not a very reactive metal (it is certainly not reactive like an alkali metal).

Y is a nonmetal since it does *not* conduct electricity. Since it is a light yellow solid, it is probably phosphorus (Group 5A).

Z is an alkali metal since it reacts with air to form a basic oxide or peroxide.

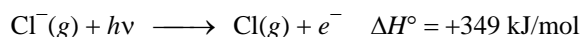
- 8.96** Plotting the melting point versus the atomic number and extrapolating the curve to francium, the estimated melting point is **23°C**.



- 8.97** The reaction representing the electron affinity of chlorine is:



It follows that the energy needed for the reverse process is +349 kJ/mol.



The energy above is the energy of 1 mole of photons. We need to convert to the energy of one photon in order to calculate the wavelength of the photon.

$$\frac{349 \text{ kJ}}{1 \text{ mol photons}} \times \frac{1 \text{ mol photons}}{6.022 \times 10^{23} \text{ photons}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 5.80 \times 10^{-19} \text{ J/photon}$$

Now, we can calculate the wavelength of a photon with this energy.

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{5.80 \times 10^{-19} \text{ J}} = 3.43 \times 10^{-7} \text{ m} = \mathbf{343 \text{ nm}}$$

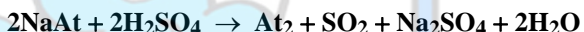
The radiation is in the **ultraviolet** region of the electromagnetic spectrum.

- 8.98**
- | | | |
|------------------------------------------------|------------------------------|-----------------------------------------|
| (a) Mg in Mg(OH) ₂ | (d) Na in NaHCO ₃ | (g) Ca in CaO |
| (b) Na, liquid | (e) K in KNO ₃ | (h) Ca |
| (c) Mg in MgSO ₄ ·7H ₂ O | (f) Mg | (i) Na in NaCl; Ca in CaCl ₂ |

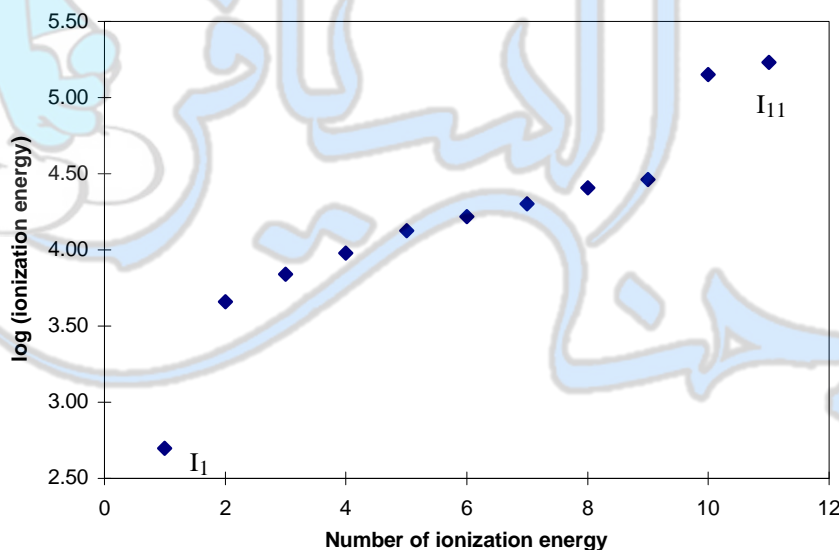
- 8.99** Z_{eff} increases from left to right across the table, so electrons are held more tightly. (This explains the electron affinity values of C and O.) Nitrogen has a zero value of electron affinity because of the stability of the half-filled $2p$ subshell (that is, N has little tendency to accept another electron).

- 8.100** Physical characteristics: Solid; metallic appearance like iodine; melting point greater than 114°C.

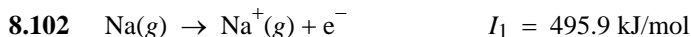
Reaction with sulfuric acid:



- 8.101** The plot is:



- (a)
- | | |
|---------------------------------------------------|------------------------------------------------------|
| I_1 corresponds to the electron in $3s^1$ | I_7 corresponds to the electron in $2p^1$ |
| I_2 corresponds to the first electron in $2p^6$ | I_8 corresponds to the first electron in $2s^2$ |
| I_3 corresponds to the first electron in $2p^5$ | I_9 corresponds to the electron in $2s^1$ |
| I_4 corresponds to the first electron in $2p^4$ | I_{10} corresponds to the first electron in $1s^2$ |
| I_5 corresponds to the first electron in $2p^3$ | I_{11} corresponds to the electron in $1s^1$ |
| I_6 corresponds to the first electron in $2p^2$ | |
- (b) It requires more energy to remove an electron from a closed shell. The breaks indicate electrons in different shells and subshells.



Energy needed to ionize one Na atom:

$$\frac{495.9 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 8.235 \times 10^{-19} \text{ J/atom}$$

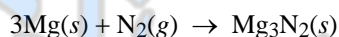
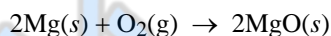
The corresponding wavelength is:

$$\lambda = \frac{hc}{I_1} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{8.235 \times 10^{-19} \text{ J}} = 2.42 \times 10^{-7} \text{ m} = \mathbf{242 \text{ nm}}$$

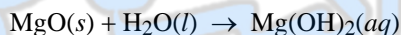
8.103 There is a large jump from the second to the third ionization energy, indicating a change in the principal quantum number n . In other words, the third electron removed is an inner, noble gas core electron, which is difficult to remove. Therefore, the element is in **Group 2A**.

8.104 (a) F_2 (b) Na (c) B (d) N_2 (e) Al

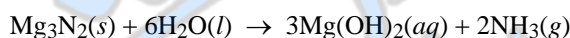
8.105 Mg will react with air (O_2 and N_2) to produce $\text{MgO}(s)$ and $\text{Mg}_3\text{N}_2(s)$. The reactions are:



$\text{MgO}(s)$ will react with water to produce the basic solution, $\text{Mg}(\text{OH})_2(aq)$. The reaction is:



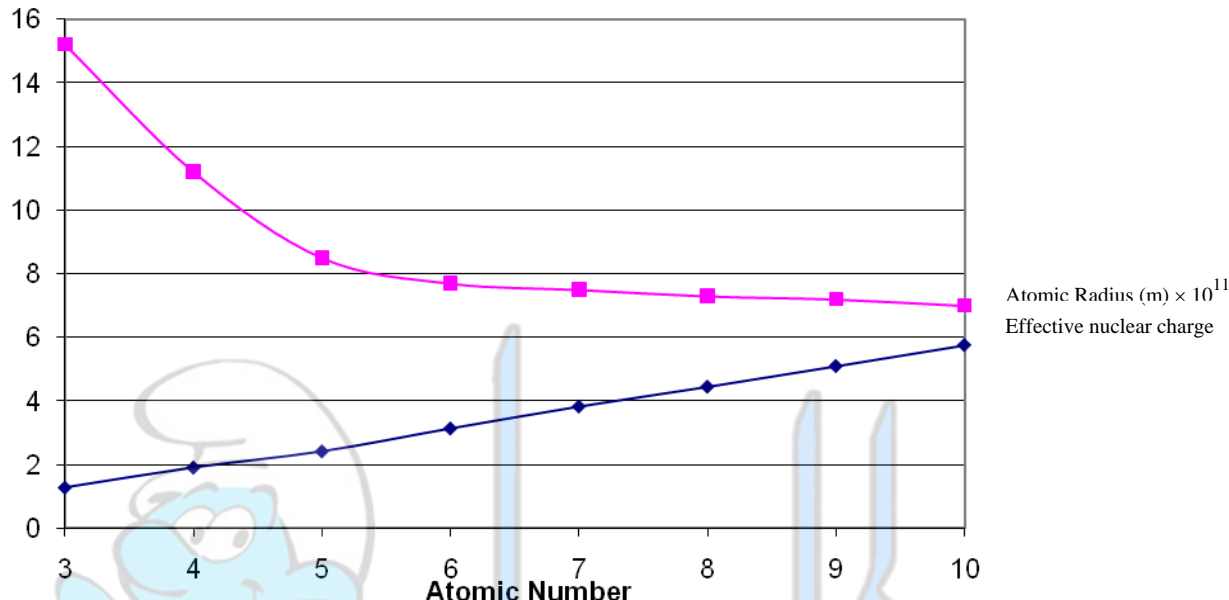
The problem states that B forms a similar solution to A, plus a gas with a pungent odor. This gas is ammonia, NH_3 . The reaction is:



A is **MgO**, and B is **Mg₃N₂**.

- 8.106**
- (a) They would have used a set up similar to Figure 7.6 of the text, except that the discharge tube was filled with argon gas. The emission spectrum of the gas did not match the spectra of any known elements.
 - (b) Argon gas is chemically unreactive, and thus would not combine with other elements to form compounds.
 - (c) Once argon was discovered, Ramsay was convinced that there were other unreactive gases belonging to the same periodic group. He went in search of these gases and amazingly discovered neon, krypton, and xenon in a three month time period.
 - (d) On Earth, the only source of helium is through radioactive decay processes— α particles emitted during nuclear decay are eventually converted to helium atoms. Because it is a light gas, its concentration in the atmosphere is very low.
 - (e) Radon, like other noble gases, is unreactive. In addition, radon is a decay product of uranium-238. Once formed, it decays by α particle emission with a half-life of 3.82 days. Its percent abundance at any given time will be very small, and thus it only forms a compound with the most electronegative element, fluorine.

8.107



Note that the atomic radius values (in meters) have been multiplied by 1×10^{11} , so that the effective nuclear charge and radius data would fit better on the same graph. As we move from Li to Ne, the number of core electrons ($1s^2$) remain constant while the nuclear charge increases. The electrons that are added across the row are valence electrons which do not shield each other well. Therefore, moving across a period of the table, the valence electrons experience a greater effective nuclear charge and the atomic radius decreases.

- 8.108** The ionization energy of 412 kJ/mol represents the energy difference between the ground state and the dissociation limit, whereas the ionization energy of 126 kJ/mol represents the energy difference between the first excited state and the dissociation limit. Therefore, the energy difference between the ground state and the excited state is:

$$\Delta E = (412 - 126) \text{ kJ/mol} = 286 \text{ kJ/mol}$$

The energy of light emitted in a transition from the first excited state to the ground state is therefore 286 kJ/mol. We first convert this energy to units of J/photon, and then we can calculate the wavelength of light emitted in this electronic transition.

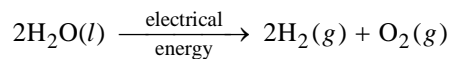
$$E = \frac{286 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}} = 4.75 \times 10^{-19} \text{ J/photon}$$

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{4.75 \times 10^{-19} \text{ J}} = 4.19 \times 10^{-7} \text{ m} = 419 \text{ nm}$$

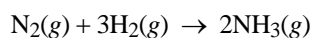
- 8.109** In He, r is greater than that in H. Also, the shielding in He makes Z_{eff} less than 2. Therefore, $I_1(\text{He}) < 2I(\text{H})$. In He^+ , there is only one electron so there is no shielding. The greater attraction between the nucleus and the lone electron reduces r to less than the r of hydrogen. Therefore, $I_2(\text{He}) > 2I(\text{H})$.

8.110 Air contains O_2 and N_2 . Our aims are first to prepare NH_3 and HNO_3 . The reaction of NH_3 and HNO_3 produces NH_4NO_3 .

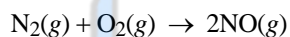
To prepare NH_3 , we isolate N_2 from air. H_2 can be obtained by the electrolysis of water.



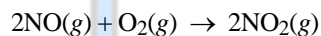
Under suitable conditions,



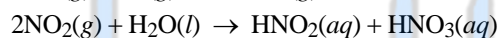
To prepare HNO_3 , we first react N_2 with O_2 (from air or water).



Next,



Then,

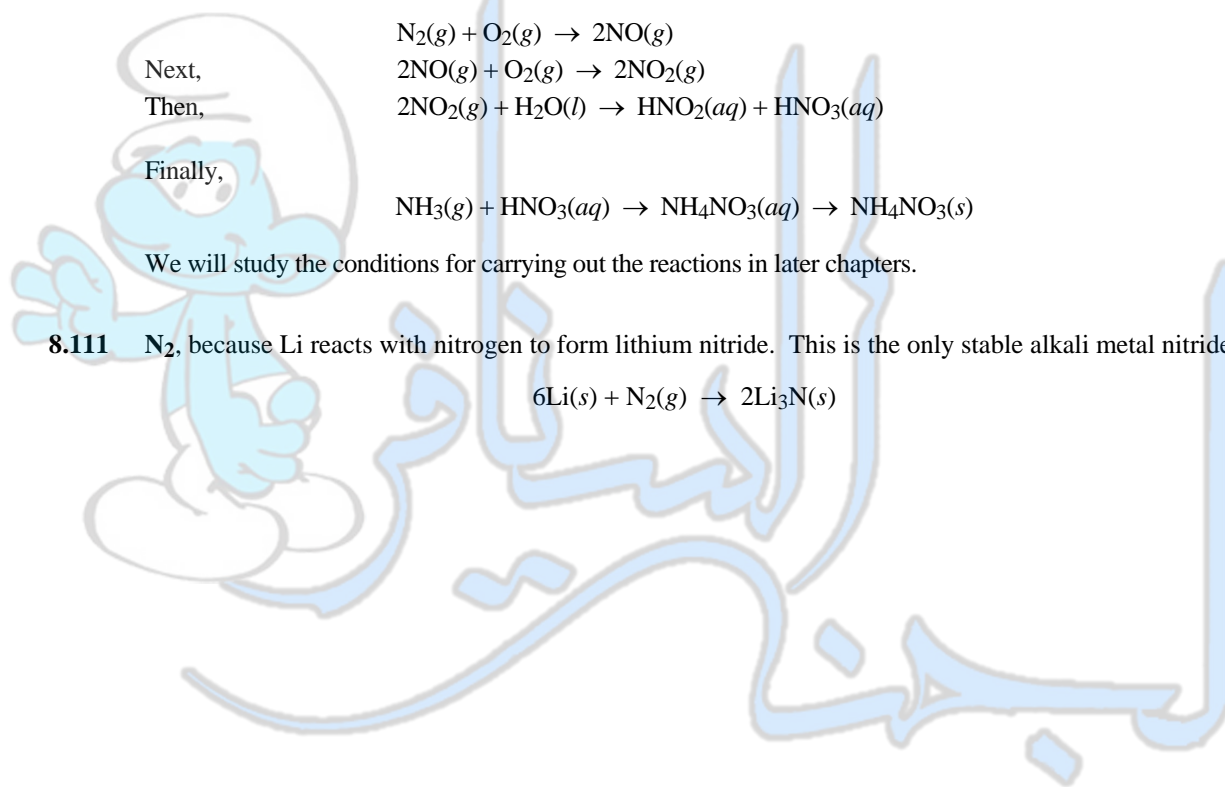
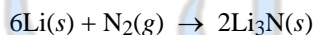


Finally,



We will study the conditions for carrying out the reactions in later chapters.

8.111 N_2 , because Li reacts with nitrogen to form lithium nitride. This is the only stable alkali metal nitride.



CHAPTER 14

CHEMICAL KINETICS

- 14.1** The rate of a reaction measures how fast a reactant is consumed or how fast a product is formed. The rate is expressed as a ratio of the change in concentration to elapsed time.
- 14.2** The units of reaction rate are molarity per second (M/s).
- 14.3** It is preferable to measure the initial rate because as the reaction proceeds, the concentrations of the reactants decrease and it may become difficult to measure the changes accurately. Also, there may be a reverse reaction such that, products \rightarrow reactants, which would introduce error in the rate measurement. Both of these complications are virtually absent during the early stages of the reaction.
- 14.4** The corrosion of iron and the conversion of diamond to graphite at standard conditions are very slow. The combustion of gasoline and the reaction between a strong acid and a strong base are very fast.

14.5 In general for a reaction $aA + bB \rightarrow cC + dD$

$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

(a) $\text{rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[HI]}{\Delta t}$

(b) $\text{rate} = -\frac{1}{2} \frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[H_2O]}{\Delta t}$

(c) $\text{rate} = -\frac{1}{5} \frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[H^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[Br_2]}{\Delta t}$

Note that because the reaction is carried out in the aqueous phase, we do not monitor the concentration of water.

- 14.6 Strategy:** The rate is defined as the change in concentration of a reactant or product with time. Each “change in concentration” term is divided by the corresponding stoichiometric coefficient. Terms involving reactants are preceded by a minus sign.

$$\text{rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[NH_3]}{\Delta t}$$

Solution:

- (a) If hydrogen is reacting at the rate of $0.074 M/s$ $\left(\frac{\Delta[H_2]}{\Delta t} = -0.074 M/s \right)$, the rate at which ammonia is being formed is:

$$\frac{1}{2} \frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t}$$

$$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[H_2]}{\Delta t}$$

$$\frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{2}{3}(-0.074 \text{ M/s}) = \mathbf{0.049 \text{ M/s}}$$

$$\text{(b)} \quad \frac{\Delta[\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{3}(-0.074 \text{ M/s}) = -0.025 \text{ M/s}$$

The rate at which molecular nitrogen is reacting is **0.025 M/s**. Will the rate at which ammonia forms always be twice the rate of reaction of nitrogen, or is this true only at the instant described in this problem?

14.7 The rate law is an expression relating the rate of a reaction to the rate constant and the concentrations of the reactants.

14.8 First order: s^{-1} . Second order: $\text{M}^{-1}\text{s}^{-1}$.

14.9 $\ln \frac{[A]_t}{[A]_0} = -kt$, where \ln is the natural logarithm, $[A]_0$ and $[A]_t$ are the concentrations of A at times $t = 0$ and $t = t$, respectively, k is the rate constant, and t is time.

14.10 (a) Rate = k (b) M/s
(c) The rate is constant. The plot will be a straight line with a slope of zero.

14.11 (b) and (c).

14.12 (a) potassium (b) magnesium (c) magnesium powder (d) 1.0 M HCl

14.13 rate = $k[\text{NH}_4^+][\text{NO}_2^-] = (3.0 \times 10^{-4} \text{ M/s})(0.26 \text{ M})(0.080 \text{ M}) = \mathbf{6.2 \times 10^{-6} \text{ M/s}}$

14.14 (a) Assume the rate law has the form:

$$\text{rate} = k[\text{F}_2]^x[\text{ClO}_2]^y$$

To determine the order of the reaction with respect to F_2 , find two experiments in which the $[\text{ClO}_2]$ is held constant. Compare the data from experiments 1 and 3. When the concentration of F_2 is doubled, the reaction rate doubles. Thus, the reaction is *first-order* in F_2 .

To determine the order with respect to ClO_2 , compare experiments 1 and 2. When the ClO_2 concentration is quadrupled, the reaction rate quadruples. Thus, the reaction is *first-order* in ClO_2 .

The rate law is:

$$\text{rate} = k[\text{F}_2][\text{ClO}_2]$$

(b) The value of k can be found using the data from any of the experiments. If we take the numbers from the second experiment we have:

$$k = \frac{\text{rate}}{[\text{F}_2][\text{ClO}_2]} = \frac{4.8 \times 10^{-3} \text{ M/s}}{(0.10 \text{ M})(0.040 \text{ M})} = \mathbf{1.2 \text{ M}^{-1}\text{s}^{-1}}$$

Verify that the same value of k can be obtained from the other sets of data.

- (c) Since we now know the rate law and the value of the rate constant, we can calculate the rate at any concentration of reactants.

$$\text{rate} = k[\text{F}_2][\text{ClO}_2] = (1.2 \text{ M}^{-1} \text{ s}^{-1})(0.010 \text{ M})(0.020 \text{ M}) = 2.4 \times 10^{-4} \text{ M/s}$$

- 14.15** By comparing the first and second sets of data, we see that changing [B] does not affect the rate of the reaction. Therefore, the reaction is zero-order in B. By comparing the first and third sets of data, we see that doubling [A] doubles the rate of the reaction. This shows that the reaction is **first-order** in A.

$$\text{rate} = k[\text{A}]$$

From the first set of data:

$$3.20 \times 10^{-1} \text{ M/s} = k(1.50 \text{ M})$$

$$k = 0.213 \text{ s}^{-1}$$

What would be the value of k if you had used the second or third set of data? Should k be constant?

- 14.16 Strategy:** We are given a set of concentrations and rate data and asked to determine the order of the reaction and the initial rate for specific concentrations of X and Y. To determine the order of the reaction, we need to find the rate law for the reaction. We assume that the rate law takes the form

$$\text{rate} = k[\text{X}]^x[\text{Y}]^y$$

How do we use the data to determine x and y ? Once the orders of the reactants are known, we can calculate k for any set of rate and concentrations. Finally, the rate law enables us to calculate the rate at any concentrations of X and Y.

Solution:

- (a) Experiments 2 and 5 show that when we double the concentration of X at constant concentration of Y, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_5}{\text{rate}_2} = \frac{0.508 \text{ M/s}}{0.127 \text{ M/s}} \approx 4 = \frac{k(0.40)^x(0.30)^y}{k(0.20)^x(0.30)^y}$$

Therefore,

$$\frac{(0.40)^x}{(0.20)^x} = 2^x = 4$$

or, $x = 2$. That is, the reaction is second-order in X. Experiments 2 and 4 indicate that doubling [Y] at constant [X] increases the rate by eight-fold. Here we write the ratio as

$$\frac{\text{rate}_4}{\text{rate}_2} = \frac{1.016 \text{ M/s}}{0.127 \text{ M/s}} = 8 = \frac{k(0.20)^x(0.60)^y}{k(0.20)^x(0.30)^y}$$

Therefore,

$$\frac{(0.60)^y}{(0.30)^y} = 2^y = 8$$

or, $y = 3$. That is, the reaction is third-order in Y. Hence, the rate law is given by:

$$\text{rate} = k[\text{X}]^2[\text{Y}]^3$$

The order of the reaction is $(2 + 3) = 5$. The reaction is *5th-order*.

- (b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law and using the first set of data, we find:

$$k = \frac{\text{rate}}{[\text{X}]^2[\text{Y}]} = \frac{0.147 \text{ M/s}}{(0.10 \text{ M})^2 (0.50 \text{ M})^3} = 118 \text{ M}^{-4} \text{ s}^{-1}$$

Next, using the known rate constant and substituting the concentrations of X and Y into the rate law, we can calculate the initial rate of disappearance of X.

$$\text{rate} = (118 \text{ M}^{-4} \text{ s}^{-1})(0.30 \text{ M})^2 (0.40 \text{ M})^3 = \mathbf{0.68 \text{ M/s}}$$

- 14.17 (a) second-order, (b) zero-order, (c) 1.5 order, (d) third-order

- 14.18 (a) For a reaction first-order in A,

$$\text{Rate} = k[\text{A}]$$

$$1.6 \times 10^{-2} \text{ M/s} = k(0.35 \text{ M})$$

$$k = \mathbf{0.046 \text{ s}^{-1}}$$

- (b) For a reaction second-order in A,

$$\text{Rate} = k[\text{A}]^2$$

$$1.6 \times 10^{-2} \text{ M/s} = k(0.35 \text{ M})^2$$

$$k = \mathbf{0.13 \text{ M}^{-1} \text{ s}^{-1}}$$

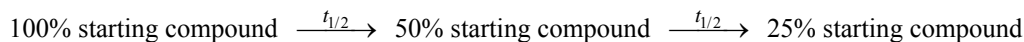
- 14.19 The half-life of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half of its initial concentration. The equation relating the half-life of a first-order reaction to the rate constant is,

$$t_{1/2} = \frac{0.693}{k}$$

- 14.20 The concentration of reactant will fall to one-eighth of its original value after three half-lives, which equals

$$3 \times \frac{0.693}{k}$$

- 14.21 We know that half of the substance decomposes in a time equal to the half-life, $t_{1/2}$. This leaves half of the compound. Half of what is left decomposes in a time equal to another half-life, so that only one quarter of the original compound remains. We see that 75% of the original compound has decomposed after two half-lives. Thus two half-lives equal one hour, or the half-life of the decay is **30 min**.



This problem can also be solved using first-order kinetics. We can solve for k using Equation (14.3) of the text, with $[\text{A}]_0 = 100$ and $[\text{A}] = 25$,

$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$$

$$\ln \frac{25}{100} = -k(60 \text{ min})$$

$$k = -\frac{\ln(0.25)}{60 \text{ min}} = 0.023 \text{ min}^{-1}$$

Then, substituting k into Equation (14.5) of the text, you arrive at the same answer for $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.023 \text{ min}^{-1}} = 30 \text{ min}$$

14.22 (a)

Strategy: To calculate the rate constant, k , from the half-life of a first-order reaction, we use Equation (14.5) of the text.

Solution: For a first-order reaction, we only need the half-life to calculate the rate constant. From Equation (14.5)

$$k = \frac{0.693}{t_{1/2}}$$

$$k = \frac{0.693}{35.0 \text{ s}} = 0.0198 \text{ s}^{-1}$$

(b)

Strategy: The relationship between the concentration of a reactant at different times in a first-order reaction is given by Equations (14.3) and (14.4) of the text. We are asked to determine the time required for 95% of the phosphine to decompose. If we initially have 100% of the compound and 95% has reacted, then what is left must be (100% – 95%), or 5%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]_t/[A]_0 = 5\%/100\%$, or 0.05/1.00.

Solution: The time required for 95% of the phosphine to decompose can be found using Equation (14.3) of the text.

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{(0.05)}{(1.00)} = -(0.0198 \text{ s}^{-1})t$$

$$t = -\frac{\ln(0.0500)}{0.0198 \text{ s}^{-1}} = 151 \text{ s}$$

- 14.23 (a)** Since the reaction is known to be second-order, the relationship between reactant concentration and time is given by Equation (14.6) of the text. The problem supplies the rate constant and the initial concentration of NOBr (time = 0). The concentration after 22 s can be found easily.

$$\frac{1}{[\text{NOBr}]_t} = kt + \frac{1}{[\text{NOBr}]_0}$$

$$\frac{1}{[\text{NOBr}]_t} = (0.80/M \cdot s)(22 \cancel{s}) + \frac{1}{0.086 M}$$

$$\frac{1}{[\text{NOBr}]_t} = 29 M^{-1}$$

$$[\text{NOBr}] = 0.034 M$$

If the reaction were first-order with the same k and initial concentration, could you calculate the concentration after 22 s? If the reaction were first-order and you were given $t_{1/2}$, could you calculate the concentration after 22 s?

- (b) The half-life for a second-order reaction *is* dependent on the initial concentration. The half-lives can be calculated using Equation (14.7) of the text.

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

$$t_{\frac{1}{2}} = \frac{1}{(0.80 / M \cdot s)(0.072 M)}$$

$$t_{\frac{1}{2}} = \mathbf{17 \text{ s}}$$

For an initial concentration of $0.054 M$, you should find $t_{\frac{1}{2}} = \mathbf{23 \text{ s}}$. Note that the half-life of a second-order reaction is inversely proportional to the initial reactant concentration.

14.24 (a) $\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$

$$\frac{1}{0.28} = \frac{1}{0.62} + 0.54t$$

$$t = \mathbf{3.6 \text{ s}}$$

(b) $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

At $0.62 M$, $t_{\frac{1}{2}} = \frac{1}{\left(0.54 \frac{1}{M \cdot s}\right)(0.62 M)} = \mathbf{3.0 \text{ s}}$

At $0.28 M$, $t_{\frac{1}{2}} = \frac{1}{\left(0.54 \frac{1}{M \cdot s}\right)(0.28 M)} = \mathbf{6.6 \text{ s}}$

- 14.25 (a)** Notice that there are 16 A molecules at $t = 0 \text{ s}$ and that there are 8 A molecules at $t = 10 \text{ s}$. The time of 10 seconds represents the first half-life of this reaction. We can calculate the rate constant, k , from the half-life of this first-order reaction.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{10 \text{ s}} = \mathbf{0.0693 \text{ s}^{-1}}$$

- (b) For a first-order reaction, the half-life is independent of reactant concentration. Therefore, $t = 20 \text{ s}$ represents the second half-life and $t = 30 \text{ s}$ represents the third half-life. At the first half-life ($t = 10 \text{ s}$), there are 8 A molecules and 8 B molecules. At $t = 20 \text{ s}$, the concentration of A will decrease to half of its concentration at $t = 10 \text{ s}$. There will be **4 A molecules** at $t = 20 \text{ s}$. Because the mole ratio between A and B is 1:1, four more B molecules will be produced and there will be **12 B molecules** present at $t = 20 \text{ s}$.

At $t = 30$ s, the concentration of A will decrease to half of its concentration at $t = 20$ s. There will be **2 A molecules** at $t = 30$ s. Because the mole ratio between A and B is 1:1, two more B molecules will be produced and there will be **14 B molecules** present at $t = 30$ s.

- 14.26 (a)** For a reaction that follows first-order kinetics, the rate will be directly proportional to the reactant concentration. In this case,

$$\text{Rate} = k[X]$$

Because the containers are equal volume, we can use the number of molecules to represent the concentration. Therefore, the relative rates of reaction for the three containers are:

- (i) Rate = $8k$
- (ii) Rate = $6k$
- (iii) Rate = $12k$

We can divide each rate by $2k$ to show that,

$$\text{Ratio of rates} = 4 : 3 : 6$$

- (b) Doubling the volume of each container will have **no effect** on the relative rates of reaction compared to part (a). Doubling the volume would halve each of the concentrations, but the ratio of the concentrations for containers (i) – (iii) would still be 4 : 3 : 6. Therefore, the relative rates between the three containers would remain the same. The actual (absolute) rate would decrease by 50%.
- (c) The reaction follows first-order kinetics. For a first-order reaction, the half-life is independent of the initial concentration of the reactant. Therefore, the half-lives for containers (i), (ii), and (iii), will be the **same**.

- 14.27** Activation energy (E_a) is the minimum amount of energy required to initiate a chemical reaction. The rate constant, and hence the reaction rate, decreases with increasing activation energy and increases with increasing temperature.

- 14.28** $k = Ae^{-E_a/RT}$, where E_a is the activation energy of the reaction (in kJ/mol), R is the gas constant (8.314 J/mol·K), T is the absolute temperature (in K), and e is the base of the natural logarithm scale.

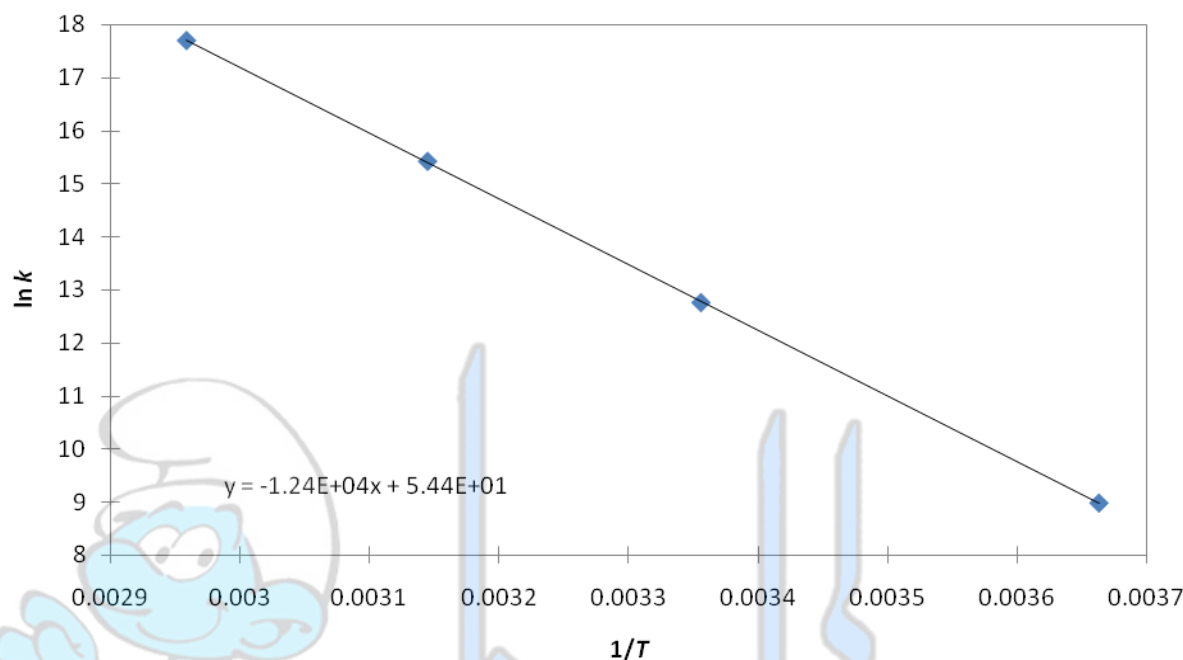
- 14.29** Because of the minus sign associated with the exponent, E_a/RT , in the Arrhenius equation, $k = Ae^{-E_a/RT}$, the rate constant decreases with increasing activation energy and increases with increasing temperature.

- 14.30** Reactions have an activation energy (E_a), which is the minimum amount of energy required to initiate a chemical reaction.

- 14.31** Please see Figure 14.14 of the text. For (a), your sketch should match Figure 14.14a with a $\Delta H = -296.06$ kJ/mol. For (b), your sketch should match Figure 14.14b with a $\Delta H = 242.7$ kJ/mol.

- 14.32** See Figure 14.14 of the text. In your sketch for the $\text{H} + \text{H}_2$ reaction, the potential energies of reactants and products will be the same. The activated complex will be H_3 .

14.33 Graphing Equation (14.12) of the text requires plotting $\ln k$ versus $1/T$. The graph is shown below.



The slope of the line is $-1.24 \times 10^4 \text{ K}$, which equals $-E_a/R$. The activation energy is:

$$-E_a = \text{slope} \times R = (-1.24 \times 10^4 \text{ K})(8.314 \text{ J/K}\cdot\text{mol})$$

$$E_a = 1.03 \times 10^5 \text{ J/mol} = 103 \text{ kJ/mol}$$

Do you need to know the order of the reaction to find the activation energy? Is it possible to have a negative activation energy? What would a potential energy versus reaction coordinate diagram look like in such a case?

14.34 Strategy: A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (14.13) of the text]. Make sure the units of R and E_a are consistent. Since the rate of the reaction at 250°C is 1.50×10^3 times faster than the rate at 150°C , the ratio of the rate constants, k , is also $1.50 \times 10^3 : 1$, because rate and rate constant are directly proportional.

Solution: The data are: $T_1 = 250^\circ\text{C} = 523 \text{ K}$, $T_2 = 150^\circ\text{C} = 423 \text{ K}$, and $k_1/k_2 = 1.50 \times 10^3$. Substituting into Equation (14.13) of the text,

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\ln(1.50 \times 10^3) = \frac{E_a}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{523 \text{ K} - 423 \text{ K}}{(523 \text{ K})(423 \text{ K})} \right)$$

$$7.31 = \frac{E_a}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left(4.52 \times 10^{-4} \frac{1}{\text{K}} \right)$$

$$E_a = 1.35 \times 10^5 \text{ J/mol} = 135 \text{ kJ/mol}$$

- 14.35** The appropriate value of R is 8.314 J/K mol , not $0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$. You must also use the activation energy value of 63000 J/mol (why?). Once the temperature has been converted to Kelvin, the rate constant is:

$$k = Ae^{-E_a/RT} = (8.7 \times 10^{12} \text{ s}^{-1})e^{-\left[\frac{63000 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(348 \text{ K})}\right]} = (8.7 \times 10^{12} \text{ s}^{-1})(3.5 \times 10^{-10})$$

$$k = 3.0 \times 10^3 \text{ s}^{-1}$$

Can you tell from the units of k what the order of the reaction is?

- 14.36** Use a modified form of the Arrhenius equation to calculate the temperature at which the rate constant is $8.80 \times 10^{-4} \text{ s}^{-1}$. We carry an extra significant figure throughout this calculation to minimize rounding errors.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left(\frac{4.60 \times 10^{-4} \text{ s}^{-1}}{8.80 \times 10^{-4} \text{ s}^{-1}} \right) = \frac{1.04 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{T_2} - \frac{1}{623 \text{ K}} \right)$$

$$\ln(0.5227) = (1.251 \times 10^4 \text{ K}) \left(\frac{1}{T_2} - \frac{1}{623 \text{ K}} \right)$$

$$-0.6487 + 20.08 = \frac{1.251 \times 10^4 \text{ K}}{T_2}$$

$$19.43T_2 = 1.251 \times 10^4 \text{ K}$$

$$T_2 = 644 \text{ K} = 371^\circ\text{C}$$

- 14.37** Let k_1 be the rate constant at 295 K and $2k_1$ the rate constant at 305 K . We write:

$$\ln \frac{k_1}{2k_1} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$-0.693 = \frac{E_a}{8.314 \text{ J/K}\cdot\text{mol}} \left(\frac{295 \text{ K} - 305 \text{ K}}{(295 \text{ K})(305 \text{ K})} \right)$$

$$E_a = 5.18 \times 10^4 \text{ J/mol} = 51.8 \text{ kJ/mol}$$

- 14.38** Since the ratio of rates is equal to the ratio of rate constants, we can write:

$$\ln \frac{\text{rate}_1}{\text{rate}_2} = \ln \frac{k_1}{k_2}$$

$$\ln \frac{k_1}{k_2} = \ln \left(\frac{2.0 \times 10^2}{39.6} \right) = \frac{E_a}{8.314 \text{ J/K}\cdot\text{mol}} \left(\frac{(300 \text{ K} - 278 \text{ K})}{(300 \text{ K})(278 \text{ K})} \right)$$

$$E_a = 5.10 \times 10^4 \text{ J/mol} = 51.0 \text{ kJ/mol}$$

- 14.39** With very few exceptions, reaction rates increase with increasing temperature. The diagram that represents the faster rate and hence is run at the higher temperature is diagram (a).

- 14.40** Elementary steps, or elementary reactions, are a series of simple reactions that represent the progress of the overall reaction at the molecular level. The term for the sequence of elementary steps that leads to product formation is reaction mechanism.
- 14.41** (a) termolecular, (b) unimolecular, and (c) bimolecular.
- 14.42** A unimolecular reaction is an elementary step in which only one reacting molecule participates. There are no zero-molecular reactions because at least one molecule must participate for a reaction to occur.
- 14.43** Very few termolecular reactions, reactions that involve the participation of three molecules in one elementary step, are known, because the simultaneous encounter of three molecules is a far less likely event than a bimolecular collision.
- 14.44** The rate-determining step is the slowest step in the sequence of steps leading to product formation. If you are competing as a team in an adventure race, the “rate” at which you complete the event can be no faster than the time of your slowest team member.
- 14.45** There are nine molecules on the reactant side of the equation. It is highly unlikely that all nine molecules would combine in one elementary step.
- 14.46** Activated complex.
- 14.47** (a) The order of the reaction is simply the sum of the exponents in the rate law (Section 14.2 of the text). The order of this reaction is 2.
- (b) The rate law reveals the identity of the substances participating in the slow or rate-determining step of a reaction mechanism. This rate law implies that the slow step involves the reaction of a molecule of NO with a molecule of Cl₂. If this is the case, then the first reaction shown must be the rate-determining (slow) step, and the second reaction must be much faster.

- 14.48** (a) **Strategy:** We are given information as to how the concentrations of X₂, Y, and Z affect the rate of the reaction and are asked to determine the rate law. We assume that the rate law takes the form

$$\text{rate} = k[\text{X}_2]^x[\text{Y}]^y[\text{Z}]^z$$

How do we use the information to determine x , y , and z ?

Solution: Since the reaction rate doubles when the X₂ concentration is doubled, the reaction is first-order in X. The reaction rate triples when the concentration of Y is tripled, so the reaction is also first-order in Y. The concentration of Z has no effect on the rate, so the reaction is zero-order in Z.

The rate law is:

$$\text{rate} = k[\text{X}_2][\text{Y}]$$

- (b) If a change in the concentration of Z has no effect on the rate, the concentration of Z is not a term in the rate law. This implies that Z does not participate in the rate-determining step of the reaction mechanism.

(c)

Strategy: The rate law, determined in part (a), shows that the slow step involves reaction of a molecule of X_2 with a molecule of Y. Since Z is not present in the rate law, it does not take part in the slow step and must appear in a fast step at a later time. (If the fast step involving Z happened before the rate-determining step, the rate law would involve Z in a more complex way.)

Solution: A mechanism that is consistent with the rate law could be:



The rate law only tells us about the slow step. Other mechanisms with different subsequent fast steps are possible. Try to invent one.

Check: The rate law written from the rate-determining step in the proposed mechanism matches the rate law determined in part (a). Also, the two elementary steps add to the overall balanced equation given in the problem.

- 14.49** A catalyst is a substance that increases the rate of a reaction by lowering the activation energy. It does so by providing an alternate reaction pathway.
- 14.50** A catalyst is a substance that increases the rate of a reaction by lowering the activation energy. It does so by providing an alternate reaction pathway. The catalyst may react to form an intermediate with the reactant, but it is regenerated in a subsequent step so it is not consumed in the reaction.
- 14.51** Yes, a catalyst could be added to the reaction.
- 14.52** In heterogeneous catalysis, the reactants and the catalyst are in different phases. In homogeneous catalysis, the reactants and the catalyst are in the same phase. See Section 14.6 of the text which describes a number of industrial processes that utilize heterogeneous catalysis.
- 14.53** Enzyme catalyses are usually homogeneous with the substrate and enzyme present in the same aqueous solution.
- 14.54** Enzymes are present in small amounts because they are not altered during the reaction. Enzymes are very efficient catalysts so we only need small amounts to carry out biological processes. In addition, enzymes are highly specific. A cell may contain 3000 different enzymes (present in small amounts) each one catalyzing a specific reaction.
- 14.55** Higher temperatures may disrupt the intricate three dimensional structure of the enzyme, thereby reducing or totally destroying its catalytic activity.
- 14.56** The rate-determining step involves the breakdown of ES to E and P. The rate law for this step is:

$$\text{rate} = k_2[\text{ES}]$$

In the first elementary step, the intermediate ES is in equilibrium with E and S. The equilibrium relationship is:

$$\frac{[\text{ES}]}{[\text{E}][\text{S}]} = \frac{k_1}{k_{-1}}$$

or

$$[\text{ES}] = \frac{k_1}{k_{-1}}[\text{E}][\text{S}]$$

Substitute $[\text{ES}]$ into the rate law expression.

$$\text{rate} = k_2[\text{ES}] = \frac{k_1 k_2}{k_{-1}}[\text{E}][\text{S}]$$

14.57 In each case, the gas pressure will either increase or decrease. The pressure can be related to the progress of the reaction through the balanced equation.

14.58 Let's count the number of molecules present at times of 0 s, 20 s, and 40 s.

0 s,	12 A molecules
20 s,	6 A molecules, 6 B molecules
40 s,	3 A molecules, 9 B molecules

Note that the concentration of A molecules is halved at $t = 20$ s and is halved again at $t = 40$ s. We notice that the half-life is independent of the concentration of the reactant, A, and hence the reaction is *first-order* in A. The rate constant, k , can now be calculated using the equation for the half-life of a first-order reaction.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{20 \text{ s}} = \mathbf{0.0347 \text{ s}^{-1}}$$

14.59 Let's count the number of molecules present at times of 0 min, 15 min, and 30 min.

0 min,	16 A atoms
15 min,	8 A atoms, 4 A ₂ molecules
30 min,	4 A atoms, 6 A ₂ molecules

Note that the concentration of A atoms is halved at $t = 15$ min and is halved again at $t = 30$ min. We notice that the half-life is independent of the concentration of the reactant, A, and hence the reaction is **first-order** in A. The rate constant, k , can now be calculated using the equation for the half-life of a first-order reaction.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{15 \text{ min}} = \mathbf{0.046 \text{ min}^{-1}}$$

14.60 First, calculate the radius of the 10.0 cm^3 sphere.

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

$$10.0 \text{ cm}^3 = \frac{4}{3}\pi r^3$$

$$r = 1.34 \text{ cm}$$

The surface area of the sphere is:

$$\text{area} = 4\pi r^2 = 4\pi(1.34 \text{ cm})^2 = \mathbf{22.6 \text{ cm}^2}$$

Next, calculate the radius of the 1.25 cm^3 sphere.

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

$$1.25 \text{ cm}^3 = \frac{4}{3}\pi r^3$$

$$r = 0.668 \text{ cm}$$

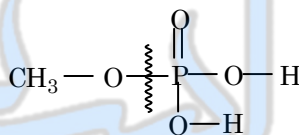
The surface area of one sphere is:

$$\text{area} = 4\pi r^2 = 4\pi(0.668 \text{ cm})^2 = 5.61 \text{ cm}^2$$

$$\text{The total area of 8 spheres} = 5.61 \text{ cm}^2 \times 8 = \mathbf{44.9 \text{ cm}^2}$$

Obviously, the surface area of the eight spheres (44.9 cm^2) is greater than that of one larger sphere (22.6 cm^2). A greater surface area promotes the catalyzed reaction more effectively.

- 14.61** Since the methanol contains no oxygen-18, the oxygen atom must come from the phosphate group and not the water. The mechanism must involve a bond-breaking process like:



- 14.62** If water is also the solvent in this reaction, it is present in vast excess over the other reactants and products. Throughout the course of the reaction, the concentration of the water will not change by a measurable amount. As a result, the reaction rate will not appear to depend on the concentration of water.
- 14.63** Most transition metals have several stable oxidation states. This allows the metal atoms to act as either a source or a receptor of electrons in a broad range of reactions.
- 14.64 (a)** To determine the rate law, we must determine the exponents in the equation

$$\text{rate} = k[\text{CH}_3\text{COCH}_3]^x[\text{Br}_2]^y[\text{H}^+]^z$$

To determine the order of the reaction with respect to CH_3COCH_3 , find two experiments in which the $[\text{Br}_2]$ and $[\text{H}^+]$ are held constant. Compare the data from experiments (a) and (e). When the concentration of CH_3COCH_3 is increased by a factor of 1.33, the reaction rate increases by a factor of 1.33. Thus, the reaction is *first-order* in CH_3COCH_3 .

To determine the order with respect to Br_2 , compare experiments (a) and (b). When the Br_2 concentration is doubled, the reaction rate does not change. Thus, the reaction is *zero-order* in Br_2 .

To determine the order with respect to H^+ , compare experiments (a) and (c). When the H^+ concentration is doubled, the reaction rate doubles. Thus, the reaction is *first-order* in H^+ .

The rate law is:

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

(b) Rearrange the rate law from part (a), solving for k .

$$k = \frac{\text{rate}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]}$$

Substitute the data from any one of the experiments to calculate k . Using the data from Experiment (a),

$$k = \frac{5.7 \times 10^{-5} \cancel{M/s}}{(0.30 \cancel{M})(0.050 M)} = 3.8 \times 10^{-3} /M \cdot s$$

14.65 Since the reaction is first-order in both A and B, then we can write the rate law expression:

$$\text{rate} = k[A][B]$$

Substituting in the values for the rate, $[A]$, and $[B]$:

$$4.1 \times 10^{-4} M/s = k(1.6 \times 10^{-2} M)(2.4 \times 10^{-3} M)$$

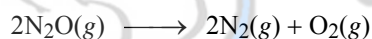
$$k = 10.7 M^{-1}s^{-1}$$

Knowing that the overall reaction was second-order, could you have predicted the units for k ?

14.66 Recall that the pressure of a gas is directly proportional to the number of moles of gas. This comes from the ideal gas equation.

$$P = \frac{nRT}{V}$$

The balanced equation is:



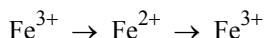
From the stoichiometry of the balanced equation, for every one mole of N_2O that decomposes, one mole of N_2 and 0.5 moles of O_2 will be formed. Let's assume that we had 2 moles of N_2O at $t = 0$. After one half-life there will be one mole of N_2O remaining and one mole of N_2 and 0.5 moles of O_2 will be formed. The total number of moles of gas after one half-life will be:

$$n_T = n_{\text{N}_2\text{O}} + n_{\text{N}_2} + n_{\text{O}_2} = 1 \text{ mol} + 1 \text{ mol} + 0.5 \text{ mol} = 2.5 \text{ mol}$$

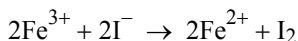
At $t = 0$, there were 2 mol of gas. Now, at $t_{1/2}$, there are 2.5 mol of gas. Since the pressure of a gas is directly proportional to the number of moles of gas, we can write:

$$\frac{2.10 \text{ atm}}{2 \cancel{\text{mol gas}} (t = 0)} \times 2.5 \cancel{\text{mol gas}} \left(\text{at } t_{1/2} \right) = 2.63 \text{ atm after one half-life}$$

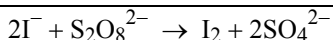
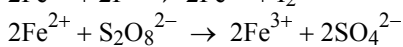
14.67 Fe^{3+} undergoes a redox cycle:



Fe^{3+} oxidizes I^- :



Fe^{2+} reduces $\text{S}_2\text{O}_8^{2-}$:



The uncatalyzed reaction is slow because both I^- and $\text{S}_2\text{O}_8^{2-}$ are negatively charged, which makes their mutual approach unfavorable.

14.68 The rate expression for a third-order reaction is:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^3$$

The units for the rate law are:

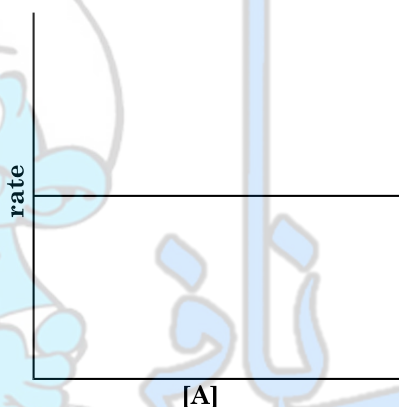
$$\frac{M}{s} = kM^3$$

$$k = M^{-2}s^{-1}$$

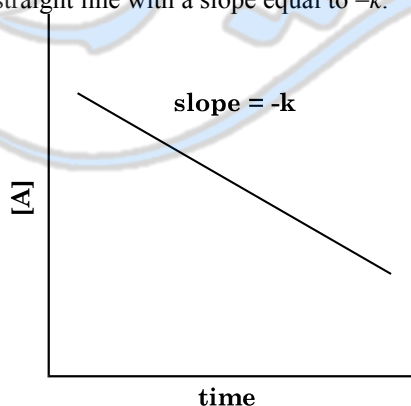
14.69 For a rate law, *zero-order* means that the exponent is zero. In other words, the reaction rate is just equal to a constant; it doesn't change as time passes.

(a) The rate law would be:

$$\text{rate} = k[A]^0 = k$$



(b) The integrated zero-order rate law is: $[A] = -kt + [A]_0$. Therefore, a plot of $[A]$ versus time should be a straight line with a slope equal to $-k$.



14.70 Both compounds, A and B, decompose by first-order kinetics. Therefore, we can write a first-order rate equation for A and also one for B.

$$\ln \frac{[A]_t}{[A]_0} = -k_A t$$

$$\frac{[A]_t}{[A]_0} = e^{-k_A t}$$

$$[A]_t = [A]_0 e^{-k_A t}$$

$$\ln \frac{[B]_t}{[B]_0} = -k_B t$$

$$\frac{[B]_t}{[B]_0} = e^{-k_B t}$$

$$[B]_t = [B]_0 e^{-k_B t}$$

We can calculate each of the rate constants, k_A and k_B , from their respective half-lives.

$$k_A = \frac{0.693}{50.0 \text{ min}} = 0.0139 \text{ min}^{-1} \qquad k_B = \frac{0.693}{18.0 \text{ min}} = 0.0385 \text{ min}^{-1}$$

The initial concentration of A and B are equal. $[A]_0 = [B]_0$. Therefore, from the first-order rate equations, we can write:

$$\frac{[A]_t}{[B]_t} = 4 = \frac{[A]_0 e^{-k_A t}}{[B]_0 e^{-k_B t}} = \frac{e^{-k_A t}}{e^{-k_B t}} = e^{(k_B - k_A)t} = e^{(0.0385 - 0.0139)t}$$

$$4 = e^{0.0246t}$$

$$\ln 4 = 0.0246t$$

$$t = 56.4 \text{ min}$$

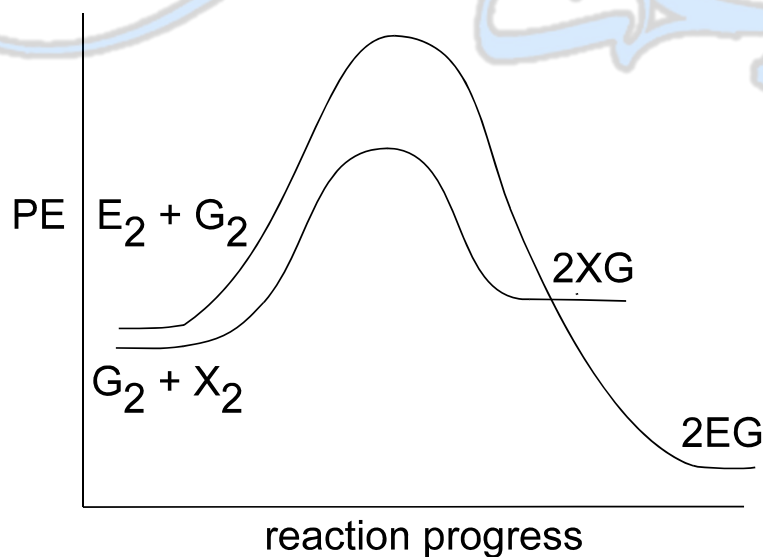
- 14.71** There are three gases present and we can measure only the total pressure of the gases. To measure the partial pressure of N_2O_5 at a particular time, we must withdraw a sample of the mixture, analyze and determine the mole fractions. Then,

$$P_{\text{N}_2\text{O}_5} = P_T X_{\text{N}_2\text{O}_5}$$

This is a rather tedious process if many measurements are required. A mass spectrometer will help (see Section 3.4 of the text).

- 14.72** (a) Changing the concentration of a reactant has no effect on k .
 (b) If a reaction is run in a solvent other than in the gas phase, then the reaction mechanism will probably change and will thus change k .
 (c) Cutting the pressure in half simply changes the concentration. No effect on k , as in (a).
 (d) The rate constant k changes with temperature.
 (e) A catalyst changes the reaction mechanism and therefore changes k .

14.73



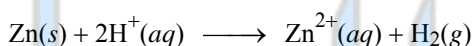
14.74 Mathematically, the fraction left after ten half-lives is:

$$\left(\frac{1}{2}\right)^{10} = 9.8 \times 10^{-4}$$

or, 0.098% of original sample is left.

- 14.75**
- (a) A catalyst works by changing the reaction mechanism, thus lowering the activation energy.
 - (b) A catalyst changes the reaction mechanism.
 - (c) A catalyst does not change the enthalpy of reaction.
 - (d) A catalyst increases the forward rate of reaction.
 - (e) A catalyst increases the reverse rate of reaction.

14.76 The net ionic equation is:



- (a) Changing from the same mass of granulated zinc to powdered zinc **increases** the rate because the surface area of the zinc (and thus its concentration) has increased.
- (b) Decreasing the mass of zinc (in the same granulated form) will **decrease** the rate because the total surface area of zinc has decreased.
- (c) The concentration of protons has decreased in changing from the strong acid (hydrochloric) to the weak acid (acetic); the rate will **decrease**.
- (d) An increase in temperature will **increase** the rate constant k ; therefore, the rate of reaction increases.

14.77 The overall rate law is of the general form: $\text{rate} = k[\text{H}_2]^x[\text{NO}]^y$

- (a) Comparing Experiment #1 and Experiment #2, we see that the concentration of NO is constant and the concentration of H_2 has decreased by one-half. The initial rate has also decreased by one-half. Therefore, the initial rate is directly proportional to the concentration of H_2 ; $x = 1$.

Comparing Experiment #1 and Experiment #3, we see that the concentration of H_2 is constant and the concentration of NO has decreased by one-half. The initial rate has decreased by one-fourth. Therefore, the initial rate is proportional to the squared concentration of NO; $y = 2$.

The overall rate law is: **$\text{rate} = k[\text{H}_2][\text{NO}]^2$**

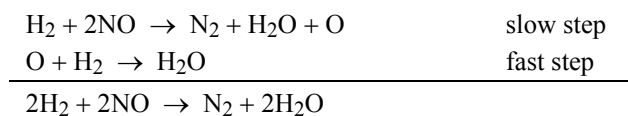
- (b) Using Experiment #1 to calculate the rate constant,

$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

$$k = \frac{\text{rate}}{[\text{H}_2][\text{NO}]^2}$$

$$k = \frac{2.4 \times 10^{-6} \text{ M/s}}{(0.010 \text{ M})(0.025 \text{ M})^2} = 0.38 \text{ M}^{-2}\text{s}^{-1}$$

- (c) Consulting the rate law, we assume that the slow step in the reaction mechanism will probably involve one H_2 molecule and two NO molecules. Additionally the hint tells us that O atoms are an intermediate.



- 14.78** If the reaction is 35.5% complete, the amount of A remaining is 64.5%. The ratio of $[A]_t/[A]_0$ is 64.5%/100% or 0.645/1.00. Using the first-order integrated rate law, Equation (14.3) of the text, we have

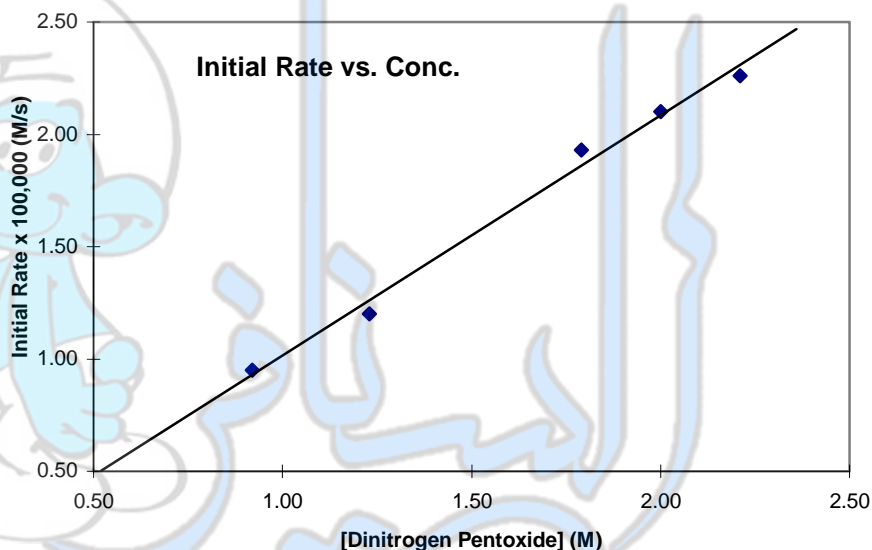
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{0.645}{1.00} = -k(4.90 \text{ min})$$

$$-0.439 = -k(4.90 \text{ min})$$

$$k = 0.0896 \text{ min}^{-1}$$

- 14.79** First we plot the data for the reaction: $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$



The plot is linear, which means that the initial rate is directly proportional to the concentration of N_2O_5 .

Thus, the rate law is:

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

The rate constant k can be determined from the slope of the graph $\frac{\Delta(\text{Initial Rate})}{\Delta[\text{N}_2\text{O}_5]}$ or by using any set of data.

$$k = 1.0 \times 10^{-5} \text{ s}^{-1}$$

Note that the rate law is **not** $\text{Rate} = k[\text{N}_2\text{O}_5]^2$, as we might expect from the balanced equation. In general, the order of a reaction must be determined by experiment; it cannot be deduced from the coefficients in the balanced equation.

- 14.80** The first-order rate equation can be arranged to take the form of a straight line.

$$\ln[A]_t = -kt + \ln[A]_0$$

If a reaction obeys first-order kinetics, a plot of $\ln[A]$ vs. t will be a straight line with a slope of $-k$.

The slope of a plot of $\ln[\text{N}_2\text{O}_5]$ vs. t is $-6.18 \times 10^{-4} \text{ min}^{-1}$. Thus,

$$k = 6.18 \times 10^{-4} \text{ min}^{-1}$$

The equation for the half-life of a first-order reaction is:

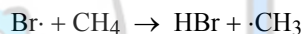
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$t_{\frac{1}{2}} = \frac{0.693}{6.18 \times 10^{-4} \text{ min}^{-1}} = 1.12 \times 10^3 \text{ min}$$

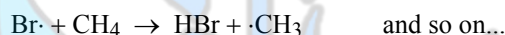
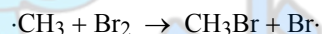
- 14.81** The red bromine vapor absorbs photons of blue light and dissociates to form bromine atoms.



The bromine atoms collide with methane molecules and abstract hydrogen atoms.



The methyl radical then reacts with Br_2 , giving the observed product and regenerating a bromine atom to start the process over again:



- 14.82 (a)** We can write the rate law for an elementary step directly from the stoichiometry of the balanced reaction. In this rate-determining elementary step three molecules must collide simultaneously (one X and two Y's). This makes the reaction termolecular, and consequently the rate law must be third-order: first-order in X and second-order in Y.

The rate law is:

$$\text{rate} = k[\text{X}][\text{Y}]^2$$

- (b)** The value of the rate constant can be found by solving algebraically for k .

$$k = \frac{\text{rate}}{[\text{X}][\text{Y}]^2} = \frac{3.8 \times 10^{-3} \text{ M/s}}{(0.26 \text{ M})(0.88 \text{ M})^2} = 1.9 \times 10^{-2} \text{ M}^{-2}\text{s}^{-1}$$

Could you write the rate law if the reaction shown were the overall balanced equation and not an elementary step?

- 14.83** Neither of the reactants is an electrolyte, so initially the solution will be a poor conductor. As the reaction progresses, hydrogen ions and iodide ions are produced (HI is a strong electrolyte), and the conductivity increases. One could relate the change in conductivity to the fact that two moles of ions form per mole of $\text{C}_2\text{H}_5\text{I}$ consumed, and thus follow the progress of the reaction.

- 14.84** We can calculate the ratio of k_1/k_2 at 40°C using the Arrhenius equation.

$$\frac{k_1}{k_2} = \frac{Ae^{-E_{a1}/RT}}{Ae^{-E_{a2}/RT}} = e^{-(E_{a1} - E_{a2})/RT} = e^{-\Delta E_a/RT}$$

$$8.0 = e^{\frac{-\Delta E_a}{(8.314 \text{ J/K}\cdot\text{mol})(313 \text{ K})}}$$

$$\ln(8.0) = \frac{-\Delta E_a}{(8.314 \text{ J/K}\cdot\text{mol})(313 \text{ K})}$$

$$\Delta E_a = -5.4 \times 10^3 \text{ J/mol}$$

Having calculated ΔE_a , we can substitute back into the equation to calculate the ratio k_1/k_2 at 300°C (573 K).

$$\frac{k_1}{k_2} = e^{\frac{-5.4 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(573 \text{ K})}} = \mathbf{3.1}$$

- 14.85** (a) $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$
 (b) Cl is a catalyst; ClO is an intermediate.
 (c) The C–F bond is stronger than the C–Cl bond.
 (d) Ethane will remove the Cl atoms:
 $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5$

- 14.86** During the first ten minutes or so the engine is relatively cold, so the exhaust gases will not fully react with the components of the catalytic converter. Remember, for almost all reactions, the rate of reaction increases with temperature.

- 14.87** (a) The first-order rate constant can be determined from the half-life.

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1 \text{ yr}} = \mathbf{0.0247 \text{ yr}^{-1}}$$

- (b) Mathematically, the amount left after ten half-lives is:

$$\left(\frac{1}{2}\right)^{10} = \mathbf{9.8 \times 10^{-4}}$$

- (c) If 99.0% has disappeared, then 1.0% remains. The ratio of $[\text{A}]/[\text{A}]_0$ is 1.0%/100% or 0.010/1.00. Substitute into the first-order integrated rate law, Equation (14.3) of the text, to determine the time.

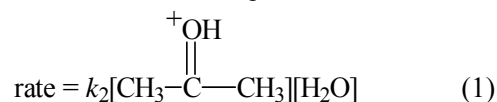
$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$$

$$\ln \frac{0.010}{1.0} = -(0.0247 \text{ yr}^{-1})t$$

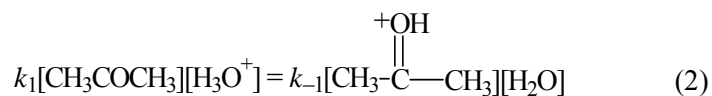
$$-4.6 = -(0.0247 \text{ yr}^{-1})t$$

$$t = \mathbf{186 \text{ yr}}$$

14.88 Let k_2 be the rate constant for the slow step:



Let k_1 and k_{-1} be the rate constants for the forward and reverse steps in the fast equilibrium.



Therefore, Equation (1) becomes

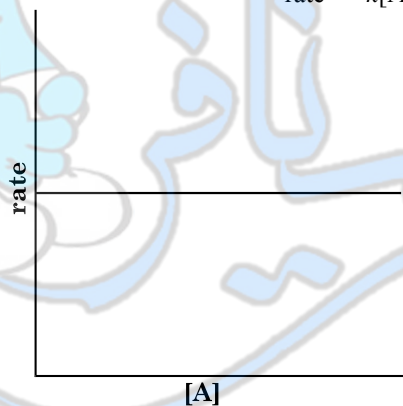
$$\text{rate} = \frac{k_1 k_2}{k_{-1}}[\text{CH}_3\text{COCH}_3][\text{H}_3\text{O}^+]$$

which is the same as (a) in Problem 14.64.

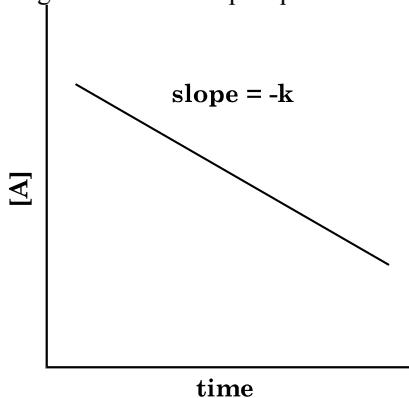
14.89 For a rate law, *zero-order* means that the exponent is zero. In other words, the reaction rate is just equal to a constant; it doesn't change as time passes.

(a) The rate law would be:

$$\text{rate} = k[\text{A}]^0 = k$$



The integrated zero-order rate law is: $[\text{A}] = -kt + [\text{A}]_0$. Therefore, a plot of $[\text{A}]$ versus time should be a straight line with a slope equal to $-k$.



(b) $[A] = [A]_0 - kt$

At $t_{\frac{1}{2}}$, $[A] = \frac{[A]_0}{2}$. Substituting into the above equation:

$$\frac{[A]_0}{2} = [A]_0 - kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

$$k = \frac{[A]_0}{2t_{\frac{1}{2}}}$$

(c) When $[A] = 0$,

$$[A]_0 = kt$$

$$t = \frac{[A]_0}{k}$$

Substituting for k ,

$$t = \frac{[A]_0}{\frac{[A]_0}{2t_{\frac{1}{2}}}}$$

$$t = 2t_{\frac{1}{2}}$$

This indicates that the integrated rate law is no longer valid after **two** half-lives.

14.90 At very high $[H_2]$,

$$k_2[H_2] \gg 1$$

$$\text{rate} = \frac{k_1[\text{NO}]^2[H_2]}{k_2[H_2]} = \frac{k_1}{k_2}[\text{NO}]^2$$

At very low $[H_2]$,

$$k_2[H_2] \ll 1$$

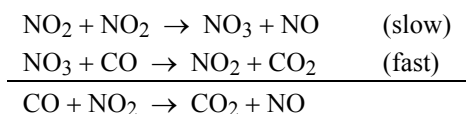
$$\text{rate} = \frac{k_1[\text{NO}]^2[H_2]}{1} = k_1[\text{NO}]^2[H_2]$$

The result from Problem 14.77 agrees with the rate law determined for low $[H_2]$.

14.91 (a) E_a has a large value.

(b) $E_a \approx 0$. Orientation factor is not important.

14.92 A plausible two-step mechanism is:



14.93 First, solve for the rate constant, k , from the half-life of the decay.

$$t_{\frac{1}{2}} = 2.44 \times 10^5 \text{ yr} = \frac{0.693}{k}$$

$$k = \frac{0.693}{2.44 \times 10^5 \text{ yr}} = 2.84 \times 10^{-6} \text{ yr}^{-1}$$

Now, we can calculate the time for the plutonium to decay from $5.0 \times 10^2 \text{ g}$ to $1.0 \times 10^2 \text{ g}$ using the equation for a first-order reaction relating concentration and time.

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{1.0 \times 10^2}{5.0 \times 10^2} = -(2.84 \times 10^{-6} \text{ yr}^{-1})t$$

$$-1.61 = -(2.84 \times 10^{-6} \text{ yr}^{-1})t$$

$$t = 5.7 \times 10^5 \text{ yr}$$

14.94 At high pressure of PH_3 , all the sites on W are occupied, so the rate is independent of $[\text{PH}_3]$.

14.95 (a) Catalyst: Mn^{2+} ; intermediate: Mn^{3+} , Mn^{4+} .

First step is rate-determining.

(b) Without the catalyst, the reaction would be a termolecular one involving 3 cations! (Ti^+ and two Ce^{4+}). The reaction would be slow.

(c) The catalyst is a homogeneous catalyst because it has the same phase (aqueous) as the reactants.

14.96 (a) $\frac{\Delta[\text{B}]}{\Delta t} = k_1[\text{A}] - k_2[\text{B}]$

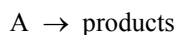
(b) If, $\frac{\Delta[\text{B}]}{\Delta t} = 0$

Then, from part (a) of this problem:

$$k_1[\text{A}] = k_2[\text{B}]$$

$$[\text{B}] = \frac{k_1}{k_2}[\text{A}]$$

14.97 (a) Consider the first-order reaction:



Using the ideal gas equation, we can write:

$$PV = n_{\text{A}}RT$$

Rearranging,

$$\frac{n_A}{V} = [A] = \frac{P}{RT}$$

Substituting $[A] = P/RT$ into Equation (14.3) of the text gives:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{P_t/RT}{P_0/RT} = -kt$$

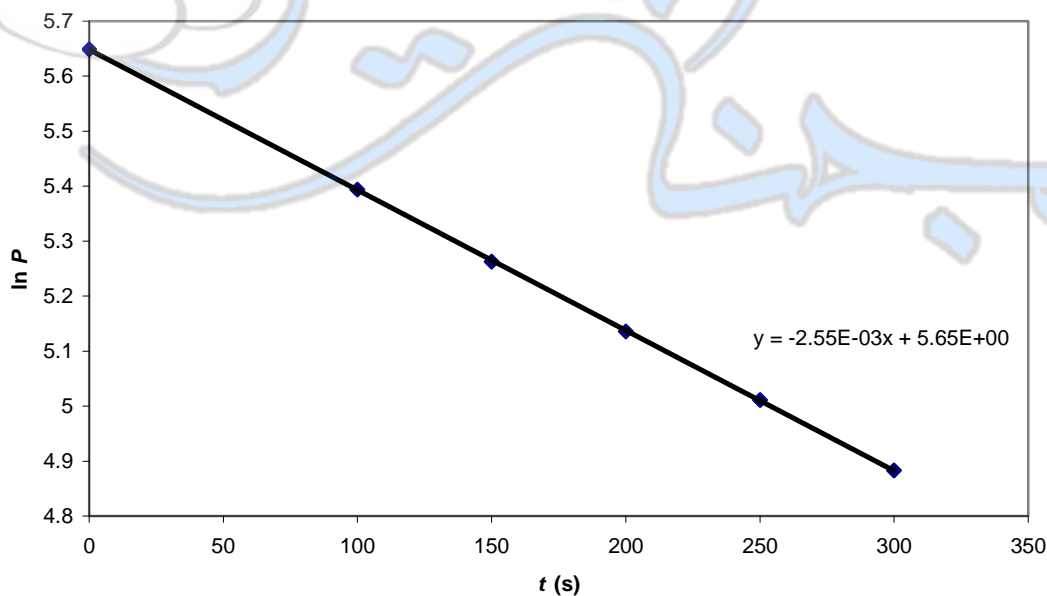
$$\ln \frac{P_t}{P_0} = -kt$$

(b) Rearranging the equation derived above, we find

$$\ln P_t = -kt + \ln P_0$$

This equation has the form of a linear equation, $y = mx + b$. If the reaction is first-order, a plot of $\ln P$ vs. t will give a straight line with a slope of $-k$.

t (s)	$\ln P$
0	5.649
100	5.394
150	5.263
200	5.136
250	5.011
300	4.883



A plot of $\ln P$ vs. t yields a straight line, so the reaction is indeed first-order. The slope of the line is $-2.55 \times 10^{-3} \text{ s}^{-1}$. The slope is equal to $-k$, so $k = 2.55 \times 10^{-3} \text{ s}^{-1}$.

- (c) We estimate the half-life to be approximately 275 s. Note that the pressure at the first half-life would be 142 mmHg. Solving for the rate constant,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{275 \text{ s}}$$

$$k = 2.52 \times 10^{-3} \text{ s}^{-1}$$

- 14.98** Run the reaction with H_2O enriched with the ^{18}O isotope. If mechanism (a) is correct, only the product acetic acid (CH_3COOH) will contain the ^{18}O isotope. On the other hand, if mechanism (b) is correct, only the product methanol (CH_3OH) will contain the ^{18}O isotope.

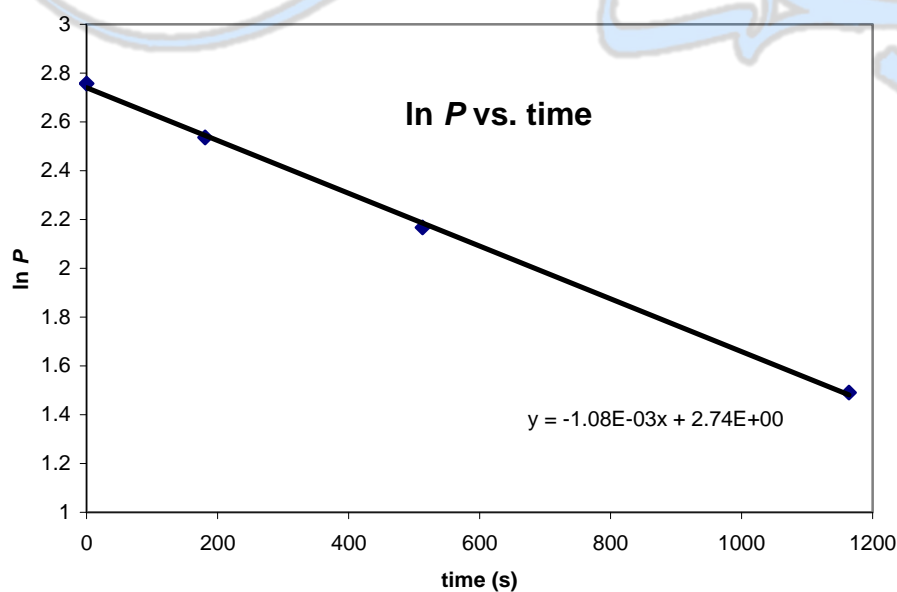
- 14.99** Let P_0 be the pressure of $\text{ClCO}_2\text{CCl}_3$ at $t = 0$, and let x be the decrease in pressure after time t . Note that from the coefficients in the balanced equation that the loss of 1 atmosphere of $\text{ClCO}_2\text{CCl}_3$ results in the formation of two atmospheres of COCl_2 . We write: $\text{ClCO}_2\text{CCl}_3 \rightarrow 2\text{COCl}_2$

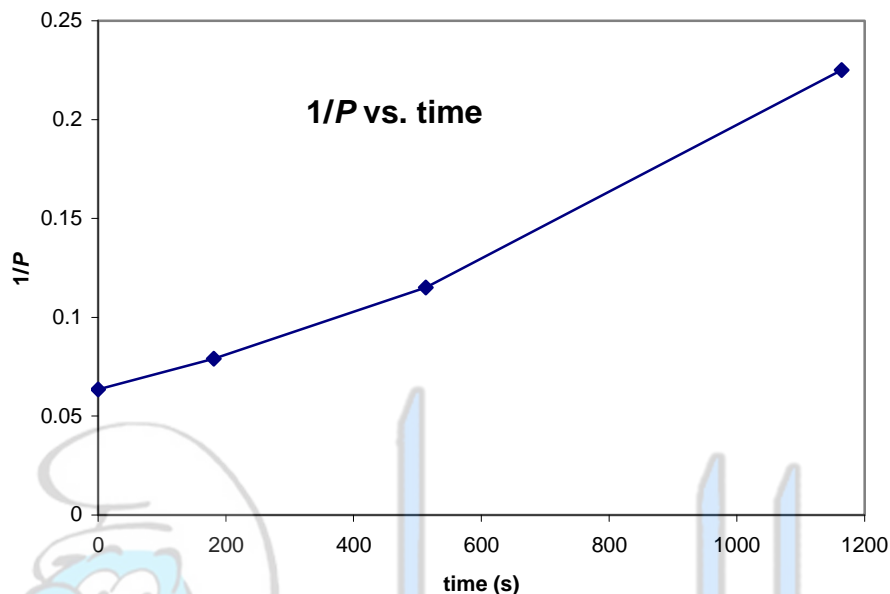
Time	$[\text{ClCO}_2\text{CCl}_3]$	$[\text{COCl}_2]$
$t = 0$	P_0	0
$t = t$	$P_0 - x$	$2x$

Thus the change (increase) in pressure (ΔP) is $2x - x = x$. We have:

$t(\text{s})$	$P(\text{mmHg})$	$\Delta P = x$	$P_{\text{ClCO}_2\text{CCl}_3}$	$\ln P_{\text{ClCO}_2\text{CCl}_3}$	$\frac{1}{P_{\text{ClCO}_2\text{CCl}_3}}$
0	15.76	0.00	15.76	2.757	0.0635
181	18.88	3.12	12.64	2.537	0.0791
513	22.79	7.03	8.73	2.167	0.115
1164	27.08	11.32	4.44	1.491	0.225

If the reaction is first-order, then a plot of $\ln P_{\text{ClCO}_2\text{CCl}_3}$ vs. t would be linear. If the reaction is second-order, a plot of $1/P_{\text{ClCO}_2\text{CCl}_3}$ vs. t would be linear. The two plots are shown below.





From the graphs we see that the reaction must be **first-order**. For a first-order reaction, the slope is equal to $-k$. The equation of the line is given on the graph. The rate constant is: $k = 1.08 \times 10^{-3} \text{ s}^{-1}$.

- 14.100 (1)** Assuming the reactions have roughly the same frequency factors, the one with the largest activation energy will be the slowest, and the one with the smallest activation energy will be the fastest. The reactions ranked from slowest to fastest are:

$$(b) < (c) < (a)$$

(2) Reaction (a): $\Delta H = -40 \text{ kJ/mol}$

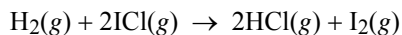
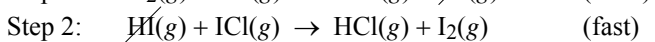
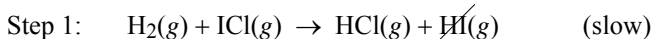
Reaction (b): $\Delta H = 20 \text{ kJ/mol}$

Reaction (c): $\Delta H = -20 \text{ kJ/mol}$

(a) and (c) are exothermic, and (b) is endothermic.

- 14.101 (a)** There are three elementary steps: $A \rightarrow B$, $B \rightarrow C$, and $C \rightarrow D$.
- (b)** There are two intermediates: B and C.
- (c)** The third step, $C \rightarrow D$, is rate determining because it has the largest activation energy.
- (d)** The overall reaction is exothermic.

- 14.102** The rate law, $\text{Rate} = k[\text{H}_2][\text{ICl}]$, indicates that one molecule of H_2 and one molecule of ICl collide in the rate-determining step of the reaction. A possible mechanism for this reaction is:



14.103 Let $k_{\text{cat}} = k_{\text{uncat}}$

Then,

$$Ae^{\frac{-E_a(\text{cat})}{RT_1}} = Ae^{\frac{-E_a(\text{uncat})}{RT_2}}$$

Since the frequency factor is the same, we can write:

$$e^{\frac{-E_a(\text{cat})}{RT_1}} = e^{\frac{-E_a(\text{uncat})}{RT_2}}$$

Taking the natural log (\ln) of both sides of the equation gives:

$$\frac{-E_a(\text{cat})}{RT_1} = \frac{-E_a(\text{uncat})}{RT_2}$$

or,

$$\frac{E_a(\text{cat})}{T_1} = \frac{E_a(\text{uncat})}{T_2}$$

Substituting in the given values:

$$\frac{7.0 \text{ kJ/mol}}{293 \text{ K}} = \frac{42 \text{ kJ/mol}}{T_2}$$

$$T_2 = 1.8 \times 10^3 \text{ K}$$

This temperature is much too high to be practical.

14.104 (a) The rate law for the reaction is:

$$\text{rate} = k[\text{Hb}][\text{O}_2]$$

We are given the rate constant and the concentration of Hb and O_2 , so we can substitute in these quantities to solve for rate.

$$\text{rate} = (2.1 \times 10^6 \text{ /M}\cdot\text{s})(8.0 \times 10^{-6} \text{ M})(1.5 \times 10^{-6} \text{ M})$$

$$\text{rate} = 2.5 \times 10^{-5} \text{ M/s}$$

(b) If HbO_2 is being formed at the rate of $2.5 \times 10^{-5} \text{ M/s}$, then O_2 is being consumed at the same rate, $2.5 \times 10^{-5} \text{ M/s}$. Note the 1:1 mole ratio between O_2 and HbO_2 .

(c) The rate of formation of HbO_2 increases, but the concentration of Hb remains the same. Assuming that temperature is constant, we can use the same rate constant as in part (a). We substitute rate, $[\text{Hb}]$, and the rate constant into the rate law to solve for O_2 concentration.

$$\text{rate} = k[\text{Hb}][\text{O}_2]$$

$$1.4 \times 10^{-4} \text{ M/s} = (2.1 \times 10^6 \text{ /M}\cdot\text{s})(8.0 \times 10^{-6} \text{ M})[\text{O}_2]$$

$$[\text{O}_2] = 8.3 \times 10^{-6} \text{ M}$$

- 14.105 (a)** The relationship between half-life and rate constant is given in Equation (14.5) of the text.

$$k = \frac{0.693}{t_{1/2}}$$

$$k = \frac{0.693}{19.8 \text{ min}}$$

$$k = 0.0350 \text{ min}^{-1}$$

- (b)** Following the same procedure as in part (a), we find the rate constant at 70°C to be $1.58 \times 10^{-3} \text{ min}^{-1}$. We now have two values of rate constants (k_1 and k_2) at two temperatures (T_1 and T_2). This information allows us to calculate the activation energy, E_a , using Equation (14.13) of the text.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\ln \left(\frac{0.0350 \text{ min}^{-1}}{1.58 \times 10^{-3} \text{ min}^{-1}} \right) = \frac{E_a}{(8.314 \text{ J/mol} \cdot \text{K})} \left(\frac{373 \text{ K} - 343 \text{ K}}{(373 \text{ K})(343 \text{ K})} \right)$$

$$E_a = 1.10 \times 10^5 \text{ J/mol} = 1.10 \times 10^2 \text{ kJ/mol}$$

- (c)** Since all the above steps are elementary steps, we can deduce the rate law simply from the equations representing the steps. The rate laws are:

Initiation: $\text{rate} = k_i[\text{R}_2]$

Propagation: $\text{rate} = k_p[\text{M}][\text{M}_1\cdot]$

Termination: $\text{rate} = k_t[\text{M}'\cdot][\text{M}''\cdot]$

The reactant molecules are the ethylene monomers, and the product is polyethylene. Recalling that intermediates are species that are formed in an early elementary step and consumed in a later step, we see that they are the radicals $\text{M}'\cdot$, $\text{M}''\cdot$, and so on. (The $\text{R}\cdot$ species also qualifies as an intermediate.)

- (d)** The growth of long polymers would be favored by a high rate of propagations and a low rate of termination. Since the rate law of propagation depends on the concentration of monomer, an increase in the concentration of ethylene would increase the propagation (growth) rate. From the rate law for termination we see that a low concentration of the radical fragment $\text{M}'\cdot$ or $\text{M}''\cdot$ would lead to a slower rate of termination. This can be accomplished by using a low concentration of the initiator, R_2 .
- 14.106 (a)** Drinking too much alcohol too fast means all the alcohol dehydrogenase (ADH) active sites are tied up and the excess alcohol will damage the central nervous system.
- (b)** Both ethanol and methanol will compete for the same site at ADH. An excess of ethanol will replace methanol at the active site, leading to methanol's discharge from the body.

- 14.107** Initially, the rate increases with increasing pressure (concentration) of NH_3 . The straight-line relationship in the first half of the plot shows that the rate of reaction is directly proportional to the concentration of ammonia. $\text{Rate} = k[\text{NH}_3]$. The more ammonia that is adsorbed on the tungsten surface, the faster the reaction. At a certain pressure (concentration), the rate is no longer dependent on the concentration of ammonia (horizontal portion of plot). The reaction is now zero-order in NH_3 concentration. At a certain concentration of NH_3 , all the reactive sites on the metal surface are occupied by NH_3 molecules, and the rate becomes constant. Increasing the concentration further has no effect on the rate.

$$14.108 \quad t_{\frac{1}{2}} \propto \frac{1}{[A]_0^{n-1}}$$

$$t_{\frac{1}{2}} = C \frac{1}{[A]_0^{n-1}}, \text{ where } C \text{ is a proportionality constant.}$$

Substituting in for zero, first, and second-order reactions gives:

$$n = 0 \quad t_{\frac{1}{2}} = C \frac{1}{[A]_0^{-1}} = C[A]_0$$

$$n = 1 \quad t_{\frac{1}{2}} = C \frac{1}{[A]_0^0} = C$$

$$n = 2 \quad t_{\frac{1}{2}} = C \frac{1}{[A]_0}$$

Compare these results with those in Table 14.2 of the text. What is C in each case?

14.109 (a) The units of the rate constant show the reaction to be second-order, meaning the rate law is most likely:

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

We can use the ideal gas equation to solve for the concentrations of H_2 and I_2 . We can then solve for the initial rate in terms of H_2 and I_2 and then convert to the initial rate of formation of HI . We carry an extra significant figure throughout this calculation to minimize rounding errors.

$$n = \frac{PV}{RT}$$

$$\frac{n}{V} = M = \frac{P}{RT}$$

Since the total pressure is 1658 mmHg and there are equimolar amounts of H_2 and I_2 in the vessel, the partial pressure of each gas is 829 mmHg.

$$[\text{H}_2] = [\text{I}_2] = \frac{\left(829 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(400 + 273) \text{ K}} = 0.01974 \text{ M}$$

Let's convert the units of the rate constant to $\text{M} \cdot \text{min}$, and then we can substitute into the rate law to solve for rate.

$$k = 2.42 \times 10^{-2} \frac{1}{\text{M} \cdot \cancel{\text{s}}} \times \frac{60 \cancel{\text{s}}}{1 \text{ min}} = 1.452 \frac{1}{\text{M} \cdot \text{min}}$$

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

$$\text{Rate} = \left(1.452 \frac{1}{\cancel{\text{M}} \cdot \text{min}}\right)(0.01974 \cancel{\text{M}})(0.01974 \text{ M}) = 5.658 \times 10^{-4} \text{ M/min}$$

We know that,

$$\text{Rate} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

or

$$\frac{\Delta[\text{HI}]}{\Delta t} = 2 \times \text{Rate} = (2)(5.658 \times 10^{-4} \text{ M/min}) = \mathbf{1.13 \times 10^{-3} \text{ M/min}}$$

- (b) We can use the second-order integrated rate law to calculate the concentration of H_2 after 10.0 minutes. We can then substitute this concentration back into the rate law to solve for rate.

$$\frac{1}{[\text{H}_2]_t} = kt + \frac{1}{[\text{H}_2]_0}$$

$$\frac{1}{[\text{H}_2]_t} = \left(1.452 \frac{1}{\text{M} \cdot \text{min}}\right)(10.0 \text{ min}) + \frac{1}{0.01974 \text{ M}}$$

$$[\text{H}_2]_t = 0.01534 \text{ M}$$

We can now substitute this concentration back into the rate law to solve for rate. The concentration of I_2 after 10.0 minutes will also equal 0.01534 M.

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

$$\text{Rate} = \left(1.452 \frac{1}{\text{M} \cdot \text{min}}\right)(0.01534 \text{ M})(0.01534 \text{ M}) = 3.417 \times 10^{-4} \text{ M/min}$$

We know that,

$$\text{Rate} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

or

$$\frac{\Delta[\text{HI}]}{\Delta t} = 2 \times \text{Rate} = (2)(3.417 \times 10^{-4} \text{ M/min}) = \mathbf{6.83 \times 10^{-4} \text{ M/min}}$$

The concentration of HI after 10.0 minutes is:

$$[\text{HI}]_t = ([\text{H}_2]_0 - [\text{H}_2]_t) \times 2$$

$$[\text{HI}]_t = (0.01974 \text{ M} - 0.01534 \text{ M}) \times 2 = \mathbf{8.8 \times 10^{-3} \text{ M}}$$

14.110 The half-life is related to the initial concentration of A by

$$t_{1/2} \propto \frac{1}{[\text{A}]_0^{n-1}}$$

According to the data given, the half-life doubled when $[\text{A}]_0$ was halved. This is only possible if the half-life is inversely proportional to $[\text{A}]_0$. Substituting $n = 2$ into the above equation gives:

$$t_{1/2} \propto \frac{1}{[\text{A}]_0}$$

Looking at this equation, it is clear that if $[\text{A}]_0$ is halved, the half-life would double. The reaction is **second-order**.

We use Equation (14.7) of the text to calculate the rate constant.

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

$$k = \frac{1}{[A]_0 t_{\frac{1}{2}}} = \frac{1}{(1.20 \text{ M})(2.0 \text{ min})} = \mathbf{0.42 \text{ /M} \cdot \text{min}}$$

14.111 From Equation (14.13) of the text,

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left(\frac{k_1}{k_2} \right) = \frac{2.4 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{606 \text{ K}} - \frac{1}{600 \text{ K}} \right)$$

$$\ln \left(\frac{k_1}{k_2} \right) = -0.48$$

$$\frac{k_2}{k_1} = e^{0.48} = 1.6$$

The rate constant at 606 K is 1.6 times greater than that at 600 K. This is a **60%** increase in the rate constant for a 1% increase in temperature! The result shows the profound effect of an exponential dependence. In general, the larger the E_a , the greater the influence of T on k .

14.112 λ_1 (the absorbance of A) decreases with time. This would happen for all the mechanisms shown. Note that λ_2 (the absorbance of B) increases with time and then decreases. Therefore, B cannot be a product as shown in mechanisms (a) or (b). If B were a product its absorbance would increase with time and level off, but it would not decrease. Since the concentration of B increases and then after some time begins to decrease, it must mean that it is produced and then it reacts to produce product as in mechanisms (c) and (d). In mechanism (c), two products are C and D, so we would expect to see an increase in absorbance for two species. Since we see an increase in absorbance for only one species, then the mechanism that is consistent with the data must be (d). λ_3 is the absorbance of C.

14.113 The rate law can be written directly from an elementary reaction.

$$\text{Rate} = k[\text{CH}_3][\text{C}_2\text{H}_6]$$

The rate constant, k , is given. If the concentrations of CH_3 and C_2H_6 can be determined, the initial rate of the reaction can be calculated. The partial pressures of CH_3 and C_2H_6 can be calculated from the respective mole fractions and the total pressure. Once the partial pressures are known, the molar concentrations can be calculated using the ideal gas equation.

$$P_{\text{CH}_3} = X_{\text{CH}_3} P_T = (0.00093)(5.42 \text{ atm}) = 0.0050 \text{ atm}$$

$$P_{\text{C}_2\text{H}_6} = X_{\text{C}_2\text{H}_6} P_T = (0.00077)(5.42 \text{ atm}) = 0.0042 \text{ atm}$$

The ideal gas equation can be rearranged to solve for molar concentration.

$$\frac{n}{V} = \frac{P}{RT}$$

$$M_{\text{CH}_3} = \frac{P_{\text{CH}_3}}{RT} = \frac{(0.0050 \text{ atm})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(600 \text{ K})} = 1.0 \times 10^{-4} \text{ M}$$

$$M_{\text{C}_2\text{H}_6} = \frac{P_{\text{C}_2\text{H}_6}}{RT} = \frac{(0.0042 \text{ atm})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(600 \text{ K})} = 8.5 \times 10^{-5} \text{ M}$$

Substitute the concentrations and the rate constant into the rate law to solve for the initial rate of the reaction.

$$\text{Rate} = k[\text{CH}_3][\text{C}_2\text{H}_6]$$

$$\text{Rate} = (3.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})(1.0 \times 10^{-4} \text{ M})(8.5 \times 10^{-5} \text{ M})$$

$$\text{Rate} = 2.6 \times 10^{-4} \text{ M/s}$$

14.114 During a cardiac arrest, there is a diminished rate of oxygen reaching the brain. As temperature is lowered, reaction rate decreases. Lowering body temperature will reduce the metabolic rate of oxygen needed for the brain, thereby reducing cell damage and hence damage to the brain.

14.115 See Figure 14.14(a) of the text. This diagram represents an exothermic reaction in the forward direction. For the reaction given in the problem, $E_a = 240 \text{ kJ/mol}$ and $\Delta H = -164 \text{ kJ/mol}$ for the reaction in the forward direction. The ΔH value on this diagram would be represented by the difference in energy between the reactants (A + B) and the products (C + D). The activation energy for the reverse reaction would be the energy needed to go from the products (C + D) to the activated complex. This energy difference includes ΔH for the reverse reaction (+164 kJ/mol) and the activation energy for the forward reaction.

$$E_a(\text{reverse}) = (+164 \text{ kJ/mol}) + (240 \text{ kJ/mol}) = 404 \text{ kJ/mol}$$

CHAPTER 18

ENTROPY, FREE ENERGY, AND EQUILIBRIUM

Problem Categories

Biological: 18.79, 18.91, 18.99.

Conceptual: 18.9, 18.10, 18.13, 18.14, 18.32, 18.37, 18.40, 18.41, 18.42, 18.43, 18.44, 18.47, 18.51, 18.53, 18.54, 18.57, 18.58, 18.61, 18.65, 18.66, 18.71, 18.83, 18.87, 18.93, 18.94, 18.95, 18.97.

Descriptive: 18.36, 18.48a,b, 18.68.

Environmental: 18.48, 18.67, 18.76.

Industrial: 18.52, 18.62, 18.74, 18.78, 18.84.

Organic: 18.81, 18.82.

Difficulty Level

Easy: 18.9, 18.10, 18.11, 18.12, 18.13, 18.14, 18.17, 18.18, 18.19, 18.20, 18.23, 18.24, 18.25, 18.26, 18.35, 18.37, 18.43, 18.51, 18.57, 18.58, 18.62, 18.63, 18.66, 18.72, 18.92.

Medium: 18.6, 18.27, 18.28, 18.29, 18.30, 18.31, 18.32, 18.36, 18.38, 18.39, 18.40, 18.41, 18.42, 18.44, 18.45, 18.50, 18.52, 18.54, 18.55, 18.56, 18.59, 18.60, 18.61, 18.64, 18.65, 18.68, 18.70, 18.74, 18.75, 18.76, 18.77, 18.78, 18.79, 18.83, 18.85, 18.86, 18.87, 18.88, 18.89, 18.90, 18.91, 18.93, 18.94, 18.97, 18.98.

Difficult: 18.46, 18.47, 18.48, 18.49, 18.53, 18.67, 18.69, 18.71, 18.73, 18.80, 18.81, 18.82, 18.84, 18.95, 18.96, 18.99, 18.100, 18.101, 18.102.

- 18.5 (a) increases (b) decreases (c) increases (d) decreases (e) decreases (f) increases
(g) increases

- 18.6 The probability (P) of finding all the molecules in the same flask becomes progressively smaller as the number of molecules increases. An equation that relates the probability to the number of molecules is given by:

$$P = \left(\frac{1}{2}\right)^N$$

where, N is the total number of molecules present.

Using the above equation, we find:

- (a) $P = 0.25$ (b) $P = 8 \times 10^{-31}$ (c) $P \approx 0$

Extending the calculation to a macroscopic system would result in such a small number for the probability (similar to the calculation with Avogadro's number above) that for all practical purposes, there is zero probability that all molecules would be found in the same bulb.

- 18.9 (a) This is easy. The liquid form of any substance always has greater entropy (more microstates).
(b) This is hard. At first glance there may seem to be no apparent difference between the two substances that might affect the entropy (molecular formulas identical). However, the first has the --O--H structural feature which allows it to participate in hydrogen bonding with other molecules. This allows a more ordered arrangement of molecules in the liquid state. The standard entropy of CH_3OCH_3 is larger.
(c) This is also difficult. Both are monatomic species. However, the Xe atom has a greater molar mass than Ar. Xenon has the higher standard entropy.
(d) Same argument as part (c). Carbon dioxide gas has the higher standard entropy (see Appendix 3).
(e) O_3 has a greater molar mass than O_2 and thus has the higher standard entropy.

- (f) Using the same argument as part (c), one mole of N_2O_4 has a larger standard entropy than one mole of NO_2 . Compare values in Appendix 3.

Use the data in Appendix 3 to compare the standard entropy of one mole of N_2O_4 with that of two moles of NO_2 . In this situation the number of atoms is the same for both. Which is higher and why?

18.10 In order of increasing entropy per mole at 25°C :

(c) < (d) < (e) < (a) < (b)

- (c) $\text{Na}(s)$: ordered, crystalline material.
 (d) $\text{NaCl}(s)$: ordered crystalline material, but with more particles per mole than $\text{Na}(s)$.
 (e) H_2 : a diatomic gas, hence of higher entropy than a solid.
 (a) $\text{Ne}(g)$: a monatomic gas of higher molar mass than H_2 .
 (b) $\text{SO}_2(g)$: a polyatomic gas of higher molar mass than Ne .

18.11 Using Equation (18.7) of the text to calculate $\Delta S^\circ_{\text{rxn}}$

(a) $\Delta S^\circ_{\text{rxn}} = S^\circ(\text{SO}_2) - [S^\circ(\text{O}_2) + S^\circ(\text{S})]$

$$\Delta S^\circ_{\text{rxn}} = (1)(248.5 \text{ J/K}\cdot\text{mol}) - (1)(205.0 \text{ J/K}\cdot\text{mol}) - (1)(31.88 \text{ J/K}\cdot\text{mol}) = \mathbf{11.6 \text{ J/K}\cdot\text{mol}}$$

(b) $\Delta S^\circ_{\text{rxn}} = S^\circ(\text{MgO}) + S^\circ(\text{CO}_2) - S^\circ(\text{MgCO}_3)$

$$\Delta S^\circ_{\text{rxn}} = (1)(26.78 \text{ J/K}\cdot\text{mol}) + (1)(213.6 \text{ J/K}\cdot\text{mol}) - (1)(65.69 \text{ J/K}\cdot\text{mol}) = \mathbf{174.7 \text{ J/K}\cdot\text{mol}}$$

18.12 Strategy: To calculate the standard entropy change of a reaction, we look up the standard entropies of reactants and products in Appendix 3 of the text and apply Equation (18.7). As in the calculation of enthalpy of reaction, the stoichiometric coefficients have no units, so $\Delta S^\circ_{\text{rxn}}$ is expressed in units of $\text{J/K}\cdot\text{mol}$.

Solution: The standard entropy change for a reaction can be calculated using the following equation.

$$\Delta S^\circ_{\text{rxn}} = \sum n S^\circ(\text{products}) - \sum m S^\circ(\text{reactants})$$

(a) $\Delta S^\circ_{\text{rxn}} = S^\circ(\text{Cu}) + S^\circ(\text{H}_2\text{O}) - [S^\circ(\text{H}_2) + S^\circ(\text{CuO})]$

$$\begin{aligned} &= (1)(33.3 \text{ J/K}\cdot\text{mol}) + (1)(188.7 \text{ J/K}\cdot\text{mol}) - [(1)(131.0 \text{ J/K}\cdot\text{mol}) + (1)(43.5 \text{ J/K}\cdot\text{mol})] \\ &= \mathbf{47.5 \text{ J/K}\cdot\text{mol}} \end{aligned}$$

(b) $\Delta S^\circ_{\text{rxn}} = S^\circ(\text{Al}_2\text{O}_3) + 3S^\circ(\text{Zn}) - [2S^\circ(\text{Al}) + 3S^\circ(\text{ZnO})]$

$$\begin{aligned} &= (1)(50.99 \text{ J/K}\cdot\text{mol}) + (3)(41.6 \text{ J/K}\cdot\text{mol}) - [(2)(28.3 \text{ J/K}\cdot\text{mol}) + (3)(43.9 \text{ J/K}\cdot\text{mol})] \\ &= \mathbf{-12.5 \text{ J/K}\cdot\text{mol}} \end{aligned}$$

(c) $\Delta S^\circ_{\text{rxn}} = S^\circ(\text{CO}_2) + 2S^\circ(\text{H}_2\text{O}) - [S^\circ(\text{CH}_4) + 2S^\circ(\text{O}_2)]$

$$\begin{aligned} &= (1)(213.6 \text{ J/K}\cdot\text{mol}) + (2)(69.9 \text{ J/K}\cdot\text{mol}) - [(1)(186.2 \text{ J/K}\cdot\text{mol}) + (2)(205.0 \text{ J/K}\cdot\text{mol})] \\ &= \mathbf{-242.8 \text{ J/K}\cdot\text{mol}} \end{aligned}$$

Why was the entropy value for water different in parts (a) and (c)?

18.13 All parts of this problem rest on two principles. First, the entropy of a solid is always less than the entropy of a liquid, and the entropy of a liquid is always much smaller than the entropy of a gas. Second, in comparing systems in the same phase, the one with the most complex particles has the higher entropy.

- (a) Positive entropy change (increase). One of the products is in the gas phase (more microstates).
- (b) Negative entropy change (decrease). Liquids have lower entropies than gases.
- (c) Positive. Same as (a).
- (d) Positive. There are two gas-phase species on the product side and only one on the reactant side.

18.14 (a) $\Delta S < 0$; gas reacting with a liquid to form a solid (decrease in number of moles of gas, hence a decrease in microstates).
 (b) $\Delta S > 0$; solid decomposing to give a liquid and a gas (an increase in microstates).
 (c) $\Delta S > 0$; increase in number of moles of gas (an increase in microstates).
 (d) $\Delta S < 0$; gas reacting with a solid to form a solid (decrease in number of moles of gas, hence a decrease in microstates).

18.17 Using Equation (18.12) of the text to solve for the change in standard free energy,

(a) $\Delta G^\circ = 2\Delta G_f^\circ(\text{NO}) - \Delta G_f^\circ(\text{N}_2) - \Delta G_f^\circ(\text{O}_2) = (2)(86.7 \text{ kJ/mol}) - 0 - 0 = \mathbf{173.4 \text{ kJ/mol}}$

(b) $\Delta G^\circ = \Delta G_f^\circ[\text{H}_2\text{O}(g)] - \Delta G_f^\circ[\text{H}_2\text{O}(l)] = (1)(-228.6 \text{ kJ/mol}) - (1)(-237.2 \text{ kJ/mol}) = \mathbf{8.6 \text{ kJ/mol}}$

(c) $\Delta G^\circ = 4\Delta G_f^\circ(\text{CO}_2) + 2\Delta G_f^\circ(\text{H}_2\text{O}) - 2\Delta G_f^\circ(\text{C}_2\text{H}_2) - 5\Delta G_f^\circ(\text{O}_2)$
 $= (4)(-394.4 \text{ kJ/mol}) + (2)(-237.2 \text{ kJ/mol}) - (2)(209.2 \text{ kJ/mol}) - (5)(0) = \mathbf{-2470 \text{ kJ/mol}}$

18.18 Strategy: To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 3 of the text and apply Equation (18.12). Note that all the stoichiometric coefficients have no units so $\Delta G_{\text{rxn}}^\circ$ is expressed in units of kJ/mol. The standard free energy of formation of any element in its stable allotropic form at 1 atm and 25°C is zero.

Solution: The standard free energy change for a reaction can be calculated using the following equation.

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ(\text{products}) - \sum m \Delta G_f^\circ(\text{reactants})$$

(a) $\Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ(\text{MgO}) - [2\Delta G_f^\circ(\text{Mg}) + \Delta G_f^\circ(\text{O}_2)]$

$$\Delta G_{\text{rxn}}^\circ = (2)(-569.6 \text{ kJ/mol}) - [(2)(0) + (1)(0)] = \mathbf{-1139 \text{ kJ/mol}}$$

(b) $\Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ(\text{SO}_3) - [2\Delta G_f^\circ(\text{SO}_2) + \Delta G_f^\circ(\text{O}_2)]$

$$\Delta G_{\text{rxn}}^\circ = (2)(-370.4 \text{ kJ/mol}) - [(2)(-300.4 \text{ kJ/mol}) + (1)(0)] = \mathbf{-140.0 \text{ kJ/mol}}$$

(c) $\Delta G_{\text{rxn}}^\circ = 4\Delta G_f^\circ[\text{CO}_2(g)] + 6\Delta G_f^\circ[\text{H}_2\text{O}(l)] - \{2\Delta G_f^\circ[\text{C}_2\text{H}_6(g)] + 7\Delta G_f^\circ[\text{O}_2(g)]\}$

$$\Delta G_{\text{rxn}}^\circ = (4)(-394.4 \text{ kJ/mol}) + (6)(-237.2 \text{ kJ/mol}) - [(2)(-32.89 \text{ kJ/mol}) + (7)(0)] = \mathbf{-2935.0 \text{ kJ/mol}}$$

18.19 Reaction A: First apply Equation (18.10) of the text to compute the free energy change at 25°C (298 K)

$$\Delta G = \Delta H - T\Delta S = 10,500 \text{ J/mol} - (298 \text{ K})(30 \text{ J/K}\cdot\text{mol}) = 1560 \text{ J/mol}$$

The +1560 J/mol shows the reaction is not spontaneous at 298 K. The ΔG will change sign (i.e., the reaction will become spontaneous) above the temperature at which $\Delta G = 0$.

$$T = \frac{\Delta H}{\Delta S} = \frac{10500 \text{ J/mol}}{30 \text{ J/K} \cdot \text{mol}} = \mathbf{350 \text{ K}}$$

Reaction B: Calculate ΔG .

$$\Delta G = \Delta H - T\Delta S = 1800 \text{ J/mol} - (298 \text{ K})(-113 \text{ J/K} \cdot \text{mol}) = \mathbf{35,500 \text{ J/mol}}$$

The free energy change is positive, which shows that the reaction is not spontaneous at 298 K. Since both terms are positive, there is no temperature at which their sum is negative. The reaction is not spontaneous at any temperature.

18.20 Reaction A: Calculate ΔG from ΔH and ΔS .

$$\Delta G = \Delta H - T\Delta S = -126,000 \text{ J/mol} - (298 \text{ K})(84 \text{ J/K} \cdot \text{mol}) = -151,000 \text{ J/mol}$$

The free energy change is negative so the reaction is spontaneous at 298 K. Since ΔH is negative and ΔS is positive, **the reaction is spontaneous at all temperatures.**

Reaction B: Calculate ΔG .

$$\Delta G = \Delta H - T\Delta S = -11,700 \text{ J/mol} - (298 \text{ K})(-105 \text{ J/K} \cdot \text{mol}) = +19,600 \text{ J}$$

The free energy change is positive at 298 K which means the reaction is not spontaneous at that temperature. The positive sign of ΔG results from the large negative value of ΔS . At lower temperatures, the $-T\Delta S$ term will be smaller thus allowing the free energy change to be negative.

ΔG will equal zero when $\Delta H = T\Delta S$.

Rearranging,

$$T = \frac{\Delta H}{\Delta S} = \frac{-11700 \text{ J/mol}}{-105 \text{ J/K} \cdot \text{mol}} = \mathbf{111 \text{ K}}$$

At temperatures **below 111 K**, ΔG will be negative and the reaction will be spontaneous.

18.23 Find the value of K by solving Equation (18.14) of the text.

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-2.60 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}} = e^{-1.05} = \mathbf{0.35}$$

18.24 Strategy: According to Equation (18.14) of the text, the equilibrium constant for the reaction is related to the standard free energy change; that is, $\Delta G^\circ = -RT \ln K$. Since we are given the equilibrium constant in the problem, we can solve for ΔG° . What temperature unit should be used?

Solution: The equilibrium constant is related to the standard free energy change by the following equation.

$$\Delta G^\circ = -RT \ln K$$

Substitute K_w , R , and T into the above equation to calculate the standard free energy change, ΔG° . The temperature at which $K_w = 1.0 \times 10^{-14}$ is $25^\circ\text{C} = 298 \text{ K}$.

$$\Delta G^\circ = -RT \ln K_w$$

$$\Delta G^\circ = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = \mathbf{8.0 \times 10^4 \text{ J/mol} = 8.0 \times 10^1 \text{ kJ/mol}}$$

$$18.25 \quad K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-14}$$

$$\Delta G^\circ = -RT \ln K_{\text{sp}} = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(1.6 \times 10^{-14}) = 7.9 \times 10^4 \text{ J/mol} = 79 \text{ kJ/mol}$$

18.26 Use standard free energies of formation from Appendix 3 to find the standard free energy difference.

$$\Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ[\text{H}_2(\text{g})] + \Delta G_f^\circ[\text{O}_2(\text{g})] - 2\Delta G_f^\circ[\text{H}_2\text{O}(\text{g})]$$

$$\Delta G_{\text{rxn}}^\circ = (2)(0) + (1)(0) - (2)(-228.6 \text{ kJ/mol})$$

$$\Delta G_{\text{rxn}}^\circ = 457.2 \text{ kJ/mol} = 4.572 \times 10^5 \text{ J/mol}$$

We can calculate K_P using the following equation. We carry additional significant figures in the calculation to minimize rounding errors when calculating K_P .

$$\Delta G^\circ = -RT \ln K_P$$

$$4.572 \times 10^5 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K_P$$

$$-184.54 = \ln K_P$$

Taking the antiln of both sides,

$$e^{-184.54} = K_P$$

$$K_P = 7.2 \times 10^{-81}$$

18.27 (a) We first find the standard free energy change of the reaction.

$$\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ[\text{PCl}_3(\text{g})] + \Delta G_f^\circ[\text{Cl}_2(\text{g})] - \Delta G_f^\circ[\text{PCl}_5(\text{g})]$$

$$= (1)(-286 \text{ kJ/mol}) + (1)(0) - (1)(-325 \text{ kJ/mol}) = 39 \text{ kJ/mol}$$

We can calculate K_P using Equation (18.14) of the text.

$$K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-39 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-16} = 1 \times 10^{-7}$$

(b) We are finding the free energy difference between the reactants and the products at their nonequilibrium values. The result tells us the direction of and the potential for further chemical change. We use the given nonequilibrium pressures to compute Q_P .

$$Q_P = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{(0.27)(0.40)}{0.0029} = 37$$

The value of ΔG (notice that this is not the standard free energy difference) can be found using Equation (18.13) of the text and the result from part (a).

$$\Delta G = \Delta G^\circ + RT \ln Q = (39 \times 10^3 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(37) = 48 \text{ kJ/mol}$$

Which way is the direction of spontaneous change for this system? What would be the value of ΔG if the given data were equilibrium pressures? What would be the value of Q_P in that case?

- 18.28 (a)** The equilibrium constant is related to the standard free energy change by the following equation.

$$\Delta G^\circ = -RT \ln K$$

Substitute K_P , R , and T into the above equation to the standard free energy change, ΔG° .

$$\Delta G^\circ = -RT \ln K_P$$

$$\Delta G^\circ = -(8.314 \text{ J/mol}\cdot\text{K})(2000 \text{ K}) \ln(4.40) = -2.464 \times 10^4 \text{ J/mol} = \mathbf{-24.6 \text{ kJ/mol}}$$

(b)

Strategy: From the information given we see that neither the reactants nor products are at their standard state of 1 atm. We use Equation (18.13) of the text to calculate the free-energy change under non-standard-state conditions. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient Q_P .

Solution: Under non-standard-state conditions, ΔG is related to the reaction quotient Q by the following equation.

$$\Delta G = \Delta G^\circ + RT \ln Q_P$$

We are using Q_P in the equation because this is a gas-phase reaction.

Step 1: ΔG° was calculated in part (a). We must calculate Q_P . We carry additional significant figures in this calculation to minimize rounding errors.

$$Q_P = \frac{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}}{P_{\text{H}_2} \cdot P_{\text{CO}_2}} = \frac{(0.66)(1.20)}{(0.25)(0.78)} = 4.062$$

Step 2: Substitute $\Delta G^\circ = -2.46 \times 10^4 \text{ J/mol}$ and Q_P into the following equation to calculate ΔG .

$$\Delta G = \Delta G^\circ + RT \ln Q_P$$

$$\Delta G = -2.464 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol}\cdot\text{K})(2000 \text{ K}) \ln(4.062)$$

$$\Delta G = (-2.464 \times 10^4 \text{ J/mol}) + (2.331 \times 10^4 \text{ J/mol})$$

$$\Delta G = -1.33 \times 10^3 \text{ J/mol} = \mathbf{-1.33 \text{ kJ/mol}}$$

- 18.29** The expression of K_P is: $K_P = P_{\text{CO}_2}$

Thus you can predict the equilibrium pressure directly from the value of the equilibrium constant. The only task at hand is computing the values of K_P using Equations (18.10) and (18.14) of the text.

- (a)** At 25°C, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (298 \text{ K})(160.5 \text{ J/K}\cdot\text{mol}) = 130.0 \times 10^3 \text{ J/mol}$

$$P_{\text{CO}_2} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-130.0 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-52.47} = \mathbf{1.6 \times 10^{-23} \text{ atm}}$$

- (b)** At 800°C, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (1073 \text{ K})(160.5 \text{ J/K}\cdot\text{mol}) = 5.58 \times 10^3 \text{ J/mol}$

$$P_{\text{CO}_2} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-5.58 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(1073 \text{ K})}} = e^{-0.625} = \mathbf{0.535 \text{ atm}}$$

What assumptions are made in the second calculation?

- 18.30** We use the given K_P to find the standard free energy change.

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(5.62 \times 10^{-5}) = 2.04 \times 10^5 \text{ J/mol} = -204 \text{ kJ/mol}$$

The standard free energy of formation of one mole of COCl_2 can now be found using the standard free energy of reaction calculated above and the standard free energies of formation of CO(g) and $\text{Cl}_2(\text{g})$.

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ (\text{products}) - \sum m \Delta G_f^\circ (\text{reactants})$$

$$\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ [\text{COCl}_2(\text{g})] - \{\Delta G_f^\circ [\text{CO}(\text{g})] + \Delta G_f^\circ [\text{Cl}_2(\text{g})]\}$$

$$-204 \text{ kJ/mol} = (1)\Delta G_f^\circ [\text{COCl}_2(\text{g})] - [(1)(-137.3 \text{ kJ/mol}) + (1)(0)]$$

$$\Delta G_f^\circ [\text{COCl}_2(\text{g})] = -341 \text{ kJ/mol}$$

- 18.31** The equilibrium constant expression is: $K_P = P_{\text{H}_2\text{O}}$

We are actually finding the equilibrium vapor pressure of water (compare to Problem 18.29). We use Equation (18.14) of the text.

$$P_{\text{H}_2\text{O}} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-8.6 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-3.47} = 3.1 \times 10^{-2} \text{ atm}$$

The positive value of ΔG° implies that reactants are favored at equilibrium at 25°C . Is that what you would expect?

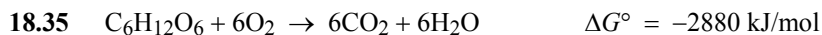
- 18.32** The standard free energy change is given by:

$$\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ (\text{graphite}) - \Delta G_f^\circ (\text{diamond})$$

You can look up the standard free energy of formation values in Appendix 3 of the text.

$$\Delta G_{\text{rxn}}^\circ = (1)(0) - (1)(2.87 \text{ kJ/mol}) = -2.87 \text{ kJ/mol}$$

Thus, the formation of graphite from diamond is **favored** under standard-state conditions at 25°C . However, the rate of the diamond to graphite conversion is very slow (due to a high activation energy) so that it will take millions of years before the process is complete.



Maximum number of ATP molecules synthesized:

$$2880 \text{ kJ/mol} \times \frac{1 \text{ ATP molecule}}{31 \text{ kJ/mol}} = 93 \text{ ATP molecules}$$

- 18.36** The equation for the coupled reaction is:



$$\Delta G^\circ = 13.4 \text{ kJ/mol} - 31 \text{ kJ/mol} = -18 \text{ kJ/mol}$$

As an estimate:

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\ln K = \frac{-(-18 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = 7.3$$

$$K = 1 \times 10^3$$

18.37 When Humpty broke into pieces, he became more disordered (spontaneously). The king was unable to reconstruct Humpty.

18.38 In each part of this problem we can use the following equation to calculate ΔG .

$$\Delta G = \Delta G^\circ + RT \ln Q$$

or,

$$\Delta G = \Delta G^\circ + RT \ln [H^+][OH^-]$$

(a) In this case, the given concentrations are equilibrium concentrations at 25°C. Since the reaction is at equilibrium, $\Delta G = 0$. This is advantageous, because it allows us to calculate ΔG° . Also recall that at equilibrium, $Q = K$. We can write:

$$\Delta G^\circ = -RT \ln K_w$$

$$\Delta G^\circ = -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln (1.0 \times 10^{-14}) = 8.0 \times 10^4 \text{ J/mol}$$

(b) $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [H^+][OH^-]$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln [(1.0 \times 10^{-3})(1.0 \times 10^{-4})] = 4.0 \times 10^4 \text{ J/mol}$$

(c) $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [H^+][OH^-]$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln [(1.0 \times 10^{-12})(2.0 \times 10^{-8})] = -3.2 \times 10^4 \text{ J/mol}$$

(d) $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [H^+][OH^-]$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln [(3.5)(4.8 \times 10^{-4})] = 6.4 \times 10^4 \text{ J/mol}$$

18.39 Only E and H are associated with the first law alone.

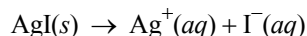
18.40 One possible explanation is simply that no reaction is possible, namely that there is an unfavorable free energy difference between products and reactants ($\Delta G > 0$).

A second possibility is that the potential for spontaneous change is there ($\Delta G < 0$), but that the reaction is extremely slow (very large activation energy).

A remote third choice is that the student accidentally prepared a mixture in which the components were already at their equilibrium concentrations.

Which of the above situations would be altered by the addition of a catalyst?

18.41 We can use data in Appendix 3 of the text to calculate the standard free energy change for the reaction. Then, we can use Equation (18.14) of the text to calculate the equilibrium constant, K .



$$\Delta G^\circ = \Delta G_f^\circ(\text{Ag}^+) + \Delta G_f^\circ(\text{I}^-) - \Delta G_f^\circ(\text{AgI})$$

$$\Delta G^\circ = (1)(77.1 \text{ kJ/mol}) + (1)(-51.67 \text{ kJ/mol}) - (1)(-66.3 \text{ kJ/mol}) = 91.73 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\frac{91.73 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = -37.024$$

$$K = 8.3 \times 10^{-17}$$

This value of K matches the K_{sp} value in Table 16.2 of the text.

- 18.42** For a solid to liquid phase transition (melting) the entropy always increases ($\Delta S > 0$) and the reaction is always endothermic ($\Delta H > 0$).

(a) Melting is always spontaneous above the melting point, so $\Delta G < 0$.

(b) At the melting point (-77.7°C), solid and liquid are in equilibrium, so $\Delta G = 0$.

(c) Melting is not spontaneous below the melting point, so $\Delta G > 0$.

- 18.43** For a reaction to be spontaneous, ΔG must be negative. If ΔS is negative, as it is in this case, then the reaction must be exothermic (why?). When water freezes, it gives off heat (exothermic). Consequently, the entropy of the surroundings increases and $\Delta S_{\text{universe}} > 0$.

- 18.44** If the process is *spontaneous* as well as *endothermic*, the signs of ΔG and ΔH must be negative and positive, respectively. Since $\Delta G = \Delta H - T\Delta S$, the sign of ΔS must be positive ($\Delta S > 0$) for ΔG to be negative.

- 18.45** The equation is: $\text{BaCO}_3(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\Delta G^\circ = \Delta G_f^\circ(\text{BaO}) + \Delta G_f^\circ(\text{CO}_2) - \Delta G_f^\circ(\text{BaCO}_3)$$

$$\Delta G^\circ = (1)(-528.4 \text{ kJ/mol}) + (1)(-394.4 \text{ kJ/mol}) - (1)(-1138.9 \text{ kJ/mol}) = 216.1 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K_P$$

$$\ln K_P = \frac{-2.16 \times 10^5 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = -87.2$$

$$K_P = P_{\text{CO}_2} = e^{-87.2} = 1 \times 10^{-38} \text{ atm}$$

- 18.46** (a) Using the relationship:

$$\frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}} = \Delta S_{\text{vap}} \approx 90 \text{ J/K} \cdot \text{mol}$$

benzene	$\Delta S_{\text{vap}} = 87.8 \text{ J/K} \cdot \text{mol}$
---------	-------------------------------------------------------------

hexane	$\Delta S_{\text{vap}} = 90.1 \text{ J/K} \cdot \text{mol}$
--------	-------------------------------------------------------------

mercury	$\Delta S_{\text{vap}} = 93.7 \text{ J/K} \cdot \text{mol}$
---------	-------------------------------------------------------------

toluene	$\Delta S_{\text{vap}} = 91.8 \text{ J/K} \cdot \text{mol}$
---------	-------------------------------------------------------------

Most liquids have ΔS_{vap} approximately equal to a constant value because the order of the molecules in the liquid state is similar. The order of most gases is totally random; thus, ΔS for liquid \rightarrow vapor should be similar for most liquids.

- (b) Using the data in Table 11.6 of the text, we find:

ethanol	$\Delta S_{\text{vap}} = 111.9 \text{ J/K}\cdot\text{mol}$
water	$\Delta S_{\text{vap}} = 109.4 \text{ J/K}\cdot\text{mol}$

Both water and ethanol have a larger ΔS_{vap} because the liquid molecules are more ordered due to hydrogen bonding (there are fewer microstates in these liquids).

- 18.47** Evidence shows that HF, which is strongly hydrogen-bonded in the liquid phase, is still considerably hydrogen-bonded in the vapor state such that its ΔS_{vap} is smaller than most other substances.

- 18.48** (a) $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$

- (b) The oxidizing agent is NO; the reducing agent is CO.

- (c) $\Delta G^\circ = 2\Delta G_f^\circ(\text{CO}_2) + \Delta G_f^\circ(\text{N}_2) - 2\Delta G_f^\circ(\text{CO}) - 2\Delta G_f^\circ(\text{NO})$

$$\Delta G^\circ = (2)(-394.4 \text{ kJ/mol}) + (0) - (2)(-137.3 \text{ kJ/mol}) - (2)(86.7 \text{ kJ/mol}) = -687.6 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K_P$$

$$\ln K_P = \frac{6.876 \times 10^5 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})} = 277.5$$

$$K_P = 3 \times 10^{120}$$

- (d) $Q_P = \frac{P_{\text{N}_2} P_{\text{CO}_2}^2}{P_{\text{CO}}^2 P_{\text{NO}}^2} = \frac{(0.80)(0.030)^2}{(5.0 \times 10^{-5})^2 (5.0 \times 10^{-7})^2} = 1.2 \times 10^{18}$

Since $Q_P \ll K_P$, the reaction will proceed from **left to right**.

- (e) $\Delta H^\circ = 2\Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{N}_2) - 2\Delta H_f^\circ(\text{CO}) - 2\Delta H_f^\circ(\text{NO})$

$$\Delta H^\circ = (2)(-393.5 \text{ kJ/mol}) + (0) - (2)(-110.5 \text{ kJ/mol}) - (2)(90.4 \text{ kJ/mol}) = -746.8 \text{ kJ/mol}$$

Since ΔH° is negative, raising the temperature will decrease K_P , thereby increasing the amount of reactants and decreasing the amount of products. **No**, the formation of N_2 and CO_2 is not favored by raising the temperature.

- 18.49** (a) At two different temperatures T_1 and T_2 ,

$$\Delta G_1^\circ = \Delta H^\circ - T_1 \Delta S^\circ = -RT \ln K_1 \quad (1)$$

$$\Delta G_2^\circ = \Delta H^\circ - T_2 \Delta S^\circ = -RT \ln K_2 \quad (2)$$

Rearranging Equations (1) and (2),

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad (3)$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad (4)$$

Subtracting equation (3) from equation (4) gives,

$$\ln K_2 - \ln K_1 = \left(\frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \right) - \left(\frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \right)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

(b) Using the equation that we just derived, we can calculate the equilibrium constant at 65°C.

$$K_1 = 4.63 \times 10^{-3} \quad T_1 = 298 \text{ K}$$

$$K_2 = ? \quad T_2 = 338 \text{ K}$$

$$\ln \frac{K_2}{4.63 \times 10^{-3}} = \frac{58.0 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left(\frac{338 \text{ K} - 298 \text{ K}}{(338 \text{ K})(298 \text{ K})} \right)$$

$$\ln \frac{K_2}{4.63 \times 10^{-3}} = 2.77$$

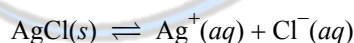
Taking the antiln of both sides of the equation,

$$\frac{K_2}{4.63 \times 10^{-3}} = e^{2.77}$$

$$K_2 = 0.074$$

$K_2 > K_1$, as we would predict for a positive ΔH° . Recall that an increase in temperature will shift the equilibrium towards the endothermic reaction; that is, the decomposition of N_2O_4 .

18.50 The equilibrium reaction is:



$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

We can calculate the standard enthalpy of reaction from the standard enthalpies of formation in Appendix 3 of the text.

$$\Delta H^\circ = \Delta H_f^\circ(\text{Ag}^+) + \Delta H_f^\circ(\text{Cl}^-) - \Delta H_f^\circ(\text{AgCl})$$

$$\Delta H^\circ = (1)(105.9 \text{ kJ/mol}) + (1)(-167.2 \text{ kJ/mol}) - (1)(-127.0 \text{ kJ/mol}) = 65.7 \text{ kJ/mol}$$

From Problem 18.49(a):

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$K_1 = 1.6 \times 10^{-10} \quad T_1 = 298 \text{ K}$$

$$K_2 = ? \quad T_2 = 333 \text{ K}$$

$$\ln \frac{K_2}{1.6 \times 10^{-10}} = \frac{6.57 \times 10^4 \text{ J}}{8.314 \text{ J/K} \cdot \text{mol}} \left(\frac{333 \text{ K} - 298 \text{ K}}{(333 \text{ K})(298 \text{ K})} \right)$$

$$\ln \frac{K_2}{1.6 \times 10^{-10}} = 2.79$$

$$\frac{K_2}{1.6 \times 10^{-10}} = e^{2.79}$$

$$K_2 = 2.6 \times 10^{-9}$$

The increase in K indicates that the solubility increases with temperature.

18.51 At absolute zero. A substance can never have a negative entropy.

18.52 Assuming that both ΔH° and ΔS° are temperature independent, we can calculate both ΔH° and ΔS° .

$$\Delta H^\circ = \Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{H}_2) - [\Delta H_f^\circ(\text{H}_2\text{O}) + \Delta H_f^\circ(\text{C})]$$

$$\Delta H^\circ = (1)(-110.5 \text{ kJ/mol}) + (1)(0) - [(1)(-241.8 \text{ kJ/mol}) + (1)(0)]$$

$$\Delta H^\circ = 131.3 \text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ(\text{CO}) + S^\circ(\text{H}_2) - [S^\circ(\text{H}_2\text{O}) + S^\circ(\text{C})]$$

$$\Delta S^\circ = [(1)(197.9 \text{ J/K} \cdot \text{mol}) + (1)(131.0 \text{ J/K} \cdot \text{mol})] - [(1)(188.7 \text{ J/K} \cdot \text{mol}) + (1)(5.69 \text{ J/K} \cdot \text{mol})]$$

$$\Delta S^\circ = 134.5 \text{ J/K} \cdot \text{mol}$$

It is obvious from the given conditions that the reaction must take place at a fairly high temperature (in order to have red-hot coke). Setting $\Delta G^\circ = 0$

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{131.3 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{134.5 \text{ J/K} \cdot \text{mol}} = 976 \text{ K} = 703^\circ\text{C}$$

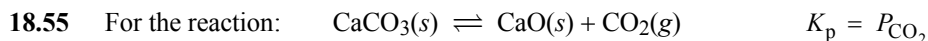
The temperature must be greater than 703°C for the reaction to be spontaneous.

- 18.53** (a) We know that HCl is a strong acid and HF is a weak acid. Thus, the equilibrium constant will be less than 1 ($K < 1$).
- (b) The number of particles on each side of the equation is the same, so $\Delta S^\circ \approx 0$. Therefore ΔH° will dominate.
- (c) HCl is a weaker bond than HF (see Table 9.4 of the text), therefore $\Delta H^\circ > 0$.

18.54 For a reaction to be spontaneous at constant temperature and pressure, $\Delta G < 0$. The process of crystallization proceeds with more order (less disorder), so $\Delta S < 0$. We also know that

$$\Delta G = \Delta H - T\Delta S$$

Since ΔG must be negative, and since the entropy term will be positive ($-T\Delta S$, where ΔS is negative), then ΔH must be negative ($\Delta H < 0$). The reaction will be exothermic.



Using the equation from Problem 18.49:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Substituting,

$$\ln \frac{1829}{22.6} = \frac{\Delta H^\circ}{8.314 \text{ J/K} \cdot \text{mol}} \left(\frac{1223 \text{ K} - 973 \text{ K}}{(973 \text{ K})(1223 \text{ K})} \right)$$

Solving,

$$\Delta H^\circ = 1.74 \times 10^5 \text{ J/mol} = 174 \text{ kJ/mol}$$

18.56 For the reaction to be spontaneous, ΔG must be negative.

$$\Delta G = \Delta H - T\Delta S$$

Given that $\Delta H = 19 \text{ kJ/mol} = 19,000 \text{ J/mol}$, then

$$\Delta G = 19,000 \text{ J/mol} - (273 \text{ K} + 72 \text{ K})(\Delta S)$$

Solving the equation with the value of $\Delta G = 0$

$$0 = 19,000 \text{ J/mol} - (273 \text{ K} + 72 \text{ K})(\Delta S)$$

$$\Delta S = 55 \text{ J/K} \cdot \text{mol}$$

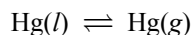
This value of ΔS which we solved for is the value needed to produce a ΔG value of zero. The *minimum* value of ΔS that will produce a spontaneous reaction will be any value of entropy *greater than* 55 J/K·mol.

18.57 (a) $\Delta S > 0$ (b) $\Delta S < 0$ (c) $\Delta S > 0$ (d) $\Delta S > 0$

18.58 The second law states that the entropy of the universe must increase in a spontaneous process. But the entropy of the universe is the sum of two terms: the entropy of the system plus the entropy of the surroundings. One of the entropies can decrease, but not both. In this case, the decrease in system entropy is offset by an increase in the entropy of the surroundings. The reaction in question is exothermic, and the heat released raises the temperature (and the entropy) of the surroundings.

Could this process be spontaneous if the reaction were endothermic?

18.59 At the temperature of the normal boiling point the free energy difference between the liquid and gaseous forms of mercury (or any other substances) is zero, i.e. the two phases are in equilibrium. We can therefore use Equation (18.10) of the text to find this temperature. For the equilibrium,



$$\Delta G = \Delta H - T\Delta S = 0$$

$$\Delta H = \Delta H_f^\circ[\text{Hg}(g)] - \Delta H_f^\circ[\text{Hg}(l)] = 60,780 \text{ J/mol} - 0 = 60780 \text{ J/mol}$$

$$\Delta S = S^\circ[\text{Hg}(g)] - S^\circ[\text{Hg}(l)] = 174.7 \text{ J/K} \cdot \text{mol} - 77.4 \text{ J/K} \cdot \text{mol} = 97.3 \text{ J/K} \cdot \text{mol}$$

$$T_{\text{bp}} = \frac{\Delta H}{\Delta S} = \frac{60780 \text{ J/mol}}{97.3 \text{ J/K} \cdot \text{mol}} = 625 \text{ K} = 352^\circ\text{C}$$

What assumptions are made? Notice that the given enthalpies and entropies are at standard conditions, namely 25°C and 1.00 atm pressure. In performing this calculation we have tacitly assumed that these quantities don't depend upon temperature. The actual normal boiling point of mercury is 356.58°C. Is the assumption of the temperature independence of these quantities reasonable?

- 18.60 Strategy:** At the boiling point, liquid and gas phase ethanol are at equilibrium, so $\Delta G = 0$. From Equation (18.10) of the text, we have $\Delta G = 0 = \Delta H - T\Delta S$ or $\Delta S = \Delta H/T$. To calculate the entropy change for the liquid ethanol \rightarrow gas ethanol transition, we write $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$. What temperature unit should we use?

Solution: The entropy change due to the phase transition (the vaporization of ethanol), can be calculated using the following equation. Recall that the temperature must be in units of Kelvin ($78.3^\circ\text{C} = 351\text{ K}$).

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}}$$

$$\Delta S_{\text{vap}} = \frac{39.3\text{ kJ/mol}}{351\text{ K}} = 0.112\text{ kJ/mol}\cdot\text{K} = 112\text{ J/mol}\cdot\text{K}$$

The problem asks for the change in entropy for the vaporization of 0.50 moles of ethanol. The ΔS calculated above is for 1 mole of ethanol.

$$\Delta S \text{ for } 0.50 \text{ mol} = (112\text{ J/mol}\cdot\text{K})(0.50 \text{ mol}) = 56\text{ J/K}$$

- 18.61** There is no connection between the spontaneity of a reaction predicted by ΔG and the rate at which the reaction occurs. A negative free energy change tells us that a reaction has the potential to happen, but gives no indication of the rate.

Does the fact that a reaction occurs at a measurable rate mean that the free energy difference ΔG is negative?

- 18.62** For the given reaction we can calculate the standard free energy change from the standard free energies of formation (see Appendix 3 of the text). Then, we can calculate the equilibrium constant, K_P , from the standard free energy change.

$$\Delta G^\circ = \Delta G_f^\circ[\text{Ni}(\text{CO})_4] - [4\Delta G_f^\circ(\text{CO}) + \Delta G_f^\circ(\text{Ni})]$$

$$\Delta G^\circ = (1)(-587.4\text{ kJ/mol}) - [(4)(-137.3\text{ kJ/mol}) + (1)(0)] = -38.2\text{ kJ/mol} = -3.82 \times 10^4\text{ J/mol}$$

Substitute ΔG° , R , and T (in K) into the following equation to solve for K_P .

$$\Delta G^\circ = -RT \ln K_P$$

$$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{-(-3.82 \times 10^4\text{ J/mol})}{(8.314\text{ J/K}\cdot\text{mol})(353\text{ K})}$$

$$K_P = 4.5 \times 10^5$$

- 18.63 (a)** $\Delta G^\circ = 2\Delta G_f^\circ(\text{HBr}) - \Delta G_f^\circ(\text{H}_2) - \Delta G_f^\circ(\text{Br}_2) = (2)(-53.2\text{ kJ/mol}) - (1)(0) - (1)(0)$

$$\Delta G^\circ = -106.4\text{ kJ/mol}$$

$$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{106.4 \times 10^3\text{ J/mol}}{(8.314\text{ J/K}\cdot\text{mol})(298\text{ K})} = 42.9$$

$$K_P = 4 \times 10^{18}$$

$$(b) \quad \Delta G^\circ = \Delta G_f^\circ(\text{HBr}) - \frac{1}{2} \Delta G_f^\circ(\text{H}_2) - \frac{1}{2} \Delta G_f^\circ(\text{Br}_2) = (1)(-53.2 \text{ kJ/mol}) - \left(\frac{1}{2}\right)(0) - \left(\frac{1}{2}\right)(0)$$

$$\Delta G^\circ = -53.2 \text{ kJ/mol}$$

$$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{53.2 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = 21.5$$

$$K_P = 2 \times 10^9$$

The K_P in (a) is the square of the K_P in (b). Both ΔG° and K_P depend on the number of moles of reactants and products specified in the balanced equation.

- 18.64** We carry additional significant figures throughout this calculation to minimize rounding errors. The equilibrium constant is related to the standard free energy change by the following equation:

$$\Delta G^\circ = -RT \ln K_P$$

$$2.12 \times 10^5 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K_P$$

$$K_P = 6.894 \times 10^{-38}$$

We can write the equilibrium constant expression for the reaction.

$$K_P = \sqrt{P_{\text{O}_2}}$$

$$P_{\text{O}_2} = (K_P)^2$$

$$P_{\text{O}_2} = (6.894 \times 10^{-38})^2 = 4.8 \times 10^{-75} \text{ atm}$$

This pressure is far too small to measure.

- 18.65** Talking involves various biological processes (to provide the necessary energy) that lead to a increase in the entropy of the universe. Since the overall process (talking) is spontaneous, the entropy of the universe must increase.
- 18.66** Both (a) and (b) apply to a reaction with a negative ΔG° value. Statement (c) is not always true. An endothermic reaction that has a positive ΔS° (increase in entropy) will have a negative ΔG° value at high temperatures.
- 18.67** (a) If ΔG° for the reaction is 173.4 kJ/mol,

$$\text{then, } \Delta G_f^\circ = \frac{173.4 \text{ kJ/mol}}{2} = 86.7 \text{ kJ/mol}$$

$$(b) \quad \Delta G^\circ = -RT \ln K_P$$

$$173.4 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln K_P$$

$$K_P = 4 \times 10^{-31}$$

$$(c) \quad \Delta H^\circ \text{ for the reaction is } 2 \times \Delta H_f^\circ(\text{NO}) = (2)(86.7 \text{ kJ/mol}) = 173.4 \text{ kJ/mol}$$

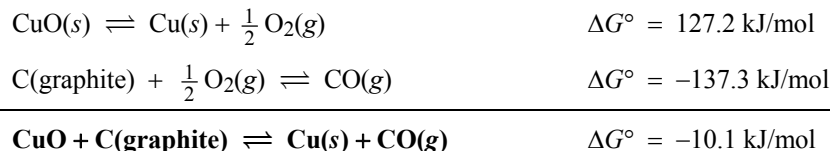
Using the equation in Problem 18.49:

$$\ln \frac{K_2}{4 \times 10^{-31}} = \frac{173.4 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1373 \text{ K} - 298 \text{ K}}{(1373 \text{ K})(298 \text{ K})} \right)$$

$$K_2 = 3 \times 10^{-7}$$

- (d) Lightning promotes the formation of NO (from N₂ and O₂ in the air) which eventually leads to the formation of nitrate ion (NO₃⁻), an essential nutrient for plants.

18.68 We write the two equations as follows. The standard free energy change for the overall reaction will be the sum of the two steps.



We can now calculate the equilibrium constant from the standard free energy change, ΔG° .

$$\begin{aligned}
 \ln K &= \frac{-\Delta G^\circ}{RT} = \frac{-(-10.1 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(673 \text{ K})} \\
 \ln K &= 1.81 \\
 K &= 6.1
 \end{aligned}$$

18.69 Using the equation in the Chemistry in Action entitled “The Efficiency of Heat Engines” in Chapter 18:

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{2473 \text{ K} - 1033 \text{ K}}{2473 \text{ K}} = 0.5823$$

The work done by moving the car:

$$mgh = (1200 \text{ kg})(9.81 \text{ m/s}^2) \times h = \text{heat generated by the engine.}$$

The heat generated by the gas:

$$1.0 \text{ gal} \times \frac{3.1 \text{ kg}}{1 \text{ gal}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{114.2 \text{ g}} \times \frac{5510 \times 10^3 \text{ J}}{1 \text{ mol}} = 1.5 \times 10^8 \text{ J}$$

The maximum use of the energy generated by the gas is:

$$(\text{energy})(\text{efficiency}) = (1.5 \times 10^8 \text{ J})(0.5823) = 8.7 \times 10^7 \text{ J}$$

Setting the (useable) energy generated by the gas equal to the work done moving the car:

$$8.7 \times 10^7 \text{ J} = (1200 \text{ kg})(9.81 \text{ m/s}^2) \times h$$

$$h = 7.4 \times 10^3 \text{ m}$$

18.70 As discussed in Chapter 18 of the text for the decomposition of calcium carbonate, a reaction favors the formation of products at equilibrium when

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$$

If we can calculate ΔH° and ΔS° , we can solve for the temperature at which decomposition begins to favor products. We use data in Appendix 3 of the text to solve for ΔH° and ΔS° .

$$\Delta H^\circ = \Delta H_f^\circ[\text{MgO}(s)] + \Delta H_f^\circ[\text{CO}_2(g)] - \Delta H_f^\circ[\text{MgCO}_3(s)]$$

$$\Delta H^\circ = -601.8 \text{ kJ/mol} + (-393.5 \text{ kJ/mol}) - (-1112.9 \text{ kJ/mol}) = 117.6 \text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ[\text{MgO}(s)] + S^\circ[\text{CO}_2(g)] - S^\circ[\text{MgCO}_3(s)]$$

$$\Delta S^\circ = 26.78 \text{ J/K}\cdot\text{mol} + 213.6 \text{ J/K}\cdot\text{mol} - 65.69 \text{ J/K}\cdot\text{mol} = 174.7 \text{ J/K}\cdot\text{mol}$$

For the reaction to begin to favor products,

$$\Delta H^\circ - T\Delta S^\circ < 0$$

or

$$T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{117.6 \times 10^3 \text{ J/mol}}{174.7 \text{ J/K}\cdot\text{mol}}$$

$$T > 673.2 \text{ K}$$

- 18.71** (a) The first law states that energy can neither be created nor destroyed. We cannot obtain energy out of nowhere.
- (b) If we calculate the efficiency of such an engine, we find that $T_h = T_c$, so the efficiency is zero! See Chemistry in Action on p. 814 of the text.

18.72 (a) $\Delta G^\circ = \Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{Fe}^{2+}) - \Delta G_f^\circ(\text{Fe}) - 2\Delta G_f^\circ(\text{H}^+)$

$$\Delta G^\circ = (1)(0) + (1)(-84.9 \text{ kJ/mol}) - (1)(0) - (2)(0)$$

$$\Delta G^\circ = -84.9 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$-84.9 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K$$

$$K = 7.6 \times 10^{14}$$

(b) $\Delta G^\circ = \Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{Cu}^{2+}) - \Delta G_f^\circ(\text{Cu}) - 2\Delta G_f^\circ(\text{H}^+)$

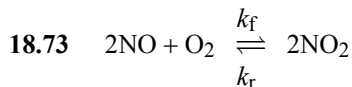
$$\Delta G^\circ = 64.98 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$64.98 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K$$

$$K = 4.1 \times 10^{-12}$$

The activity series is correct. The very large value of K for reaction (a) indicates that *products* are highly favored; whereas, the very small value of K for reaction (b) indicates that *reactants* are highly favored.



$$\Delta G^\circ = (2)(51.8 \text{ kJ/mol}) - (2)(86.7 \text{ kJ/mol}) - 0 = -69.8 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$-69.8 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K$$

$$K = 1.7 \times 10^{12} \text{ M}^{-1}$$

$$K = \frac{k_f}{k_r}$$

$$1.7 \times 10^{12} M^{-1} = \frac{7.1 \times 10^9 M^{-2} s^{-1}}{k_r}$$

$$k_r = 4.2 \times 10^{-3} M^{-1} s^{-1}$$

18.74 (a) It is a “reverse” disproportionation redox reaction.

$$(b) \Delta G^\circ = (2)(-228.6 \text{ kJ/mol}) - (2)(-33.0 \text{ kJ/mol}) - (1)(-300.4 \text{ kJ/mol})$$

$$\Delta G^\circ = -90.8 \text{ kJ/mol}$$

$$-90.8 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K$$

$$K = 8.2 \times 10^{15}$$

Because of the large value of K , this method is efficient for removing SO_2 .

$$(c) \Delta H^\circ = (2)(-241.8 \text{ kJ/mol}) + (3)(0) - (2)(-20.15 \text{ kJ/mol}) - (1)(-296.1 \text{ kJ/mol})$$

$$\Delta H^\circ = -147.2 \text{ kJ/mol}$$

$$\Delta S^\circ = (2)(188.7 \text{ J/K}\cdot\text{mol}) + (3)(31.88 \text{ J/K}\cdot\text{mol}) - (2)(205.64 \text{ J/K}\cdot\text{mol}) - (1)(248.5 \text{ J/K}\cdot\text{mol})$$

$$\Delta S^\circ = -186.7 \text{ J/K}\cdot\text{mol}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Due to the negative entropy change, ΔS° , the free energy change, ΔG° , will become positive at higher temperatures. Therefore, the reaction will be **less effective** at high temperatures.

18.75 (1) Measure K and use $\Delta G^\circ = -RT \ln K$

(2) Measure ΔH° and ΔS° and use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

18.76 $2\text{O}_3 \rightleftharpoons 3\text{O}_2$

$$\Delta G^\circ = 3\Delta G_f^\circ(\text{O}_2) - 2\Delta G_f^\circ(\text{O}_3) = 0 - (2)(163.4 \text{ kJ/mol})$$

$$\Delta G^\circ = -326.8 \text{ kJ/mol}$$

$$-326.8 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(243 \text{ K}) \ln K_P$$

$$K_P = 1.8 \times 10^{70}$$

Due to the large magnitude of K , you would expect this reaction to be spontaneous in the forward direction. However, this reaction has a **large activation energy**, so the rate of reaction is extremely slow.

18.77 First convert to moles of ice.

$$74.6 \text{ g H}_2\text{O}(s) \times \frac{1 \text{ mol H}_2\text{O}(s)}{18.02 \text{ g H}_2\text{O}(s)} = 4.14 \text{ mol H}_2\text{O}(s)$$

For a phase transition:

$$\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{sys}} = \frac{(4.14)(6010 \text{ J/mol})}{273 \text{ K}} = \mathbf{91.1 \text{ J/K} \cdot \text{mol}}$$

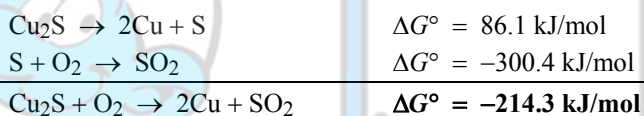
$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{-(4.14)(6010 \text{ J/mol})}{273 \text{ K}} = \mathbf{-91.1 \text{ J/K} \cdot \text{mol}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \mathbf{0}$$

This is an equilibrium process. There is no net change.

18.78 Heating the ore alone is not a feasible process. Looking at the coupled process:



Since ΔG° is a large negative quantity, the coupled reaction is feasible for extracting sulfur.

18.79 Since we are dealing with the same ion (K^+), Equation (18.13) of the text can be written as:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = 0 + (8.314 \text{ J/mol} \cdot \text{K})(310 \text{ K}) \ln \left(\frac{400 \text{ mM}}{15 \text{ mM}} \right)$$

$$\Delta G = \mathbf{8.5 \times 10^3 \text{ J/mol} = 8.5 \text{ kJ/mol}}$$

18.80 First, we need to calculate ΔH° and ΔS° for the reaction in order to calculate ΔG° .

$$\Delta H^\circ = -41.2 \text{ kJ/mol}$$

$$\Delta S^\circ = -42.0 \text{ J/K} \cdot \text{mol}$$

Next, we calculate ΔG° at 300°C or 573 K , assuming that ΔH° and ΔS° are temperature independent.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -41.2 \times 10^3 \text{ J/mol} - (573 \text{ K})(-42.0 \text{ J/K} \cdot \text{mol})$$

$$\Delta G^\circ = \mathbf{-1.71 \times 10^4 \text{ J/mol}}$$

Having solved for ΔG° , we can calculate K_P .

$$\Delta G^\circ = -RT \ln K_P$$

$$-1.71 \times 10^4 \text{ J/mol} = -(8.314 \text{ J/K} \cdot \text{mol})(573 \text{ K}) \ln K_P$$

$$\ln K_P = 3.59$$

$$\mathbf{K_P = 36}$$

Due to the negative entropy change calculated above, we expect that ΔG° will become positive at some temperature higher than 300°C . We need to find the temperature at which ΔG° becomes zero. This is the temperature at which reactants and products are equally favored ($K_P = 1$).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-41.2 \times 10^3 \text{ J/mol}}{-42.0 \text{ J/K} \cdot \text{mol}}$$

$$T = 981 \text{ K} = 708^\circ\text{C}$$

This calculation shows that at 708°C , $\Delta G^\circ = 0$ and the equilibrium constant $K_P = 1$. Above 708°C , ΔG° is positive and K_P will be smaller than 1, meaning that reactants will be favored over products. Note that the temperature 708°C is only an estimate, as we have assumed that both ΔH° and ΔS° are independent of temperature.

Using a more efficient catalyst will *not* increase K_P at a given temperature, because the catalyst will speed up both the forward and reverse reactions. The value of K_P will stay the same.

18.81 (a) ΔG° for CH_3COOH :

$$\Delta G^\circ = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln(1.8 \times 10^{-5})$$

$$\Delta G^\circ = 2.7 \times 10^4 \text{ J/mol} = \mathbf{27 \text{ kJ/mol}}$$

ΔG° for CH_2ClCOOH :

$$\Delta G^\circ = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln(1.4 \times 10^{-3})$$

$$\Delta G^\circ = 1.6 \times 10^4 \text{ J/mol} = \mathbf{16 \text{ kJ/mol}}$$

(b) The $T\Delta S^\circ$ is the dominant term.

(c) The breaking of the O–H bond in ionization of the acid and the forming of the O–H bond in H_3O^+ .

(d) The CH_3COO^- ion is smaller than $\text{CH}_2\text{ClCOO}^-$ and can participate in hydration to a greater extent, leading to a more ordered solution.

18.82 butane \rightarrow isobutane

$$\Delta G^\circ = \Delta G_f^\circ(\text{isobutane}) - \Delta G_f^\circ(\text{butane})$$

$$\Delta G^\circ = (1)(-18.0 \text{ kJ/mol}) - (1)(-15.9 \text{ kJ/mol})$$

$$\Delta G^\circ = -2.1 \text{ kJ/mol}$$

For a mixture at equilibrium at 25°C :

$$\Delta G^\circ = -RT \ln K_P$$

$$-2.1 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K_P$$

$$K_P = 2.3$$

$$K_P = \frac{P_{\text{isobutane}}}{P_{\text{butane}}} \propto \frac{\text{mol isobutane}}{\text{mol butane}}$$

$$2.3 = \frac{\text{mol isobutane}}{\text{mol butane}}$$

This shows that there are 2.3 times as many moles of isobutane as moles of butane. Or, we can say for every one mole of butane, there are 2.3 moles of isobutane.

$$\text{mol \% isobutane} = \frac{2.3 \text{ mol}}{2.3 \text{ mol} + 1.0 \text{ mol}} \times 100\% = \mathbf{70\%}$$

By difference, the mole % of butane is **30%**.

Yes, this result supports the notion that straight-chain hydrocarbons like butane are less stable than branched-chain hydrocarbons like isobutane.

18.83 Heat is absorbed by the rubber band, so ΔH is positive. Since the contraction occurs spontaneously, ΔG is negative. For the reaction to be spontaneous, ΔS must be positive meaning that the rubber becomes more disordered upon heating. This is consistent with what we know about the structure of rubber; The rubber molecules become more disordered upon contraction (See the Figure in the Chemistry in Action Essay on p. 826 of the text).

18.84 We can calculate K_P from ΔG° .

$$\Delta G^\circ = (1)(-394.4 \text{ kJ/mol}) + (0) - (1)(-137.3 \text{ kJ/mol}) - (1)(-255.2 \text{ kJ/mol})$$

$$\Delta G^\circ = -1.9 \text{ kJ/mol}$$

$$-1.9 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(1173 \text{ K}) \ln K_P$$

$$K_P = 1.2$$

Now, from K_P , we can calculate the mole fractions of CO and CO₂.

$$K_P = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 1.2 \quad P_{\text{CO}_2} = 1.2P_{\text{CO}}$$

$$X_{\text{CO}} = \frac{P_{\text{CO}}}{P_{\text{CO}} + P_{\text{CO}_2}} = \frac{P_{\text{CO}}}{P_{\text{CO}} + 1.2P_{\text{CO}}} = \frac{1}{2.2} = \mathbf{0.45}$$

$$X_{\text{CO}_2} = 1 - 0.45 = \mathbf{0.55}$$

We assumed that ΔG° calculated from ΔG_f° values was temperature independent. The ΔG_f° values in Appendix 3 of the text are measured at 25°C, but the temperature of the reaction is 900°C.

18.85 $\Delta G^\circ = -RT \ln K$

and,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Substituting,

$$\Delta G = -RT \ln K + RT \ln Q$$

$$\Delta G = RT(\ln Q - \ln K)$$

$$\Delta G = RT \ln \left(\frac{Q}{K} \right)$$

If $Q > K$, $\Delta G > 0$, and the net reaction will proceed from right to left (see Figure 14.5 of the text).

If $Q < K$, $\Delta G < 0$, and the net reaction will proceed from left to right.

If $Q = K$, $\Delta G = 0$. The system is at equilibrium.

- 18.86** For a phase transition, $\Delta G = 0$. We write:

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

Substituting ΔH and the temperature, $(-78^\circ + 273^\circ)\text{K} = 195\text{ K}$, gives

$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T} = \frac{62.4 \times 10^3 \text{ J/mol}}{195 \text{ K}} = 3.20 \times 10^2 \text{ J/K} \cdot \text{mol}$$

This value of ΔS_{sub} is for the sublimation of 1 mole of CO_2 . We convert to the ΔS value for the sublimation of 84.8 g of CO_2 .

$$84.8 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{3.20 \times 10^2 \text{ J}}{\text{K} \cdot \text{mol}} = \mathbf{617 \text{ J/K}}$$

- 18.87** The second law of thermodynamics states that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. Therefore, the entropy of the universe is increasing with time, and thus entropy could be used to determine the forward direction of time.
- 18.88** First, let's convert the age of the universe from units of years to units of seconds.

$$(13 \times 10^9 \text{ yr}) \times \frac{365 \text{ days}}{1 \text{ yr}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{3600 \text{ s}}{1 \text{ h}} = 4.1 \times 10^{17} \text{ s}$$

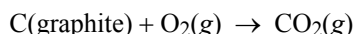
The probability of finding all 100 molecules in the same flask is 8×10^{-31} . Multiplying by the number of seconds gives:

$$(8 \times 10^{-31})(4.1 \times 10^{17} \text{ s}) = \mathbf{3 \times 10^{-13} \text{ s}}$$

- 18.89** Equation (18.10) represents the standard free-energy change for a reaction, and not for a particular compound like CO_2 . The correct form is:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

For a given reaction, ΔG° and ΔH° would need to be calculated from standard formation values (graphite, oxygen, and carbon dioxide) first, before plugging into the equation. Also, ΔS° would need to be calculated from standard entropy values.



- 18.90** We can calculate ΔS_{sys} from standard entropy values in Appendix 3 of the text. We can calculate ΔS_{surr} from the ΔH_{sys} value given in the problem. Finally, we can calculate ΔS_{univ} from the ΔS_{sys} and ΔS_{surr} values.

$$\Delta S_{\text{sys}} = (2)(69.9 \text{ J/K}\cdot\text{mol}) - [(2)(131.0 \text{ J/K}\cdot\text{mol}) + (1)(205.0 \text{ J/K}\cdot\text{mol})] = -327 \text{ J/K}\cdot\text{mol}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-(-571.6 \times 10^3 \text{ J/mol})}{298 \text{ K}} = 1918 \text{ J/K}\cdot\text{mol}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = (-327 + 1918) \text{ J/K}\cdot\text{mol} = 1591 \text{ J/K}\cdot\text{mol}$$

- 18.91** ΔH° is endothermic. Heat must be added to denature the protein. Denaturation leads to more disorder (an increase in microstates). The magnitude of ΔS° is fairly large (1600 J/K·mol). Proteins are large molecules and therefore denaturation would lead to a large increase in microstates. The temperature at which the process favors the denatured state can be calculated by setting ΔG° equal to zero.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{512 \text{ kJ/mol}}{1.60 \text{ kJ/K}\cdot\text{mol}} = 320 \text{ K} = 47^\circ\text{C}$$

- 18.92** q , and w are *not* state functions. Recall that state functions represent properties that are determined by the state of the system, regardless of how that condition is achieved. Heat and work are not state functions because they are not properties of the system. They manifest themselves only during a process (during a change). Thus their values depend on the path of the process and vary accordingly.
- 18.93** (d) will not lead to an increase in entropy of the system. The gas is returned to its original state. The entropy of the system does not change.
- 18.94** Since the adsorption is spontaneous, ΔG must be negative ($\Delta G < 0$). When hydrogen bonds to the surface of the catalyst, the system becomes more ordered ($\Delta S < 0$). Since there is a decrease in entropy, the adsorption must be exothermic for the process to be spontaneous ($\Delta H < 0$).
- 18.95** (a) An ice cube melting in a glass of water at 20°C . The value of ΔG for this process is negative so it must be spontaneous.
- (b) A "perpetual motion" machine. In one version, a model has a flywheel which, once started up, drives a generator which drives a motor which keeps the flywheel running at a constant speed and also lifts a weight.
- (c) A perfect air conditioner; it extracts heat energy from the room and warms the outside air without using any energy to do so. (Note: this process does not violate the first law of thermodynamics.)
- (d) Same example as (a).
- (e) A closed flask at 25°C containing $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ at equilibrium.
- 18.96** (a) Each CO molecule has two possible orientations in the crystal,

CO or OC

If there is no preferred orientation, then for one molecule there are two, or 2^1 , choices of orientation. Two molecules have four or 2^2 choices, and for 1 mole of CO there are 2^{N_A} choices. From Equation (18.1) of the text:

$$S = k \ln W$$

$$S = (1.38 \times 10^{-23} \text{ J/K}) \ln 2^{6.022 \times 10^{23}}$$

$$S = (1.38 \times 10^{-23} \text{ J/K})(6.022 \times 10^{23} / \text{mol}) \ln 2$$

$$S = \mathbf{5.76 \text{ J/K} \cdot \text{mol}}$$

(b) The fact that the actual residual entropy is 4.2 J/K·mol means that the orientation is not totally random.

18.97 The analogy is inappropriate. Entropy is a measure of the dispersal of molecules among available energy levels. The entropy of the room is the same whether it is tidy or not.

18.98 We use data in Appendix 3 of the text to calculate ΔH° and ΔS° .

$$\Delta H^\circ = \Delta H_{\text{vap}} = \Delta H_f^\circ[\text{C}_6\text{H}_6(g)] - \Delta H_f^\circ[\text{C}_6\text{H}_6(l)]$$

$$\Delta H^\circ = 82.93 \text{ kJ/mol} - 49.04 \text{ kJ/mol} = \mathbf{33.89 \text{ kJ/mol}}$$

$$\Delta S^\circ = S^\circ[\text{C}_6\text{H}_6(g)] - S^\circ[\text{C}_6\text{H}_6(l)]$$

$$\Delta S^\circ = 269.2 \text{ J/K} \cdot \text{mol} - 172.8 \text{ J/K} \cdot \text{mol} = \mathbf{96.4 \text{ J/K} \cdot \text{mol}}$$

We can now calculate ΔG° at 298 K.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 33.89 \text{ kJ/mol} - (298 \text{ K})(96.4 \text{ J/K} \cdot \text{mol}) \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta G^\circ = \mathbf{5.2 \text{ kJ/mol}}$$

ΔH° is positive because this is an endothermic process. We also expect ΔS° to be positive because this is a liquid \rightarrow vapor phase change. ΔG° is positive because we are at a temperature that is below the boiling point of benzene (80.1°C).

18.99 (a) $\text{A} + \text{B} \rightarrow \text{C} + x\text{H}^+$

From Equation (18.13) of the text and using the chemical standard state of 1 *M*, we write

$$\Delta G = \Delta G^\circ + RT \ln \frac{\left(\frac{[\text{C}]}{1 \text{ M}}\right)\left(\frac{[\text{H}^+]}{1 \text{ M}}\right)^x}{\left(\frac{[\text{A}]}{1 \text{ M}}\right)\left(\frac{[\text{B}]}{1 \text{ M}}\right)}$$

For the biological standard state, we write

$$\Delta G = \Delta G^{\circ'} + RT \ln \frac{\left(\frac{[\text{C}]}{1 \text{ M}}\right)\left(\frac{[\text{H}^+]}{1 \times 10^{-7} \text{ M}}\right)^x}{\left(\frac{[\text{A}]}{1 \text{ M}}\right)\left(\frac{[\text{B}]}{1 \text{ M}}\right)}$$

We set the two equations equal to each other.

$$\Delta G^\circ + RT \ln \frac{\left(\frac{[C]}{1\text{ M}}\right)\left(\frac{[H^+]}{1\text{ M}}\right)^x}{\left(\frac{[A]}{1\text{ M}}\right)\left(\frac{[B]}{1\text{ M}}\right)} = \Delta G^{\circ'} + RT \ln \frac{\left(\frac{[C]}{1\text{ M}}\right)\left(\frac{[H^+]}{1 \times 10^{-7}\text{ M}}\right)^x}{\left(\frac{[A]}{1\text{ M}}\right)\left(\frac{[B]}{1\text{ M}}\right)}$$

$$\Delta G^\circ + RT \ln \left(\frac{[H^+]}{1\text{ M}}\right)^x = \Delta G^{\circ'} + RT \ln \left(\frac{[H^+]}{1 \times 10^{-7}\text{ M}}\right)^x$$

$$\Delta G^\circ = \Delta G^{\circ'} + RT \ln \left(\frac{[H^+]}{1 \times 10^{-7}\text{ M}}\right)^x - RT \ln \left(\frac{[H^+]}{1\text{ M}}\right)^x$$

$$\Delta G^\circ = \Delta G^{\circ'} + RT \ln \left(\frac{\frac{[H^+]}{1 \times 10^{-7}\text{ M}}}{\frac{[H^+]}{1\text{ M}}} \right)^x$$

$$\Delta G^\circ = \Delta G^{\circ'} + xRT \ln \left(\frac{1}{1 \times 10^{-7}} \right) \quad (1)$$

For the reverse reaction, $C + xH^+ \rightarrow A + B$, we can show that

$$\Delta G^\circ = \Delta G^{\circ'} - xRT \ln \left(\frac{1}{1 \times 10^{-7}} \right) \quad (2)$$

(b) To calculate $\Delta G^{\circ'}$, we use Equation (2) from part (a). Because $x = 1$, Equation (2) becomes

$$\Delta G^\circ = \Delta G^{\circ'} - (1)(8.314\text{ J/mol}\cdot\text{K})(298\text{ K}) \ln \frac{1}{1 \times 10^{-7}}$$

$$\Delta G^\circ = \Delta G^{\circ'} - 39.93\text{ kJ/mol}$$

or

$$\Delta G^{\circ'} = -21.8\text{ kJ/mol} + 39.93\text{ kJ/mol} = \mathbf{18.1\text{ kJ/mol}}$$

We now calculate ΔG using both conventions.

Chemical standard state:

$$\Delta G = \Delta G^\circ + RT \ln \frac{\left(\frac{[\text{NAD}^+]}{1\text{ M}}\right)\left(\frac{P_{\text{H}_2}}{1\text{ atm}}\right)}{\left(\frac{[\text{NADH}]}{1\text{ M}}\right)\left(\frac{[\text{H}^+]}{1\text{ M}}\right)}$$

$$\Delta G = -21.8 \times 10^3\text{ J/mol} + (8.314\text{ J/mol}\cdot\text{K})(298\text{ K}) \ln \frac{(4.6 \times 10^{-3})(0.010)}{(1.5 \times 10^{-2})(3.0 \times 10^{-5})}$$

$$\Delta G = \mathbf{-10.3\text{ kJ/mol}}$$

Biological standard state:

$$\Delta G = \Delta G^{\circ'} + RT \ln \frac{\left(\frac{[\text{NAD}^+]}{1 \text{ M}} \right) \left(\frac{P_{\text{H}_2}}{1 \text{ atm}} \right)}{\left(\frac{[\text{NADH}]}{1 \text{ M}} \right) \left(\frac{[\text{H}^+]}{1 \times 10^{-7} \text{ M}} \right)}$$

$$\Delta G = 18.1 \times 10^3 \text{ J/mol} + (8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln \frac{(4.6 \times 10^{-3})(0.010)}{(1.5 \times 10^{-2})(3.0 \times 10^{-5} / 1 \times 10^{-7})}$$

$$\Delta G = -10.3 \text{ kJ/mol}$$

As expected, ΔG is the same regardless of which standard state we employ.

18.100 We can calculate ΔG° at 872 K from the equilibrium constant, K_1 .

$$\Delta G^{\circ} = -RT \ln K$$

$$\Delta G^{\circ} = -(8.314 \text{ J/mol} \cdot \text{K})(872 \text{ K}) \ln(1.80 \times 10^{-4})$$

$$\Delta G^{\circ} = 6.25 \times 10^4 \text{ J/mol} = \mathbf{62.5 \text{ kJ/mol}}$$

We use the equation derived in Problem 18.49 to calculate ΔH° .

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.0480}{1.80 \times 10^{-4}} = \frac{\Delta H^{\circ}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{872 \text{ K}} - \frac{1}{1173 \text{ K}} \right)$$

$$\Delta H^{\circ} = \mathbf{157.8 \text{ kJ/mol}}$$

Now that both ΔG° and ΔH° are known, we can calculate ΔS° at 872 K.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$62.5 \times 10^3 \text{ J/mol} = (157.8 \times 10^3 \text{ J/mol}) - (872 \text{ K})\Delta S^{\circ}$$

$$\Delta S^{\circ} = \mathbf{109 \text{ J/K} \cdot \text{mol}}$$

18.101 (a) In Problem 18.46, Trouton's rule states that the ratio of the molar heat of vaporization of a liquid (ΔH_{vap}) to its boiling point in Kelvin is approximately 90 J/K·mol. This relationship shown mathematically is:

$$\frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}} = \Delta S_{\text{vap}} \approx 90 \text{ J/K} \cdot \text{mol}$$

We solve for ΔH_{vap} of benzene.

$$\frac{\Delta H_{\text{vap}}}{353.1 \text{ K}} \approx 90 \text{ J/K} \cdot \text{mol}$$

$$\Delta H_{\text{vap}} = \mathbf{3.18 \times 10^4 \text{ J/mol} = 31.8 \text{ kJ/mol}}$$

Compare this estimated value of the molar heat of vaporization of benzene to the value in Table 11.6 of the text (31.0 kJ/mol).

(b) The phase change is, $\text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(g)$. The equilibrium constant expression is:

$$K_P = P_{\text{C}_6\text{H}_6(g)}$$

The equation derived in Problem 18.49 is:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Substituting, $K_2 = P_{\text{C}_6\text{H}_6(2)}$ and $K_1 = P_{\text{C}_6\text{H}_6(1)}$ gives

$$\ln \frac{P_{\text{C}_6\text{H}_6(2)}}{P_{\text{C}_6\text{H}_6(1)}} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$T_1 = 347 \text{ K}$ and $T_2 = 353.1 \text{ K}$

$$\ln \frac{P_{\text{C}_6\text{H}_6(2)}}{P_{\text{C}_6\text{H}_6(1)}} = \frac{31.8 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{353.1 \text{ K} - 347 \text{ K}}{(347 \text{ K})(353.1 \text{ K})} \right)$$

$$\ln \frac{P_{\text{C}_6\text{H}_6(2)}}{P_{\text{C}_6\text{H}_6(1)}} = 0.190$$

$$\frac{P_{\text{C}_6\text{H}_6(2)}}{P_{\text{C}_6\text{H}_6(1)}} = e^{0.190} = 1.21$$

This factor of 1.21 indicates that the vapor pressure of benzene at 353.1 K is 1.21 times the vapor pressure at 347 K. The vapor pressure at the normal boiling point is 760 mmHg. The estimated vapor pressure at 74°C (347 K) is therefore,

$$P_{\text{C}_6\text{H}_6(g)} = \frac{760 \text{ mmHg}}{1.21} = \mathbf{628 \text{ mmHg}}$$

18.102 First, calculate the equilibrium constant, K_P , from the ΔG° value.

$$\Delta G^\circ = -RT \ln K_P$$

$$-3.4 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K_P$$

$$\ln K_P = 1.4$$

$$K_P = 4$$

Next, calculate the Q_P value for each reaction mixture and compare the value to K_P calculated above. The problem states that the partial pressures of the gases in each frame are equal to the number of A_2 , B_2 , and AB molecules times 0.10 atm.

$$\begin{aligned} \text{(a)} \quad Q_P &= \frac{P_{\text{AB}}^2}{P_{\text{A}_2} \cdot P_{\text{B}_2}} \\ Q_P &= \frac{(0.3)^2}{(0.3)(0.2)} = 1.5 \end{aligned}$$

$$\text{(b)} \quad Q_P = \frac{(0.6)^2}{(0.2)(0.3)} = 6.0$$

$$(c) \quad Q_P = \frac{(0.4)^2}{(0.2)(0.2)} = 4.0$$

- (1) Reaction mixture (c) is at equilibrium ($Q = K$). $\Delta G = 0$.
- (2) Reaction mixture (a) has a negative ΔG value. Because $Q < K$, the system will shift right, toward products, to reach equilibrium. This shift corresponds to a negative ΔG value. The value of ΔG could also be calculated using Equation (18.13) of the text.

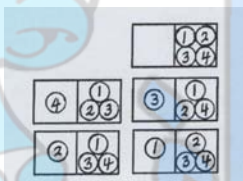
$$\Delta G = \Delta G^\circ + RT \ln Q = -2.4 \text{ kJ/mol}$$

- (3) Reaction mixture (b) has a positive ΔG value. Because $Q > K$, the system will shift left, toward reactants, to reach equilibrium. This shift corresponds to a positive ΔG value.

$$\Delta G = \Delta G^\circ + RT \ln Q = 1.0 \text{ kJ/mol}$$

Answers to Review of Concepts

Section 18.3 (p. 805)



Section 18.4 (p. 811)

(a) $A_2 + 3B_2 \rightarrow 2AB_3$. (b) $\Delta S < 0$.

Section 18.5 (p. 818)

(a) ΔS must be positive and $T\Delta S > \Delta H$ in magnitude.

(b) Because ΔS is usually quite small for solution processes, the $T\Delta S$ term is small (at room temperature) compared to ΔH in magnitude. Thus, ΔH is the predominant factor in determining the sign of ΔG .

Section 18.5 (p. 821)

196 J/K·mol

CHAPTER 19

ELECTROCHEMISTRY

Problem Categories

Biological: 19.66, 19.68, 19.126.

Conceptual: 19.67, 19.79, 19.85, 19.94, 19.103, 19.106, 19.108, 19.128.

Descriptive: 19.13, 19.14, 19.17, 19.18, 19.46a, 19.52a, 19.61, 19.77, 19.87, 19.93, 19.99, 19.100, 19.101, 19.111, 19.113, 19.123.

Environmental: 19.63.

Industrial: 19.48, 19.56, 19.89, 19.109, 19.112, 19.120.

Organic: 19.38.

Difficulty Level

Easy: 19.11, 19.12, 19.13, 19.14, 19.16, 19.17, 19.18, 19.22, 19.45, 19.63, 19.67, 19.79, 19.91, 19.97.

Medium: 19.1, 19.2, 19.15, 19.21, 19.23, 19.24, 19.25, 19.26, 19.29, 19.30, 19.31, 19.32, 19.33, 19.34, 19.38, 19.46, 19.47, 19.48, 19.49, 19.50, 19.51, 19.52, 19.53, 19.55, 19.57, 19.58, 19.59, 19.60, 19.61, 19.62, 19.64, 19.65, 19.66, 19.69, 19.70, 19.72, 19.73, 19.74, 19.75, 19.77, 19.81, 19.82, 19.83, 19.84, 19.85, 19.86, 19.87, 19.89, 19.93, 19.94, 19.96, 19.98, 19.99, 19.100, 19.103, 19.104, 19.106, 19.107, 19.108, 19.109, 19.110, 19.113, 19.114, 19.115, 19.116, 19.117, 19.122, 19.124, 19.126.

Difficult: 19.37, 19.54, 19.56, 19.68, 19.71, 19.76, 19.78, 19.80, 19.88, 19.90, 19.92, 19.95, 19.101, 19.102, 19.105, 19.111, 19.112, 19.118, 19.119, 19.120, 19.121, 19.123, 19.125, 19.127, 19.128.

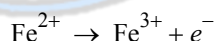
19.1 We follow the steps are described in detail in Section 19.1 of the text.

(a) The problem is given in ionic form, so combining Steps 1 and 2, the half-reactions are:

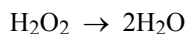


Step 3: We balance each half-reaction for number and type of atoms and charges.

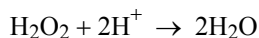
The *oxidation half-reaction* is already balanced for Fe atoms. There are three net positive charges on the right and two net positive charges on the left, we add one electrons to the right side to balance the charge.



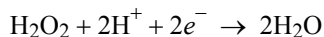
Reduction half-reaction: we add one H₂O to the right-hand side of the equation to balance the O atoms.



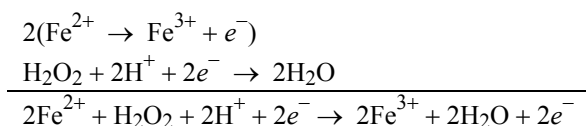
To balance the H atoms, we add 2H⁺ to the left-hand side.



There are two net positive charges on the left, so we add two electrons to the same side to balance the charge.



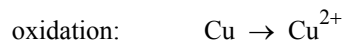
Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 2.



The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



(b) The problem is given in ionic form, so combining Steps 1 and 2, the half-reactions are:



Step 3: We balance each half-reaction for number and type of atoms and charges.

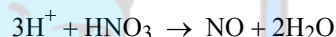
The *oxidation half-reaction* is already balanced for Cu atoms. There are two net positive charges on the right, so we add two electrons to the right side to balance the charge.



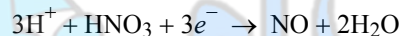
Reduction half-reaction: we add two H_2O to the right-hand side of the equation to balance the O atoms.



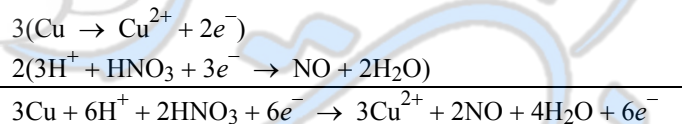
To balance the H atoms, we add 3H^+ to the left-hand side.



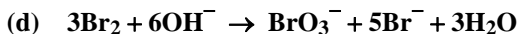
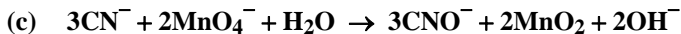
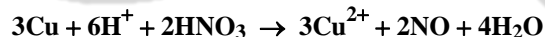
There are three net positive charges on the left, so we add three electrons to the same side to balance the charge.



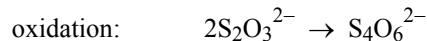
Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.



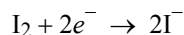
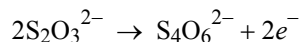
The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



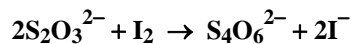
(e) Half-reactions balanced for S and I:



Both half-reactions are already balanced for O, so we balance charge with electrons



The electron count is the same on both sides. We add the equations, canceling electrons, to obtain the balanced equation.

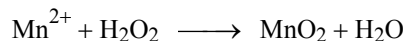


19.2 Strategy: We follow the procedure for balancing redox reactions presented in Section 19.1 of the text.

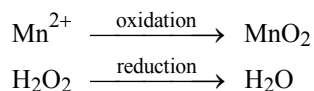
Solution:

(a)

Step 1: The unbalanced equation is given in the problem.

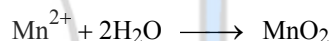


Step 2: The two half-reactions are:



Step 3: We balance each half-reaction for number and type of atoms and charges.

The *oxidation half-reaction* is already balanced for Mn atoms. To balance the O atoms, we add two water molecules on the left side.



To balance the H atoms, we add 4 H⁺ to the right-hand side.



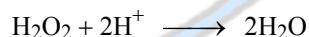
There are four net positive charges on the right and two net positive charge on the left, we add two electrons to the right side to balance the charge.



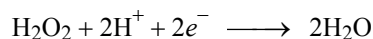
Reduction half-reaction: we add one H₂O to the right-hand side of the equation to balance the O atoms.



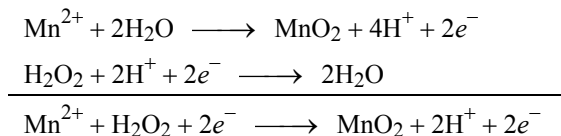
To balance the H atoms, we add 2H⁺ to the left-hand side.



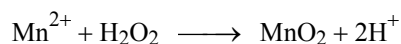
There are two net positive charges on the left, so we add two electrons to the same side to balance the charge.



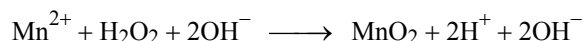
Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. Note that the number of electrons gained and lost is equal.



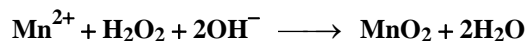
The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



Because the problem asks to balance the equation in basic medium, we add one OH[−] to both sides for each H⁺ and combine pairs of H⁺ and OH[−] on the same side of the arrow to form H₂O.

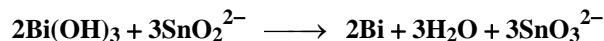


Combining the H^+ and OH^- to form water we obtain:



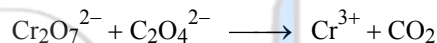
Step 5: Check to see that the equation is balanced by verifying that the equation has the same types and numbers of atoms and the same charges on both sides of the equation.

(b) This problem can be solved by the same methods used in part (a).

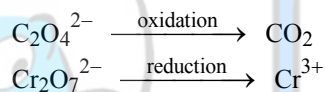


(c)

Step 1: The unbalanced equation is given in the problem.



Step 2: The two half-reactions are:

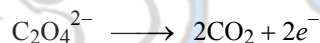


Step 3: We balance each half-reaction for number and type of atoms and charges.

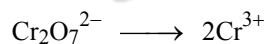
In the *oxidation half-reaction*, we first need to balance the C atoms.



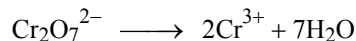
The O atoms are already balanced. There are two net negative charges on the left, so we add two electrons to the right to balance the charge.



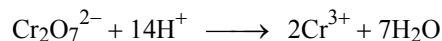
In the *reduction half-reaction*, we first need to balance the Cr atoms.



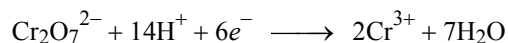
We add seven H_2O molecules on the right to balance the O atoms.



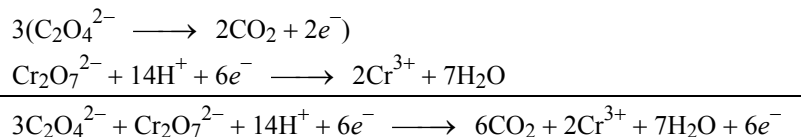
To balance the H atoms, we add 14H^+ to the left-hand side.



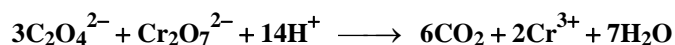
There are twelve net positive charges on the left and six net positive charges on the right. We add six electrons on the left to balance the charge.



Step 4: We now add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 3.

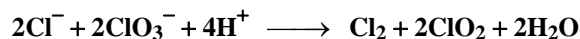


The electrons on both sides cancel, and we are left with the balanced net ionic equation in acidic medium.



Step 5: Check to see that the equation is balanced by verifying that the equation has the same types and numbers of atoms and the same charges on both sides of the equation.

(d) This problem can be solved by the same methods used in part (c).



19.11	Half-reaction	$E^\circ(\text{V})$
	$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mg}(\text{s})$	-2.37
	$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$	+0.34

The overall equation is: $\text{Mg}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

$$E^\circ = 0.34 \text{ V} - (-2.37 \text{ V}) = \mathbf{2.71 \text{ V}}$$

19.12 Strategy: At first, it may not be clear how to assign the electrodes in the galvanic cell. From Table 19.1 of the text, we write the standard reduction potentials of Al and Ag and apply the diagonal rule to determine which is the anode and which is the cathode.

Solution: The standard reduction potentials are:

$\text{Ag}^+(1.0 \text{ M}) + e^- \rightarrow \text{Ag}(\text{s})$	$E^\circ = 0.80 \text{ V}$
$\text{Al}^{3+}(1.0 \text{ M}) + 3e^- \rightarrow \text{Al}(\text{s})$	$E^\circ = -1.66 \text{ V}$

Applying the diagonal rule, we see that Ag^+ will oxidize Al.

Anode (oxidation): $\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(1.0 \text{ M}) + 3e^-$

Cathode (reduction): $3\text{Ag}^+(1.0 \text{ M}) + 3e^- \rightarrow 3\text{Ag}(\text{s})$

Overall: $\text{Al}(\text{s}) + 3\text{Ag}^+(1.0 \text{ M}) \rightarrow \text{Al}^{3+}(1.0 \text{ M}) + 3\text{Ag}(\text{s})$

Note that in order to balance the overall equation, we multiplied the reduction of Ag^+ by 3. We can do so because, as an intensive property, E° is not affected by this procedure. We find the emf of the cell using Equation (19.1) and Table 19.1 of the text.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Al}^{3+}/\text{Al}}^\circ$$

$$E_{\text{cell}}^\circ = 0.80 \text{ V} - (-1.66 \text{ V}) = \mathbf{+2.46 \text{ V}}$$

Check: The positive value of E° shows that the forward reaction is favored.

19.13 The appropriate half-reactions from Table 19.1 are

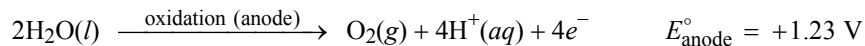
$\text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^-(\text{aq})$	$E_{\text{anode}}^\circ = 0.53 \text{ V}$
$\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$	$E_{\text{cathode}}^\circ = 0.77 \text{ V}$

Thus iron(III) should oxidize iodide ion to iodine. This makes the iodide ion/iodine half-reaction the anode. The standard emf can be found using Equation (19.1).

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.77 \text{ V} - 0.53 \text{ V} = \mathbf{0.24 \text{ V}}$$

(The emf was not required in this problem, but the fact that it is positive confirms that the reaction should favor products at equilibrium.)

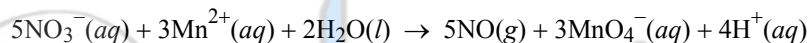
19.14 The half-reaction for oxidation is:



The species that can oxidize water to molecular oxygen must have an E_{red}° more positive than +1.23 V.

From Table 19.1 of the text we see that only $\text{Cl}_2(g)$ and $\text{MnO}_4^-(aq)$ in acid solution can oxidize water to oxygen.

19.15 The overall reaction is:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.96 \text{ V} - 1.51 \text{ V} = -0.55 \text{ V}$$

The negative emf indicates that reactants are favored at equilibrium. NO_3^- will not oxidize Mn^{2+} to MnO_4^- under standard-state conditions.

19.16 Strategy: E_{cell}° is *positive* for a spontaneous reaction. In each case, we can calculate the standard cell emf from the potentials for the two half-reactions.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

Solution:

(a) $E^\circ = -0.40 \text{ V} - (-2.87 \text{ V}) = \mathbf{2.47 \text{ V}}$. The reaction is spontaneous.

(b) $E^\circ = -0.14 \text{ V} - 1.07 \text{ V} = \mathbf{-1.21 \text{ V}}$. The reaction is not spontaneous.

(c) $E^\circ = -0.25 \text{ V} - 0.80 \text{ V} = \mathbf{-1.05 \text{ V}}$. The reaction is not spontaneous.

(d) $E^\circ = 0.77 \text{ V} - 0.15 \text{ V} = \mathbf{0.62 \text{ V}}$. The reaction is spontaneous.

19.17 From Table 19.1 of the text, we compare the standard reduction potentials for the half-reactions. The more positive the potential, the better the substance as an oxidizing agent.

(a) Au^{3+} (b) Ag^+ (c) Cd^{2+} (d) O_2 in acidic solution.

19.18 Strategy: The greater the tendency for the substance to be oxidized, the stronger its tendency to act as a reducing agent. The species that has a stronger tendency to be oxidized will have a smaller reduction potential.

Solution: In each pair, look for the one with the smaller reduction potential. This indicates a greater tendency for the substance to be oxidized.

(a) Li (b) H_2 (c) Fe^{2+} (d) Br^-

19.21 We find the standard reduction potentials in Table 19.1 of the text.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.76 \text{ V} - (-2.37 \text{ V}) = 1.61 \text{ V}$$

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

$$K = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}}$$

$$K = e^{\frac{(2)(1.61 \text{ V})}{0.0257 \text{ V}}}$$

$$K = 3 \times 10^{54}$$

19.22 Strategy: The relationship between the equilibrium constant, K , and the standard emf is given by Equation (19.5) of the text: $E_{\text{cell}}^{\circ} = (0.0257 \text{ V} / n) \ln K$. Thus, knowing n (the moles of electrons transferred) and the equilibrium constant, we can determine E_{cell}° .

Solution: The equation that relates K and the standard cell emf is:

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

We see in the reaction that Mg goes to Mg^{2+} and Zn^{2+} goes to Zn. Therefore, two moles of electrons are transferred during the redox reaction. Substitute the equilibrium constant and the moles of e^{-} transferred ($n = 2$) into the above equation to calculate E° .

$$E^{\circ} = \frac{(0.0257 \text{ V}) \ln K}{n} = \frac{(0.0257 \text{ V}) \ln(2.69 \times 10^{12})}{2} = \mathbf{0.368 \text{ V}}$$

19.23 In each case we use standard reduction potentials from Table 19.1 together with Equation (19.5) of the text.

(a) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.07 \text{ V} - 0.53 \text{ V} = 0.54 \text{ V}$

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

$$K = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}}$$

$$K = e^{\frac{(2)(0.54 \text{ V})}{0.0257 \text{ V}}} = \mathbf{2 \times 10^{18}}$$

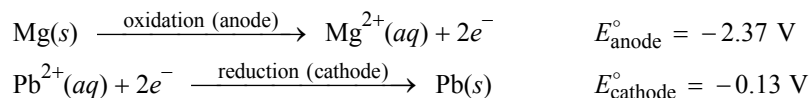
(b) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.61 \text{ V} - 1.36 \text{ V} = 0.25 \text{ V}$

$$K = e^{\frac{(2)(0.25 \text{ V})}{0.0257 \text{ V}}} = \mathbf{3 \times 10^8}$$

$$(c) \quad E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.51 \text{ V} - 0.77 \text{ V} = 0.74 \text{ V}$$

$$K = e^{\frac{(5)(0.74 \text{ V})}{0.0257 \text{ V}}} = 3 \times 10^{62}$$

19.24 (a) We break the equation into two half-reactions:



The standard emf is given by

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.13 \text{ V} - (-2.37 \text{ V}) = 2.24 \text{ V}$$

We can calculate ΔG° from the standard emf.

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G^{\circ} = -(2)(96500 \text{ J/V} \cdot \text{mol})(2.24 \text{ V}) = -432 \text{ kJ/mol}$$

Next, we can calculate K using Equation (19.5) of the text.

$$E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K$$

or

$$\ln K = \frac{nE_{\text{cell}}^{\circ}}{0.0257 \text{ V}}$$

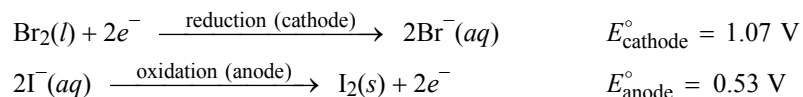
and

$$K = e^{\frac{nE^{\circ}}{0.0257}}$$

$$K = e^{\frac{(2)(2.24)}{0.0257}} = 5 \times 10^{75}$$

Tip: You could also calculate K_c from the standard free energy change, ΔG° , using the equation: $\Delta G^{\circ} = -RT \ln K_c$.

(b) We break the equation into two half-reactions:



The standard emf is

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.07 \text{ V} - 0.53 \text{ V} = 0.54 \text{ V}$$

We can calculate ΔG° from the standard emf.

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G^{\circ} = -(2)(96500 \text{ J/V} \cdot \text{mol})(0.54 \text{ V}) = -104 \text{ kJ/mol}$$

Next, we can calculate K using Equation (19.5) of the text.

$$K = e^{\frac{nE^\circ}{0.0257}}$$

$$K = e^{\frac{(2)(0.54)}{0.0257}} = 2 \times 10^{18}$$

(c) This is worked in an analogous manner to parts (a) and (b).

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.23 \text{ V} - 0.77 \text{ V} = 0.46 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -(4)(96500 \text{ J/V}\cdot\text{mol})(0.46 \text{ V}) = -178 \text{ kJ/mol}$$

$$K = e^{\frac{nE^\circ}{0.0257}}$$

$$K = e^{\frac{(4)(0.46)}{0.0257}} = 1 \times 10^{31}$$

(d) This is worked in an analogous manner to parts (a), (b), and (c).

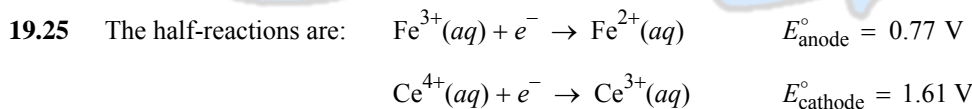
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.53 \text{ V} - (-1.66 \text{ V}) = 2.19 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -(6)(96500 \text{ J/V}\cdot\text{mol})(2.19 \text{ V}) = -1.27 \times 10^3 \text{ kJ/mol}$$

$$K = e^{\frac{nE^\circ}{0.0257}}$$

$$K = e^{\frac{(6)(2.19)}{0.0257}} = 8 \times 10^{211}$$



Thus, Ce^{4+} will oxidize Fe^{2+} to Fe^{3+} ; this makes the $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-reaction the anode. The standard cell emf is found using Equation (19.1) of the text.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.61 \text{ V} - 0.77 \text{ V} = 0.84 \text{ V}$$

The values of ΔG° and K_c are found using Equations (19.3) and (19.5) of the text.

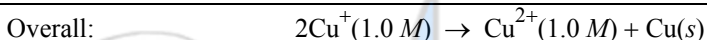
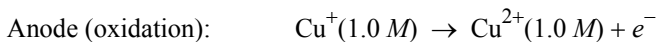
$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(1)(96500 \text{ J/V}\cdot\text{mol})(0.84 \text{ V}) = -81 \text{ kJ/mol}$$

$$\ln K = \frac{nE^\circ_{\text{cell}}}{0.0257 \text{ V}}$$

$$K_c = e^{\frac{nE^\circ_{\text{cell}}}{0.0257 \text{ V}}} = e^{\frac{(1)(0.84 \text{ V})}{0.0257 \text{ V}}} = 2 \times 10^{14}$$

19.26 Strategy: The relationship between the standard free energy change and the standard emf of the cell is given by Equation (19.3) of the text: $\Delta G^\circ = -nFE_{\text{cell}}^\circ$. The relationship between the equilibrium constant, K , and the standard emf is given by Equation (19.5) of the text: $E_{\text{cell}}^\circ = (0.0257 \text{ V}/n) \ln K$. Thus, if we can determine E_{cell}° , we can calculate ΔG° and K . We can determine the E_{cell}° of a hypothetical galvanic cell made up of two couples ($\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu) from the standard reduction potentials in Table 19.1 of the text.

Solution: The half-cell reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Cu}^+/\text{Cu}}^\circ - E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ$$

$$E_{\text{cell}}^\circ = 0.52 \text{ V} - 0.15 \text{ V} = \mathbf{0.37 \text{ V}}$$

Now, we use Equation (19.3) of the text. The overall reaction shows that $n = 1$.

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$\Delta G^\circ = -(1)(96500 \text{ J/V}\cdot\text{mol})(0.37 \text{ V}) = \mathbf{-36 \text{ kJ/mol}}$$

Next, we can calculate K using Equation (19.5) of the text.

$$E_{\text{cell}}^\circ = \frac{0.0257 \text{ V}}{n} \ln K$$

or

$$\ln K = \frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}$$

and

$$K = e^{\frac{nE_{\text{cell}}^\circ}{0.0257}}$$

$$K = e^{\frac{(1)(0.37)}{0.0257}} = e^{14.4} = \mathbf{2 \times 10^6}$$

Check: The negative value of ΔG° and the large positive value of K , both indicate that the reaction favors products at equilibrium. The result is consistent with the fact that E° for the galvanic cell is positive.

19.29 If this were a standard cell, the concentrations would all be 1.00 M , and the voltage would just be the standard emf calculated from Table 19.1 of the text. Since cell emf's depend on the concentrations of the reactants and products, we must use the Nernst equation [Equation (19.8) of the text] to find the emf of a nonstandard cell.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.25}{0.15}$$

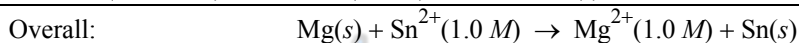
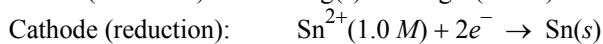
$$E = \mathbf{1.09 \text{ V}}$$

How did we find the value of 1.10 V for E° ?

19.30 Strategy: The standard emf (E°) can be calculated using the standard reduction potentials in Table 19.1 of the text. Because the reactions are not run under standard-state conditions (concentrations are not 1 M), we need Nernst's equation [Equation (19.8) of the text] to calculate the emf (E) of a hypothetical galvanic cell. Remember that solids do not appear in the reaction quotient (Q) term in the Nernst equation. We can calculate ΔG from E using Equation (19.2) of the text: $\Delta G = -nFE_{\text{cell}}$.

Solution:

(a) The half-cell reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Sn}^{2+}/\text{Sn}}^\circ - E_{\text{Mg}^{2+}/\text{Mg}}^\circ$$

$$E_{\text{cell}}^\circ = -0.14\text{ V} - (-2.37\text{ V}) = \mathbf{2.23\text{ V}}$$

From Equation (19.8) of the text, we write:

$$E = E^\circ - \frac{0.0257\text{ V}}{n} \ln Q$$

$$E = E^\circ - \frac{0.0257\text{ V}}{n} \ln \frac{[\text{Mg}^{2+}]}{[\text{Sn}^{2+}]}$$

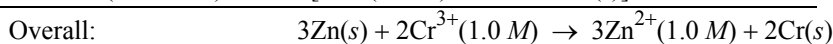
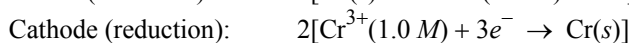
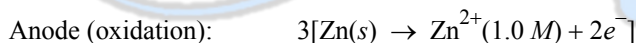
$$E = 2.23\text{ V} - \frac{0.0257\text{ V}}{2} \ln \frac{0.045}{0.035} = \mathbf{2.23\text{ V}}$$

We can now find the free energy change at the given concentrations using Equation (19.2) of the text. Note that in this reaction, $n = 2$.

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G = -(2)(96500\text{ J/V}\cdot\text{mol})(2.23\text{ V}) = \mathbf{-430\text{ kJ/mol}}$$

(b) The half-cell reactions are:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Cr}^{3+}/\text{Cr}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ$$

$$E_{\text{cell}}^\circ = -0.74\text{ V} - (-0.76\text{ V}) = \mathbf{0.02\text{ V}}$$

From Equation (19.8) of the text, we write:

$$E = E^\circ - \frac{0.0257\text{ V}}{n} \ln Q$$

$$E = E^\circ - \frac{0.0257\text{ V}}{n} \ln \frac{[\text{Zn}^{2+}]^3}{[\text{Cr}^{3+}]^2}$$

$$E = 0.02\text{ V} - \frac{0.0257\text{ V}}{6} \ln \frac{(0.0085)^3}{(0.010)^2} = \mathbf{0.04\text{ V}}$$

We can now find the free energy change at the given concentrations using Equation (19.2) of the text. Note that in this reaction, $n = 6$.

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G = -(6)(96500 \text{ J/V}\cdot\text{mol})(0.04 \text{ V}) = -23 \text{ kJ/mol}$$

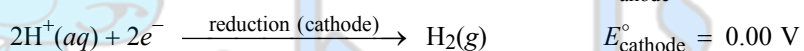
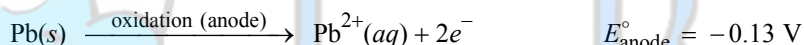
19.31 The overall reaction is: $\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.00 \text{ V} - (-0.76 \text{ V}) = 0.76 \text{ V}$$

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Zn}^{2+}]\text{P}_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E = 0.76 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.45)(2.0)}{(1.8)^2} = 0.78 \text{ V}$$

19.32 Let's write the two half-reactions to calculate the standard cell emf. (Oxidation occurs at the Pb electrode.)



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.00 \text{ V} - (-0.13 \text{ V}) = 0.13 \text{ V}$$

Using the Nernst equation, we can calculate the cell emf, E .

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Pb}^{2+}]\text{P}_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E = 0.13 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.10)(1.0)}{(0.050)^2} = 0.083 \text{ V}$$

19.33 As written, the reaction is not spontaneous under standard state conditions; the cell emf is negative.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.76 \text{ V} - 0.34 \text{ V} = -1.10 \text{ V}$$

The reaction will become spontaneous when the concentrations of zinc(II) and copper(II) ions are such as to make the emf positive. The turning point is when the emf is zero. We solve the Nernst equation for the $[\text{Cu}^{2+}]/[\text{Zn}^{2+}]$ ratio at this point.

$$E_{\text{cell}} = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

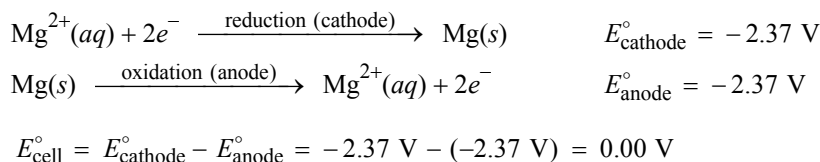
$$0 = -1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$\ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} = -85.6$$

$$\frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} = e^{-85.6} = 6.7 \times 10^{-38}$$

In other words for the reaction to be spontaneous, the $[\text{Cu}^{2+}]/[\text{Zn}^{2+}]$ ratio must be less than 6.7×10^{-38} . Is the reduction of zinc(II) by copper metal a practical use of copper?

19.34 All concentration cells have the same standard emf: *zero* volts.



We use the Nernst equation to compute the emf. There are two moles of electrons transferred from the reducing agent to the oxidizing agent in this reaction, so $n = 2$.

$$\begin{aligned}E &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \\ E &= E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Mg}^{2+}]_{\text{ox}}}{[\text{Mg}^{2+}]_{\text{red}}} \\ E &= 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.24}{0.53} = \mathbf{0.010 \text{ V}}\end{aligned}$$

What is the direction of spontaneous change in all concentration cells?

19.37 (a) The total charge passing through the circuit is

$$3.0 \cancel{\text{ h}} \times \frac{8.5 \text{ C}}{1 \cancel{\text{ s}}} \times \frac{3600 \cancel{\text{ s}}}{1 \cancel{\text{ h}}} = 9.2 \times 10^4 \text{ C}$$

From the anode half-reaction we can find the amount of hydrogen.

$$(9.2 \times 10^4 \cancel{\text{ C}}) \times \frac{2 \text{ mol H}_2}{4 \cancel{\text{ mol e}^-}} \times \frac{1 \cancel{\text{ mol e}^-}}{96500 \cancel{\text{ C}}} = 0.48 \text{ mol H}_2$$

The volume can be computed using the ideal gas equation

$$V = \frac{nRT}{P} = \frac{(0.48 \cancel{\text{ mol}})(0.0821 \text{ L} \cdot \cancel{\text{ atm/K} \cdot \cancel{\text{ mol}}})(298 \cancel{\text{ K}})}{155 \cancel{\text{ atm}}} = \mathbf{0.076 \text{ L}}$$

(b) The charge passing through the circuit in one minute is

$$\frac{8.5 \text{ C}}{1 \cancel{\text{ s}}} \times \frac{60 \cancel{\text{ s}}}{1 \text{ min}} = 510 \text{ C/min}$$

We can find the amount of oxygen from the cathode half-reaction and the ideal gas equation.

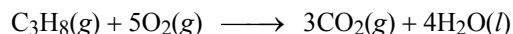
$$\frac{510 \cancel{\text{ C}}}{1 \text{ min}} \times \frac{1 \cancel{\text{ mol e}^-}}{96500 \cancel{\text{ C}}} \times \frac{1 \text{ mol O}_2}{4 \cancel{\text{ mol e}^-}} = 1.3 \times 10^{-3} \text{ mol O}_2/\text{min}$$

$$V = \frac{nRT}{P} = \left(\frac{1.3 \times 10^{-3} \cancel{\text{ mol O}_2}}{1 \text{ min}} \right) \left(\frac{(0.0821 \text{ L} \cdot \cancel{\text{ atm/K} \cdot \cancel{\text{ mol}}})(298 \cancel{\text{ K}})}{1 \cancel{\text{ atm}}} \right) = 0.032 \text{ L O}_2/\text{min}$$

$$\frac{0.032 \cancel{\text{ L O}_2}}{1 \text{ min}} \times \frac{1.0 \text{ L air}}{0.20 \cancel{\text{ L O}_2}} = \mathbf{0.16 \text{ L of air/min}}$$

- 19.38** We can calculate the standard free energy change, ΔG° , from the standard free energies of formation, ΔG_f° using Equation (18.12) of the text. Then, we can calculate the standard cell emf, E_{cell}° , from ΔG° .

The overall reaction is:



$$\Delta G_{\text{rxn}}^\circ = 3\Delta G_f^\circ[\text{CO}_2(g)] + 4\Delta G_f^\circ[\text{H}_2\text{O}(l)] - \{\Delta G_f^\circ[\text{C}_3\text{H}_8(g)] + 5\Delta G_f^\circ[\text{O}_2(g)]\}$$

$$\Delta G_{\text{rxn}}^\circ = (3)(-394.4 \text{ kJ/mol}) + (4)(-237.2 \text{ kJ/mol}) - [(1)(-23.5 \text{ kJ/mol}) + (5)(0)] = -2108.5 \text{ kJ/mol}$$

We can now calculate the standard emf using the following equation:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

or

$$E_{\text{cell}}^\circ = \frac{-\Delta G^\circ}{nF}$$

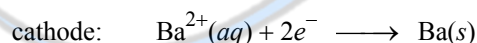
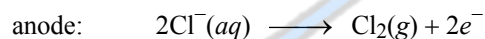
Check the half-reactions on the page of the text listed in the problem to determine that 20 moles of electrons are transferred during this redox reaction.

$$E_{\text{cell}}^\circ = \frac{-(-2108.5 \times 10^3 \text{ J/mol})}{(20)(96500 \text{ J/V} \cdot \text{mol})} = 1.09 \text{ V}$$

Does this suggest that, in theory, it should be possible to construct a galvanic cell (battery) based on any conceivable spontaneous reaction?

19.45 $\text{Mass Mg} = 1.00 \cancel{\text{ g}} \times \frac{1 \text{ mol Mg}}{2 \text{ mol } e^-} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = 12.2 \text{ g Mg}$

- 19.46** (a) The only ions present in molten BaCl_2 are Ba^{2+} and Cl^- . The electrode reactions are:



This cathode half-reaction tells us that 2 moles of e^- are required to produce 1 mole of $\text{Ba}(s)$.

(b)

Strategy: According to Figure 19.20 of the text, we can carry out the following conversion steps to calculate the quantity of Ba in grams.

$$\text{current} \times \text{time} \rightarrow \text{coulombs} \rightarrow \text{mol } e^- \rightarrow \text{mol Ba} \rightarrow \text{g Ba}$$

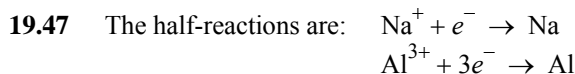
This is a large number of steps, so let's break it down into two parts. First, we calculate the coulombs of electricity that pass through the cell. Then, we will continue on to calculate grams of Ba.

Solution: First, we calculate the coulombs of electricity that pass through the cell.

$$0.50 \cancel{\text{ A}} \times \frac{1 \text{ C}}{1 \cancel{\text{ A}} \cdot \text{s}} \times \frac{60 \cancel{\text{ s}}}{1 \cancel{\text{ min}}} \times 30 \cancel{\text{ min}} = 9.0 \times 10^2 \text{ C}$$

We see that for every mole of Ba formed at the cathode, 2 moles of electrons are needed. The grams of Ba produced at the cathode are:

$$? \text{ g Ba} = (9.0 \times 10^2 \cancel{\text{ C}}) \times \frac{1 \text{ mol } e^-}{96,500 \cancel{\text{ C}}} \times \frac{1 \text{ mol Ba}}{2 \text{ mol } e^-} \times \frac{137.3 \text{ g Ba}}{1 \text{ mol Ba}} = 0.64 \text{ g Ba}$$



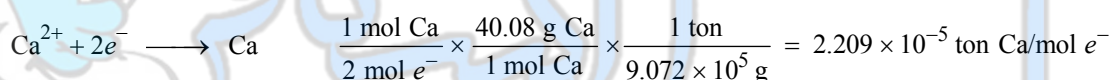
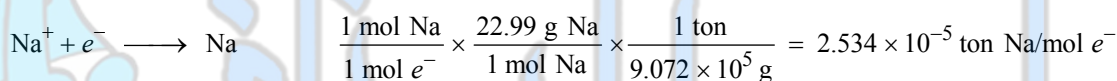
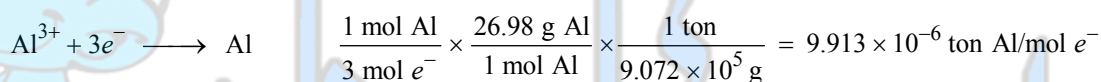
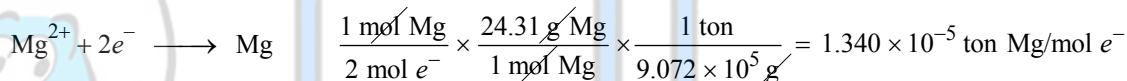
Since 1 g is the same idea as 1 ton as long as we are comparing two quantities, we can write:

$$1 \cancel{\text{g}}/\text{Na} \times \frac{1 \text{ mol}}{22.99 \cancel{\text{g}}/\text{Na}} \times 1 e^- = 0.043 \text{ mol } e^-$$

$$1 \cancel{\text{g}}/\text{Al} \times \frac{1 \text{ mol}}{26.98 \cancel{\text{g}}/\text{Al}} \times 3 e^- = 0.11 \text{ mol } e^-$$

It is cheaper to prepare 1 ton of sodium by electrolysis.

19.48 The cost for producing various metals is determined by the moles of electrons needed to produce a given amount of metal. For each reduction, let's first calculate the number of tons of metal produced per 1 mole of electrons ($1 \text{ ton} = 9.072 \times 10^5 \text{ g}$). The reductions are:



Now that we know the tons of each metal produced per mole of electrons, we can convert from \$155/ton Mg to the cost to produce the given amount of each metal.

(a) For aluminum:

$$\frac{\$155}{1 \text{ ton Mg}} \times \frac{1.340 \times 10^{-5} \cancel{\text{ton}} \text{ Mg}}{1 \cancel{\text{mol}} e^-} \times \frac{1 \cancel{\text{mol}} e^-}{9.913 \times 10^{-6} \cancel{\text{ton}} \text{ Al}} \times 10.0 \cancel{\text{tons}} \text{ Al} = \mathbf{\$2.10 \times 10^3}$$

(b) For sodium:

$$\frac{\$155}{1 \text{ ton Mg}} \times \frac{1.340 \times 10^{-5} \text{ ton Mg}}{1 \text{ mol } e^-} \times \frac{1 \text{ mol } e^-}{2.534 \times 10^{-5} \text{ ton Na}} \times 30.0 \text{ tons Na} = \mathbf{\$2.46 \times 10^3}$$

(c) For calcium:

$$\frac{\$155}{1 \text{ ton Mg}} \times \frac{1.340 \times 10^{-5} \text{ ton Mg}}{1 \text{ mol } e^-} \times \frac{1 \text{ mol } e^-}{2.209 \times 10^{-5} \text{ ton Ca}} \times 50.0 \text{ tons Ca} = \mathbf{\$4.70 \times 10^3}$$

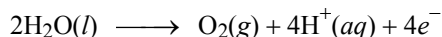
19.49 Find the amount of oxygen using the ideal gas equation

$$n = \frac{PV}{RT} = \frac{\left(755 \cancel{\text{mmHg}} \times \frac{1 \cancel{\text{atm}}}{760 \cancel{\text{mmHg}}}\right)(0.076 \cancel{\text{L}})}{(0.0821 \cancel{\text{L}} \cdot \cancel{\text{atm}}/\text{K} \cdot \cancel{\text{mol}})(298 \cancel{\text{K}})} = 3.1 \times 10^{-3} \text{ mol O}_2$$

The half-reaction shows that 4 moles of electrons are required to produce one mole of oxygen. We write:

$$(3.1 \times 10^{-3} \cancel{\text{mol O}_2}) \times \frac{4 \cancel{\text{mol e}^-}}{1 \cancel{\text{mol O}_2}} = \mathbf{0.012 \text{ mol e}^-}$$

19.50 (a) The half-reaction is:



First, we can calculate the number of moles of oxygen produced using the ideal gas equation.

$$n_{\text{O}_2} = \frac{PV}{RT}$$

$$n_{\text{O}_2} = \frac{(1.0 \cancel{\text{atm}})(0.84 \cancel{\text{L}})}{(0.0821 \cancel{\text{L} \cdot \text{atm/mol} \cdot \text{K}})(298 \cancel{\text{K}})} = 0.034 \text{ mol O}_2$$

From the half-reaction, we see that 1 mol O₂ \simeq 4 mol e[−].

$$\text{? mol e}^- = 0.034 \cancel{\text{mol O}_2} \times \frac{4 \cancel{\text{mol e}^-}}{1 \cancel{\text{mol O}_2}} = \mathbf{0.14 \text{ mol e}^-}$$

(b) The half-reaction is:



The number of moles of chlorine produced is:

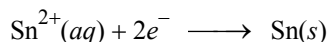
$$n_{\text{Cl}_2} = \frac{PV}{RT}$$

$$n_{\text{Cl}_2} = \frac{\left(750 \cancel{\text{mmHg}} \times \frac{1 \cancel{\text{atm}}}{760 \cancel{\text{mmHg}}}\right)(1.50 \cancel{\text{L}})}{(0.0821 \cancel{\text{L} \cdot \text{atm/mol} \cdot \text{K}})(298 \cancel{\text{K}})} = 0.0605 \text{ mol Cl}_2$$

From the half-reaction, we see that 1 mol Cl₂ \simeq 2 mol e[−].

$$\text{? mol e}^- = 0.0605 \cancel{\text{mol Cl}_2} \times \frac{2 \cancel{\text{mol e}^-}}{1 \cancel{\text{mol Cl}_2}} = \mathbf{0.121 \text{ mol e}^-}$$

(c) The half-reaction is:

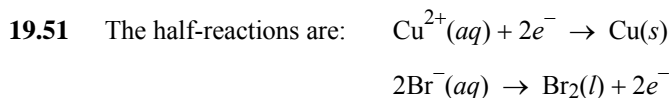


The number of moles of Sn(s) produced is

$$\text{? mol Sn} = 6.0 \cancel{\text{g Sn}} \times \frac{1 \cancel{\text{mol Sn}}}{118.7 \cancel{\text{g Sn}}} = 0.051 \text{ mol Sn}$$

From the half-reaction, we see that 1 mol Sn \simeq 2 mol e[−].

$$\text{? mol e}^- = 0.051 \cancel{\text{mol Sn}} \times \frac{2 \cancel{\text{mol e}^-}}{1 \cancel{\text{mol Sn}}} = \mathbf{0.10 \text{ mol e}^-}$$



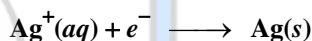
The mass of copper produced is:

$$4.50 \cancel{\text{A}} \times 1 \cancel{\text{h}} \times \frac{3600 \cancel{\text{s}}}{1 \cancel{\text{h}}} \times \frac{1 \cancel{\text{C}}}{1 \cancel{\text{A}} \cdot \cancel{\text{s}}} \times \frac{1 \cancel{\text{mol}} e^{-}}{96500 \cancel{\text{C}}} \times \frac{1 \cancel{\text{mol}} \text{Cu}}{2 \cancel{\text{mol}} e^{-}} \times \frac{63.55 \text{ g Cu}}{1 \cancel{\text{mol}} \text{Cu}} = \mathbf{5.33 \text{ g Cu}}$$

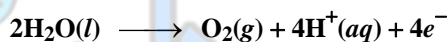
The mass of bromine produced is:

$$4.50 \text{ A} \times 1 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol } e^{-}}{96500 \text{ C}} \times \frac{1 \text{ mol Br}_2}{2 \text{ mol } e^{-}} \times \frac{159.8 \text{ g Br}_2}{1 \text{ mol Br}_2} = \mathbf{13.4 \text{ g Br}_2}$$

19.52 (a) The half-reaction is:



(b) Since this reaction is taking place in an aqueous solution, the probable oxidation is the oxidation of water. (Neither Ag^{+} nor NO_3^{-} can be further oxidized.)



(c) The half-reaction tells us that 1 mole of electrons is needed to reduce 1 mol of Ag^{+} to Ag metal. We can set up the following strategy to calculate the quantity of electricity (in C) needed to deposit 0.67 g of Ag.

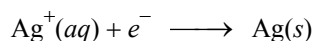
grams Ag \rightarrow mol Ag \rightarrow mol e^{-} \rightarrow coulombs

$$0.67 \cancel{\text{g}} \text{Ag} \times \frac{1 \cancel{\text{mol}} \text{Ag}}{107.9 \cancel{\text{g}} \text{Ag}} \times \frac{1 \cancel{\text{mol}} e^{-}}{1 \cancel{\text{mol}} \text{Ag}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol}} e^{-}} = \mathbf{6.0 \times 10^2 \text{ C}}$$

19.53 The half-reaction is: $\text{Co}^{2+} + 2e^{-} \rightarrow \text{Co}$

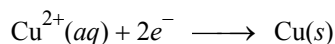
$$2.35 \cancel{\text{g}} \text{Co} \times \frac{1 \cancel{\text{mol}} \text{Co}}{58.93 \cancel{\text{g}} \text{Co}} \times \frac{2 \cancel{\text{mol}} e^{-}}{1 \cancel{\text{mol}} \text{Co}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol}} e^{-}} = \mathbf{7.70 \times 10^3 \text{ C}}$$

19.54 (a) First find the amount of charge needed to produce 2.00 g of silver according to the half-reaction:



$$2.00 \cancel{\text{g}} \text{Ag} \times \frac{1 \cancel{\text{mol}} \text{Ag}}{107.9 \cancel{\text{g}} \text{Ag}} \times \frac{1 \cancel{\text{mol}} e^{-}}{1 \cancel{\text{mol}} \text{Ag}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol}} e^{-}} = 1.79 \times 10^3 \text{ C}$$

The half-reaction for the reduction of copper(II) is:



From the amount of charge calculated above, we can calculate the mass of copper deposited in the second cell.

$$(1.79 \times 10^3 \cancel{\text{C}}) \times \frac{1 \cancel{\text{mol}} e^{-}}{96500 \cancel{\text{C}}} \times \frac{1 \cancel{\text{mol}} \text{Cu}}{2 \cancel{\text{mol}} e^{-}} \times \frac{63.55 \text{ g Cu}}{1 \cancel{\text{mol}} \text{Cu}} = \mathbf{0.589 \text{ g Cu}}$$

(b) We can calculate the current flowing through the cells using the following strategy.

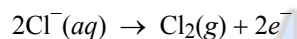
Coulombs \rightarrow Coulombs/hour \rightarrow Coulombs/second

Recall that $1 \text{ C} = 1 \text{ A}\cdot\text{s}$

The current flowing through the cells is:

$$(1.79 \times 10^3 \text{ A}\cdot\cancel{\text{s}}) \times \frac{1\cancel{\text{h}}}{3600\cancel{\text{s}}} \times \frac{1}{3.75\cancel{\text{h}}} = \mathbf{0.133 \text{ A}}$$

19.55 The half-reaction for the oxidation of chloride ion is:



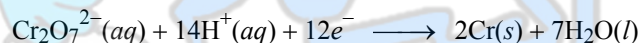
First, let's calculate the moles of e^- flowing through the cell in one hour.

$$1500\cancel{\text{A}} \times \frac{1\cancel{\text{C}}}{1\cancel{\text{A}}\cdot\text{s}} \times \frac{3600\cancel{\text{s}}}{1\text{h}} \times \frac{1\text{mol } e^-}{96500\cancel{\text{C}}} = 55.96 \text{ mol } e^-$$

Next, let's calculate the hourly production rate of chlorine gas (in kg). Note that the anode efficiency is 93.0%.

$$55.96\cancel{\text{mol } e^-} \times \frac{1\cancel{\text{mol Cl}_2}}{2\cancel{\text{mol } e^-}} \times \frac{0.07090\text{ kg Cl}_2}{1\cancel{\text{mol Cl}_2}} \times \frac{93.0\%}{100\%} = \mathbf{1.84 \text{ kg Cl}_2/\text{h}}$$

19.56 *Step 1:* Balance the half-reaction.



Step 2: Calculate the quantity of chromium metal by calculating the volume and converting this to mass using the given density.

Volume Cr = thickness \times surface area

$$\text{Volume Cr} = (1.0 \times 10^{-2} \cancel{\text{mm}}) \times \frac{1\cancel{\text{m}}}{1000\cancel{\text{mm}}} \times 0.25 \text{ m}^2 = 2.5 \times 10^{-6} \text{ m}^3$$

Converting to cm^3 ,

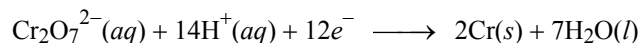
$$(2.5 \times 10^{-6} \cancel{\text{m}^3}) \times \left(\frac{1\cancel{\text{cm}}}{0.01\cancel{\text{m}}} \right)^3 = 2.5 \text{ cm}^3$$

Next, calculate the mass of Cr.

Mass = density \times volume

$$\text{Mass Cr} = 2.5 \cancel{\text{cm}^3} \times \frac{7.19\text{ g}}{1\cancel{\text{cm}^3}} = 18 \text{ g Cr}$$

Step 3: Find the number of moles of electrons required to electrodeposit 18 g of Cr from solution. The half-reaction is:



Six moles of electrons are required to reduce 1 mol of Cr metal. But, we are electrodepositing less than 1 mole of Cr(s). We need to complete the following conversions:



$$? \text{ faradays} = 18 \cancel{\text{g}}/\text{Cr} \times \frac{1 \cancel{\text{mol}} \text{Cr}}{52.00 \cancel{\text{g}}/\text{Cr}} \times \frac{6 \text{ mol } e^-}{1 \cancel{\text{mol}} \text{Cr}} = 2.1 \text{ mol } e^-$$

Step 4: Determine how long it will take for 2.1 moles of electrons to flow through the cell when the current is 25.0 C/s. We need to complete the following conversions:

$\text{mol } e^- \rightarrow \text{coulombs} \rightarrow \text{seconds} \rightarrow \text{hours}$

$$? \text{ h} = 2.1 \cancel{\text{mol}} e^- \times \frac{96,500 \cancel{\text{C}}}{1 \cancel{\text{mol}} e^-} \times \frac{1 \cancel{\text{s}}}{25.0 \cancel{\text{C}}} \times \frac{1 \text{ h}}{3600 \cancel{\text{s}}} = \mathbf{2.3 \text{ h}}$$

Would any time be saved by connecting several bumpers together in a series?

19.57 The quantity of charge passing through the solution is:

$$0.750 \cancel{\text{A}} \times \frac{1 \cancel{\text{C}}}{1 \cancel{\text{A}} \cdot \text{s}} \times \frac{60 \cancel{\text{s}}}{1 \cancel{\text{min}}} \times \frac{1 \text{ mol } e^-}{96500 \cancel{\text{C}}} \times 25.0 \cancel{\text{min}} = 1.17 \times 10^{-2} \text{ mol } e^-$$

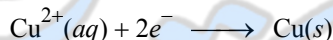
Since the charge of the copper ion is +2, the number of moles of copper formed must be:

$$(1.17 \times 10^{-2} \cancel{\text{mol}} e^-) \times \frac{1 \text{ mol Cu}}{2 \cancel{\text{mol}} e^-} = 5.85 \times 10^{-3} \text{ mol Cu}$$

The units of molar mass are grams per mole. The molar mass of copper is:

$$\frac{0.369 \text{ g}}{5.85 \times 10^{-3} \text{ mol}} = \mathbf{63.1 \text{ g/mol}}$$

19.58 Based on the half-reaction, we know that one faraday will produce half a mole of copper.



First, let's calculate the charge (in C) needed to deposit 0.300 g of Cu.

$$(3.00 \cancel{\text{A}})(304 \cancel{\text{s}}) \times \frac{1 \text{ C}}{1 \cancel{\text{A}} \cdot \text{s}} = 912 \text{ C}$$

We know that one faraday will produce half a mole of copper, but we don't have a half a mole of copper. We have:

$$0.300 \cancel{\text{g}}/\text{Cu} \times \frac{1 \text{ mol Cu}}{63.55 \cancel{\text{g}}/\text{Cu}} = 4.72 \times 10^{-3} \text{ mol}$$

We calculated the number of coulombs (912 C) needed to produce 4.72×10^{-3} mol of Cu. How many coulombs will it take to produce 0.500 moles of Cu? This will be Faraday's constant.

$$\frac{912 \text{ C}}{4.72 \times 10^{-3} \cancel{\text{mol}} \text{Cu}} \times 0.500 \cancel{\text{mol}} \text{Cu} = \mathbf{9.66 \times 10^4 \text{ C} = 1 \text{ F}}$$

19.59 The number of faradays supplied is:

$$1.44 \cancel{\text{g}}/\text{Ag} \times \frac{1 \cancel{\text{mol}} \text{Ag}}{107.9 \cancel{\text{g}}/\text{Ag}} \times \frac{1 \text{ mol } e^-}{1 \cancel{\text{mol}} \text{Ag}} = 0.0133 \text{ mol } e^-$$

Since we need three faradays to reduce one mole of X^{3+} , the molar mass of X must be:

$$\frac{0.120 \text{ g X}}{0.0133 \cancel{\text{ mol } e^-}} \times \frac{3 \cancel{\text{ mol } e^-}}{1 \text{ mol X}} = \mathbf{27.1 \text{ g/mol}}$$

19.60 First we can calculate the number of moles of hydrogen produced using the ideal gas equation.

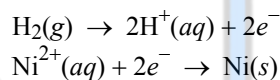
$$n_{\text{H}_2} = \frac{PV}{RT}$$

$$n_{\text{H}_2} = \frac{\left(782 \cancel{\text{ mmHg}} \times \frac{1 \cancel{\text{ atm}}}{760 \cancel{\text{ mmHg}}}\right)(0.845 \cancel{\text{ L}})}{(0.0821 \cancel{\text{ L} \cdot \text{atm/K} \cdot \text{mol}})(298 \cancel{\text{ K}})} = 0.0355 \text{ mol}$$

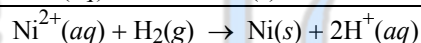
The half-reaction in the problem shows that 2 moles of electrons are required to produce 1 mole of H_2 .

$$0.0355 \cancel{\text{ mol H}_2} \times \frac{2 \text{ mol } e^-}{1 \cancel{\text{ mol H}_2}} = \mathbf{0.0710 \text{ mol } e^-}$$

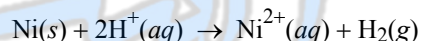
19.61 (a) The half-reactions are:



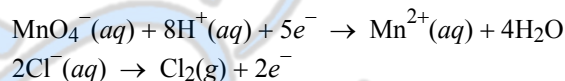
The complete balanced equation is:



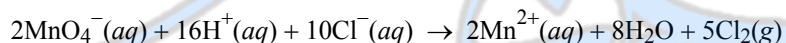
$\text{Ni}(\text{s})$ is below and to the right of $\text{H}^+(\text{aq})$ in Table 19.1 of the text (see the half-reactions at -0.25 and 0.00 V). Therefore, the spontaneous reaction is the reverse of the above reaction, that is:



(b) The half-reactions are:

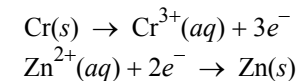


The complete balanced equation is:

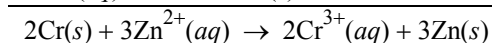


In Table 19.1 of the text, $\text{Cl}^-(\text{aq})$ is below and to the right of $\text{MnO}_4^-(\text{aq})$; therefore the spontaneous reaction is as written.

(c) The half-reactions are:

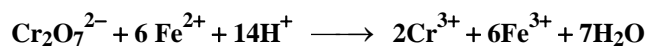


The complete balanced equation is:



In Table 19.1 of the text, $\text{Zn}(\text{s})$ is below and to the right of $\text{Cr}^{3+}(\text{aq})$; therefore the spontaneous reaction is the reverse of the reaction as written.

19.62 The balanced equation is:



The remainder of this problem is a solution stoichiometry problem.

The number of moles of potassium dichromate in 26.0 mL of the solution is:

$$26.0 \text{ mL} \times \frac{0.0250 \text{ mol}}{1000 \text{ mL soln}} = 6.50 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

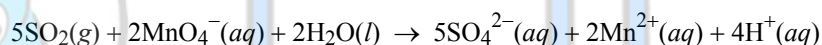
From the balanced equation it can be seen that 1 mole of dichromate is stoichiometrically equivalent to 6 moles of iron(II). The number of moles of iron(II) oxidized is therefore

$$(6.50 \times 10^{-4} \text{ mol Cr}_2\text{O}_7^{2-}) \times \frac{6 \text{ mol Fe}^{2+}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} = 3.90 \times 10^{-3} \text{ mol Fe}^{2+}$$

Finally, the molar concentration of Fe^{2+} is:

$$\frac{3.90 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} = 0.156 \text{ mol/L} = \mathbf{0.156 \text{ M Fe}^{2+}}$$

19.63 The balanced equation is:



The mass of SO_2 in the water sample is given by

$$7.37 \text{ mL} \times \frac{0.00800 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times \frac{5 \text{ mol SO}_2}{2 \text{ mol KMnO}_4} \times \frac{64.07 \text{ g SO}_2}{1 \text{ mol SO}_2} = \mathbf{9.44 \times 10^{-3} \text{ g SO}_2}$$

19.64 The balanced equation is:



First, let's calculate the number of moles of potassium permanganate in 23.30 mL of solution.

$$23.30 \text{ mL} \times \frac{0.0194 \text{ mol}}{1000 \text{ mL soln}} = 4.52 \times 10^{-4} \text{ mol KMnO}_4$$

From the balanced equation it can be seen that 1 mole of permanganate is stoichiometrically equivalent to 5 moles of iron(II). The number of moles of iron(II) oxidized is therefore

$$(4.52 \times 10^{-4} \text{ mol MnO}_4^-) \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} = 2.26 \times 10^{-3} \text{ mol Fe}^{2+}$$

The mass of Fe^{2+} oxidized is:

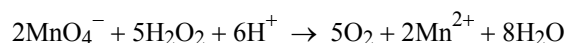
$$\text{mass Fe}^{2+} = (2.26 \times 10^{-3} \text{ mol Fe}^{2+}) \times \frac{55.85 \text{ g Fe}^{2+}}{1 \text{ mol Fe}^{2+}} = 0.126 \text{ g Fe}^{2+}$$

Finally, the mass percent of iron in the ore can be calculated.

$$\text{mass \% Fe} = \frac{\text{mass of iron}}{\text{total mass of sample}} \times 100\%$$

$$\mathbf{\%Fe} = \frac{0.126 \text{ g}}{0.2792 \text{ g}} \times 100\% = \mathbf{45.1\%}$$

- 19.65 (a)** The balanced equation is:



- (b)** The number of moles of potassium permanganate in 36.44 mL of the solution is

$$36.44 \text{ mL} \times \frac{0.01652 \text{ mol}}{1000 \text{ mL soln}} = 6.020 \times 10^{-4} \text{ mol of KMnO}_4$$

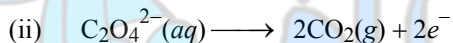
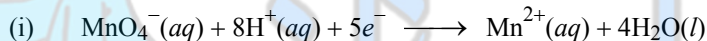
From the balanced equation it can be seen that in this particular reaction 2 moles of permanganate is stoichiometrically equivalent to 5 moles of hydrogen peroxide. The number of moles of H_2O_2 oxidized is therefore

$$(6.020 \times 10^{-4} \text{ mol MnO}_4^-) \times \frac{5 \text{ mol H}_2\text{O}_2}{2 \text{ mol MnO}_4^-} = 1.505 \times 10^{-3} \text{ mol H}_2\text{O}_2$$

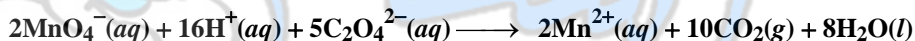
The molar concentration of H_2O_2 is:

$$[\text{H}_2\text{O}_2] = \frac{1.505 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} = 0.0602 \text{ mol/L} = \mathbf{0.0602 \text{ M}}$$

- 19.66 (a)** The half-reactions are:



We combine the half-reactions to cancel electrons, that is, $[2 \times \text{equation (i)}] + [5 \times \text{equation (ii)}]$



- (b)** We can calculate the moles of KMnO_4 from the molarity and volume of solution.

$$24.0 \text{ mL KMnO}_4 \times \frac{0.0100 \text{ mol KMnO}_4}{1000 \text{ mL soln}} = 2.40 \times 10^{-4} \text{ mol KMnO}_4$$

We can calculate the mass of oxalic acid from the stoichiometry of the balanced equation. The mole ratio between oxalate ion and permanganate ion is 5:2.

$$(2.40 \times 10^{-4} \text{ mol KMnO}_4) \times \frac{5 \text{ mol H}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} \times \frac{90.04 \text{ g H}_2\text{C}_2\text{O}_4}{1 \text{ mol H}_2\text{C}_2\text{O}_4} = 0.0540 \text{ g H}_2\text{C}_2\text{O}_4$$

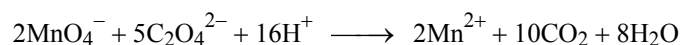
Finally, the percent by mass of oxalic acid in the sample is:

$$\% \text{ oxalic acid} = \frac{0.0540 \text{ g}}{1.00 \text{ g}} \times 100\% = \mathbf{5.40\%}$$

19.67

E	ΔG	Cell Reaction
> 0	< 0	spontaneous
< 0	> 0	nonspontaneous
$= 0$	$= 0$	at equilibrium

19.68 The balanced equation is:



Therefore, 2 mol MnO_4^- reacts with 5 mol $\text{C}_2\text{O}_4^{2-}$

$$\text{Moles of MnO}_4^- \text{ reacted} = 24.2 \text{ mL} \times \frac{9.56 \times 10^{-4} \text{ mol MnO}_4^-}{1000 \text{ mL soln}} = 2.31 \times 10^{-5} \text{ mol MnO}_4^-$$

Recognize that the mole ratio of Ca^{2+} to $\text{C}_2\text{O}_4^{2-}$ is 1:1 in CaC_2O_4 . The mass of Ca^{2+} in 10.0 mL is:

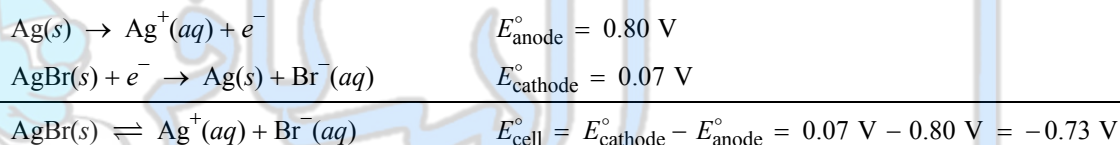
$$(2.31 \times 10^{-5} \text{ mol MnO}_4^-) \times \frac{5 \text{ mol Ca}^{2+}}{2 \text{ mol MnO}_4^-} \times \frac{40.08 \text{ g Ca}^{2+}}{1 \text{ mol Ca}^{2+}} = 2.31 \times 10^{-3} \text{ g Ca}^{2+}$$

Finally, converting to mg/mL, we have:

$$\frac{2.31 \times 10^{-3} \text{ g Ca}^{2+}}{10.0 \text{ mL}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = \mathbf{0.231 \text{ mg Ca}^{2+}/\text{mL blood}}$$

19.69 The solubility equilibrium of AgBr is: $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq)$

By reversing the second given half-reaction and adding it to the first, we obtain:



At equilibrium, we have:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln [\text{Ag}^+][\text{Br}^-]$$

$$0 = -0.73 \text{ V} - \frac{0.0257 \text{ V}}{1} \ln K_{\text{sp}}$$

$$\ln K_{\text{sp}} = -28.4$$

$$K_{\text{sp}} = \mathbf{5 \times 10^{-13}}$$

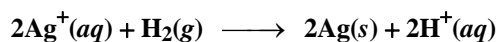
(Note that this value differs from that given in Table 16.2 of the text, since the data quoted here were obtained from a student's lab report.)

19.70 (a) The half-reactions are:



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 \text{ V} - 0.00 \text{ V} = \mathbf{0.80 \text{ V}}$$

(b) The spontaneous cell reaction under standard-state conditions is:



- (c) Using the Nernst equation we can calculate the cell potential under nonstandard-state conditions.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

- (i) The potential is:

$$E = 0.80 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(1.0 \times 10^{-2})^2}{(1.0)^2 (1.0)} = \mathbf{0.92 \text{ V}}$$

- (ii) The potential is:

$$E = 0.80 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(1.0 \times 10^{-5})^2}{(1.0)^2 (1.0)} = \mathbf{1.10 \text{ V}}$$

- (d) From the results in part (c), we deduce that this cell is a pH meter; its potential is a sensitive function of the hydrogen ion concentration. Each 1 unit increase in pH causes a voltage increase of 0.060 V.

- 19.71 (a)** If this were a standard cell, the concentrations would all be 1.00 M, and the voltage would just be the standard emf calculated from Table 19.1 of the text. Since cell emf's depend on the concentrations of the reactants and products, we must use the Nernst equation [Equation (19.8) of the text] to find the emf of a nonstandard cell.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 3.17 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$E = 3.17 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.10}{[0.10]^2}$$

$$E = \mathbf{3.14 \text{ V}}$$

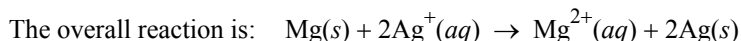
- (b) First we calculate the concentration of silver ion remaining in solution after the deposition of 1.20 g of silver metal

$$\text{Ag originally in solution: } \frac{0.100 \text{ mol Ag}^+}{1 \cancel{\text{L}}} \times 0.346 \cancel{\text{L}} = 3.46 \times 10^{-2} \text{ mol Ag}^+$$

$$\text{Ag deposited: } 1.20 \cancel{\text{g Ag}} \times \frac{1 \text{ mol}}{107.9 \cancel{\text{g}}} = 1.11 \times 10^{-2} \text{ mol Ag}$$

$$\text{Ag remaining in solution: } (3.46 \times 10^{-2} \text{ mol Ag}) - (1.11 \times 10^{-2} \text{ mol Ag}) = 2.35 \times 10^{-2} \text{ mol Ag}$$

$$[\text{Ag}^+] = \frac{2.35 \times 10^{-2} \text{ mol}}{0.346 \text{ L}} = 6.79 \times 10^{-2} \text{ M}$$



We use the balanced equation to find the amount of magnesium metal suffering oxidation and dissolving.

$$(1.11 \times 10^{-2} \cancel{\text{mol Ag}}) \times \frac{1 \text{ mol Mg}}{2 \cancel{\text{mol Ag}}} = 5.55 \times 10^{-3} \text{ mol Mg}$$

The amount of magnesium originally in solution was

$$0.288 \cancel{\text{L}} \times \frac{0.100 \text{ mol}}{1 \cancel{\text{L}}} = 2.88 \times 10^{-2} \text{ mol}$$

The new magnesium ion concentration is:

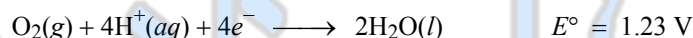
$$\frac{[(5.55 \times 10^{-3}) + (2.88 \times 10^{-2})] \text{ mol}}{0.288 \text{ L}} = 0.119 \text{ M}$$

The new cell emf is:

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 3.17 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.119}{(6.79 \times 10^{-2})^2} = \mathbf{3.13 \text{ V}}$$

- 19.72** The overvoltage of oxygen is not large enough to prevent its formation at the anode. Applying the diagonal rule, we see that water is oxidized before fluoride ion.



The very positive standard reduction potential indicates that F^- has essentially no tendency to undergo oxidation. The oxidation potential of chloride ion is much smaller (-1.36 V), and hence $\text{Cl}_2(\text{g})$ can be prepared by electrolyzing a solution of NaCl .

This fact was one of the major obstacles preventing the discovery of fluorine for many years. HF was usually chosen as the substance for electrolysis, but two problems interfered with the experiment. First, any water in the HF was oxidized before the fluoride ion. Second, pure HF without any water in it is a nonconductor of electricity (HF is a weak acid!). The problem was finally solved by dissolving KF in liquid HF to give a conducting solution.

- 19.73** The cell voltage is given by:

$$E = E^\circ - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Cu}^{2+}]_{\text{dilute}}}{[\text{Cu}^{2+}]_{\text{concentrated}}}$$

$$E = 0 - \frac{0.0257 \text{ V}}{2} \ln \frac{0.080}{1.2} = \mathbf{0.035 \text{ V}}$$

- 19.74** We can calculate the amount of charge that 4.0 g of MnO_2 can produce.

$$4.0 \cancel{\text{g}} \text{ MnO}_2 \times \frac{1 \cancel{\text{mol}}}{86.94 \cancel{\text{g}}} \times \frac{2 \cancel{\text{mol}} \text{ e}^-}{2 \cancel{\text{mol}} \text{ MnO}_2} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol}} \text{ e}^-} = 4.44 \times 10^3 \text{ C}$$

Since a current of one ampere represents a flow of one coulomb per second, we can find the time it takes for this amount of charge to pass.

$$0.0050 \text{ A} = 0.0050 \text{ C/s}$$

$$(4.44 \times 10^3 \cancel{\text{C}}) \times \frac{1 \cancel{\text{s}}}{0.0050 \cancel{\text{C}}} \times \frac{1 \text{ h}}{3600 \cancel{\text{s}}} = \mathbf{2.5 \times 10^2 \text{ h}}$$

- 19.75** The two electrode processes are:
- anode: $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$
- cathode: $4\text{H}_2\text{O}(l) + 4e^- \rightarrow 2\text{H}_2(g) + 4\text{OH}^-(aq)$

The amount of hydrogen formed is twice the amount of oxygen. Notice that the solution at the anode will become acidic and that the solution at the cathode will become basic (test with litmus paper). What are the relative amounts of H^+ and OH^- formed in this process? Would the solutions surrounding the two electrodes neutralize each other exactly? If not, would the resulting solution be acidic or basic?

- 19.76** Since this is a concentration cell, the standard emf is zero. (Why?) Using the Nernst equation, we can write equations to calculate the cell voltage for the two cells.

$$(1) \quad E_{\text{cell}} = -\frac{RT}{nF} \ln Q = -\frac{RT}{2F} \ln \frac{[\text{Hg}_2^{2+}]_{\text{soln A}}}{[\text{Hg}_2^{2+}]_{\text{soln B}}}$$

$$(2) \quad E_{\text{cell}} = -\frac{RT}{nF} \ln Q = -\frac{RT}{1F} \ln \frac{[\text{Hg}^+]_{\text{soln A}}}{[\text{Hg}^+]_{\text{soln B}}}$$

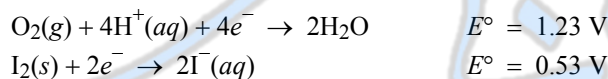
In the first case, two electrons are transferred per mercury ion ($n = 2$), while in the second only one is transferred ($n = 1$). Note that the concentration ratio will be 1:10 in both cases. The voltages calculated at 18°C are:

$$(1) \quad E_{\text{cell}} = \frac{-(8.314 \text{ J/K} \cdot \text{mol})(291 \text{ K})}{2(96500 \text{ J} \cdot \text{V}^{-1} \text{mol}^{-1})} \ln 10^{-1} = 0.0289 \text{ V}$$

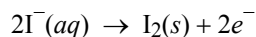
$$(2) \quad E_{\text{cell}} = \frac{-(8.314 \text{ J/K} \cdot \text{mol})(291 \text{ K})}{1(96500 \text{ J} \cdot \text{V}^{-1} \text{mol}^{-1})} \ln 10^{-1} = 0.0577 \text{ V}$$

Since the calculated cell potential for cell (1) agrees with the measured cell emf, we conclude that the mercury(I) ion exists as Hg_2^{2+} in solution.

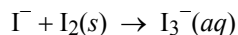
- 19.77** According to the following standard reduction potentials:



we see that it is easier to oxidize the iodide ion than water (because O_2 is a stronger oxidizing agent than I_2). Therefore, the anode reaction is:



The solution surrounding the anode will become brown because of the formation of the triiodide ion:



The cathode reaction will be the same as in the NaCl electrolysis. (Why?) Since OH^- is a product, the solution around the cathode will become basic which will cause the phenolphthalein indicator to turn red.

- 19.78** We begin by treating this like an ordinary stoichiometry problem (see Chapter 3).

Step 1: Calculate the number of moles of Mg and Ag^+ .

The number of moles of magnesium is:

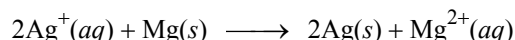
$$1.56 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} = 0.0642 \text{ mol Mg}$$

The number of moles of silver ion in the solution is:

$$\frac{0.100 \text{ mol Ag}^+}{1 \cancel{\text{L}}} \times 0.1000 \cancel{\text{L}} = 0.0100 \text{ mol Ag}^+$$

Step 2: Calculate the mass of Mg remaining by determining how much Mg reacts with Ag^+ .

The balanced equation for the reaction is:



Since you need twice as much Ag^+ compared to Mg for complete reaction, Ag^+ is the limiting reagent. The amount of Mg consumed is:

$$0.0100 \cancel{\text{mol Ag}^+} \times \frac{1 \text{ mol Mg}}{2 \cancel{\text{mol Ag}^+}} = 0.00500 \text{ mol Mg}$$

The amount of magnesium remaining is:

$$(0.0642 - 0.00500) \cancel{\text{mol Mg}} \times \frac{24.31 \text{ g Mg}}{1 \cancel{\text{mol Mg}}} = \mathbf{1.44 \text{ g Mg}}$$

Step 3: Assuming complete reaction, calculate the concentration of Mg^{2+} ions produced.

Since the mole ratio between Mg and Mg^{2+} is 1:1, the mol of Mg^{2+} formed will equal the mol of Mg reacted. The concentration of Mg^{2+} is:

$$[\text{Mg}^{2+}]_0 = \frac{0.00500 \text{ mol}}{0.100 \text{ L}} = 0.0500 \text{ M}$$

Step 4: We can calculate the equilibrium constant for the reaction from the standard cell emf.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.80 \text{ V} - (-2.37 \text{ V}) = 3.17 \text{ V}$$

We can then compute the equilibrium constant.

$$K = e^{\frac{nE_{\text{cell}}^{\circ}}{0.0257}}$$

$$K = e^{\frac{(2)(3.17)}{0.0257}} = 1 \times 10^{107}$$

Step 5: To find equilibrium concentrations of Mg^{2+} and Ag^+ , we have to solve an equilibrium problem.

Let x be the small amount of Mg^{2+} that reacts to achieve equilibrium. The concentration of Ag^+ will be $2x$ at equilibrium. Assume that essentially all Ag^+ has been reduced so that the initial concentration of Ag^+ is zero.

	$2\text{Ag}^+(aq) + \text{Mg}(s) \rightleftharpoons 2\text{Ag}(s) + \text{Mg}^{2+}(aq)$	
Initial (M):	0.0000	0.0500
Change (M):	+2x	-x
Equilibrium (M):	2x	(0.0500 - x)

$$K = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$1 \times 10^{107} = \frac{(0.0500 - x)}{(2x)^2}$$

We can assume $0.0500 - x \approx 0.0500$.

$$1 \times 10^{107} \approx \frac{0.0500}{(2x)^2}$$

$$(2x)^2 = \frac{0.0500}{1 \times 10^{107}} = 0.0500 \times 10^{-107}$$

$$(2x)^2 = 5.00 \times 10^{-109} = 50.0 \times 10^{-110}$$

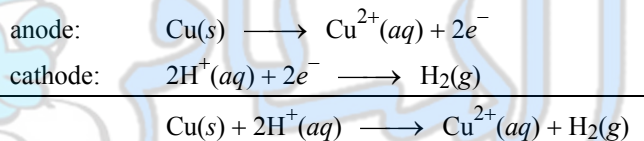
$$2x = 7 \times 10^{-55} M$$

$$[\text{Ag}^+] = 2x = 7 \times 10^{-55} M$$

$$[\text{Mg}^{2+}] = 0.0500 - x = 0.0500 M$$

19.79 Weigh the zinc and copper electrodes before operating the cell and re-weigh afterwards. The anode (Zn) should lose mass and the cathode (Cu) should gain mass.

19.80 (a) Since this is an acidic solution, the gas must be hydrogen gas from the reduction of hydrogen ion. The two electrode reactions and the overall cell reaction are:



Since 0.584 g of copper was consumed, the amount of hydrogen gas produced is:

$$0.584 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Cu}} = 9.20 \times 10^{-3} \text{ mol H}_2$$

At STP, 1 mole of an ideal gas occupies a volume of 22.41 L. Thus, the volume of H_2 at STP is:

$$V_{\text{H}_2} = (9.20 \times 10^{-3} \text{ mol H}_2) \times \frac{22.41 \text{ L}}{1 \text{ mol}} = 0.206 \text{ L}$$

(b) From the current and the time, we can calculate the amount of charge:

$$1.18 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times (1.52 \times 10^3 \text{ s}) = 1.79 \times 10^3 \text{ C}$$

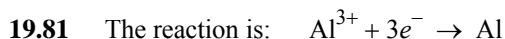
Since we know the charge of an electron, we can compute the number of electrons.

$$(1.79 \times 10^3 \text{ C}) \times \frac{1 e^-}{1.6022 \times 10^{-19} \text{ C}} = 1.12 \times 10^{22} e^-$$

Using the amount of copper consumed in the reaction and the fact that 2 mol of e^- are produced for every 1 mole of copper consumed, we can calculate Avogadro's number.

$$\frac{1.12 \times 10^{22} e^-}{9.20 \times 10^{-3} \text{ mol Cu}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} = 6.09 \times 10^{23} / \text{mol } e^-$$

In practice, Avogadro's number can be determined by electrochemical experiments like this. The charge of the electron can be found independently by Millikan's experiment.



First, let's calculate the number of coulombs of electricity that must pass through the cell to deposit 60.2 g of Al.

$$60.2 \cancel{\text{g Al}} \times \frac{1 \cancel{\text{mol Al}}}{26.98 \cancel{\text{g Al}}} \times \frac{3 \cancel{\text{mol } e^{-}}}{1 \cancel{\text{mol Al}}} \times \frac{96500 \cancel{\text{C}}}{1 \cancel{\text{mol } e^{-}}} = 6.46 \times 10^5 \text{ C}$$

The time (in min) needed to pass this much charge is:

$$t_{\text{min}} = (6.46 \times 10^5 \cancel{\text{C}}) \times \frac{1 \cancel{\text{A} \cdot \text{s}}}{1 \cancel{\text{C}}} \times \frac{1}{0.352 \cancel{\text{A}}} \times \frac{1 \text{ min}}{60 \cancel{\text{s}}} = 3.06 \times 10^4 \text{ min}$$

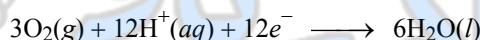
19.82 (a) We can calculate ΔG° from standard free energies of formation.

$$\Delta G^{\circ} = 2\Delta G_f^{\circ}(\text{N}_2) + 6\Delta G_f^{\circ}(\text{H}_2\text{O}) - [4\Delta G_f^{\circ}(\text{NH}_3) + 3\Delta G_f^{\circ}(\text{O}_2)]$$

$$\Delta G = 0 + (6)(-237.2 \text{ kJ/mol}) - [(4)(-16.6 \text{ kJ/mol}) + 0]$$

$$\Delta G = -1356.8 \text{ kJ/mol}$$

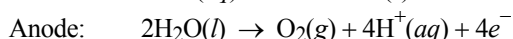
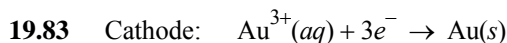
(b) The half-reactions are:



The overall reaction is a 12-electron process. We can calculate the standard cell emf from the standard free energy change, ΔG° .

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = \frac{-\Delta G^{\circ}}{nF} = \frac{-\left(\frac{-1356.8 \cancel{\text{kJ}}}{1 \cancel{\text{mol}}} \times \frac{1000 \cancel{\text{J}}}{1 \cancel{\text{kJ}}}\right)}{(12)(96500 \cancel{\text{J/V} \cdot \text{mol}})} = 1.17 \text{ V}$$



(a) First, from the amount of gold deposited, we can calculate the moles of O_2 produced. Then, using the ideal gas equation, we can calculate the volume of O_2 .

$$9.26 \cancel{\text{g Au}} \times \frac{1 \cancel{\text{mol Au}}}{197.0 \cancel{\text{g Au}}} \times \frac{3 \cancel{\text{mol } e^{-}}}{1 \cancel{\text{mol Au}}} \times \frac{1 \text{ mol O}_2}{4 \cancel{\text{mol } e^{-}}} = 0.03525 \text{ mol O}_2$$

$$V_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{P} = \frac{(0.03525 \cancel{\text{mol}}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\cancel{\text{mol}} \cdot \text{K}} \right) (296 \cancel{\text{K}})}{\left(747 \cancel{\text{mmHg}} \times \frac{1 \text{ atm}}{760 \cancel{\text{mmHg}}} \right)} = 0.872 \text{ L}$$

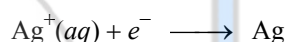
(b) $\text{Current } (I) = \frac{\text{charge } (Q)}{t \text{ (s)}}$

$$t = 2.00 \cancel{\text{h}} \times \frac{60 \cancel{\text{min}}}{1 \cancel{\text{h}}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 7.20 \times 10^3 \text{ s}$$

$$Q = 9.26 \cancel{\text{g Au}} \times \frac{1 \cancel{\text{mol Au}}}{197.0 \cancel{\text{g Au}}} \times \frac{3 \cancel{\text{mol e}^-}}{1 \cancel{\text{mol Au}}} \times \frac{96500 \cancel{\text{C}}}{1 \cancel{\text{mol e}^-}} \times \frac{1 \text{ A} \cdot \text{s}}{1 \cancel{\text{C}}} = 1.36 \times 10^4 \text{ A} \cdot \text{s}$$

$$\text{Current } (I) = \frac{\text{charge } (Q)}{t \text{ (s)}} = \frac{1.36 \times 10^4 \cancel{\text{A} \cdot \text{s}}}{7.20 \times 10^3 \cancel{\text{s}}} = \mathbf{1.89 \text{ A}}$$

19.84 The reduction of Ag^+ to Ag metal is:



We can calculate both the moles of Ag deposited and the moles of Au deposited.

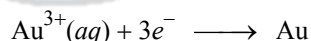
$$? \text{ mol Ag} = 2.64 \cancel{\text{g Ag}} \times \frac{1 \text{ mol Ag}}{107.9 \cancel{\text{g Ag}}} = 2.45 \times 10^{-2} \text{ mol Ag}$$

$$? \text{ mol Au} = 1.61 \cancel{\text{g Au}} \times \frac{1 \text{ mol Au}}{197.0 \cancel{\text{g Au}}} = 8.17 \times 10^{-3} \text{ mol Au}$$

We do not know the oxidation state of Au ions, so we will represent the ions as Au^{n+} . If we divide the mol of Ag by the mol of Au, we can determine the ratio of Ag^+ reduced compared to Au^{n+} reduced.

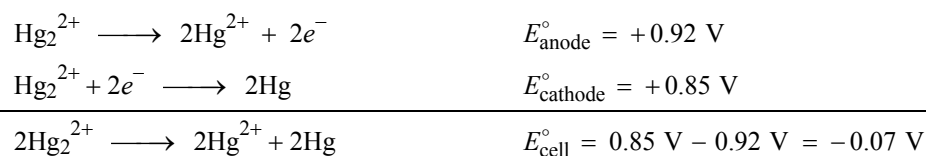
$$\frac{2.45 \times 10^{-2} \text{ mol Ag}}{8.17 \times 10^{-3} \text{ mol Au}} = 3$$

That is, the same number of electrons that reduced the Ag^+ ions to Ag reduced only one-third the number of moles of the Au^{n+} ions to Au. Thus, each Au^{n+} required three electrons per ion for every one electron for Ag^+ . The oxidation state for the gold ion is **+3**; the ion is Au^{3+} .

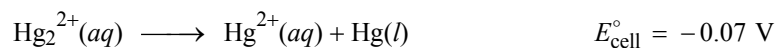


19.85 Heating the garage will melt the snow on the car which is contaminated with salt. The aqueous salt will hasten corrosion.

19.86 We reverse the first half-reaction and add it to the second to come up with the overall balanced equation



Since the standard cell potential is an intensive property,



We calculate ΔG° from E° .

$$\Delta G^\circ = -nFE^\circ = -(1)(96500 \text{ J/V}\cdot\text{mol})(-0.07 \text{ V}) = \mathbf{6.8 \text{ kJ/mol}}$$

The corresponding equilibrium constant is:

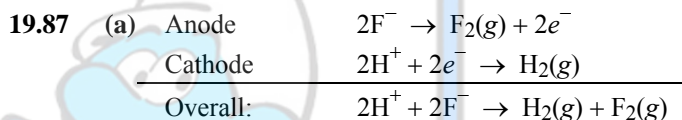
$$K = \frac{[\text{Hg}^{2+}]}{[\text{Hg}_2^{2+}]}$$

We calculate K from ΔG° .

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = \frac{-6.8 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}$$

$$K = \mathbf{0.064}$$



(b) KF increases the electrical conductivity (what type of electrolyte is $\text{HF}(\text{l})$)? The K^+ is not reduced.

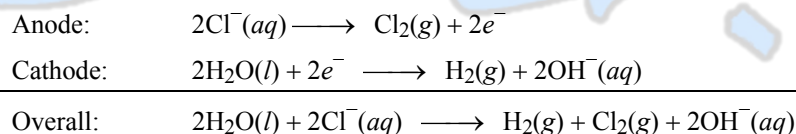
(c) Calculating the moles of F_2

$$502 \text{ A} \times 15 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A}\cdot\text{s}} \times \frac{1 \text{ mol e}^-}{96500 \text{ C}} \times \frac{1 \text{ mol F}_2}{2 \text{ mol e}^-} = 140 \text{ mol F}_2$$

Using the ideal gas law:

$$V = \frac{nRT}{P} = \frac{(140 \text{ mol})(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(297 \text{ K})}{1.2 \text{ atm}} = \mathbf{2.8 \times 10^3 \text{ L}}$$

19.88 The reactions for the electrolysis of $\text{NaCl}(\text{aq})$ are:



From the pH of the solution, we can calculate the OH^- concentration. From the $[\text{OH}^-]$, we can calculate the moles of OH^- produced. Then, from the moles of OH^- we can calculate the average current used.

$$\text{pH} = 12.24$$

$$\text{pOH} = 14.00 - 12.24 = 1.76$$

$$[\text{OH}^-] = 1.74 \times 10^{-2} \text{ M}$$

The moles of OH^- produced are:

$$\frac{1.74 \times 10^{-2} \text{ mol}}{1 \text{ L}} \times 0.300 \text{ L} = 5.22 \times 10^{-3} \text{ mol OH}^-$$

From the balanced equation, it takes 1 mole of e^- to produce 1 mole of OH^- ions.

$$(5.22 \times 10^{-3} \cancel{\text{mol OH}^-}) \times \frac{1 \cancel{\text{mol } e^-}}{1 \cancel{\text{mol OH}^-}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol } e^-}} = 504 \text{ C}$$

Recall that $1 \text{ C} = 1 \text{ A} \cdot \text{s}$

$$504 \cancel{\text{C}} \times \frac{1 \text{ A} \cdot \cancel{\text{s}}}{1 \cancel{\text{C}}} \times \frac{1 \cancel{\text{min}}}{60 \cancel{\text{s}}} \times \frac{1}{6.00 \cancel{\text{min}}} = \mathbf{1.4 \text{ A}}$$

- 19.89** (a) Anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2e^-$
 Cathode: $\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)}$

The overall reaction is: $\text{Cu(s)} \rightarrow \text{Cu(s)}$ Cu is transferred from the anode to cathode.

- (b) Consulting Table 19.1 of the text, the Zn will be oxidized, but Zn^{2+} will not be reduced at the cathode. Ag will not be oxidized at the anode.

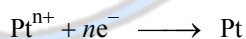
- (c) The moles of Cu: $1000 \cancel{\text{g Cu}} \times \frac{1 \text{ mol Cu}}{63.55 \cancel{\text{g Cu}}} = 15.7 \text{ mol Cu}$

The coulombs required: $15.7 \cancel{\text{mol Cu}} \times \frac{2 \cancel{\text{mol } e^-}}{1 \cancel{\text{mol Cu}}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol } e^-}} = 3.03 \times 10^6 \text{ C}$

The time required: $? \text{ s} = \frac{3.03 \times 10^6 \text{ C}}{18.9 \text{ A}} = 1.60 \times 10^5 \text{ s}$

$$(1.60 \times 10^5 \cancel{\text{s}}) \times \frac{1 \text{ h}}{3600 \cancel{\text{s}}} = \mathbf{44.4 \text{ h}}$$

- 19.90** The reaction is:



Thus, we can calculate the charge of the platinum ions by realizing that n mol of e^- are required per mol of Pt formed.

The moles of Pt formed are:

$$9.09 \cancel{\text{g Pt}} \times \frac{1 \text{ mol Pt}}{195.1 \cancel{\text{g Pt}}} = 0.0466 \text{ mol Pt}$$

Next, calculate the charge passed in C.

$$\text{C} = 2.00 \cancel{\text{h}} \times \frac{3600 \cancel{\text{s}}}{1 \cancel{\text{h}}} \times \frac{2.50 \text{ C}}{1 \cancel{\text{s}}} = 1.80 \times 10^4 \text{ C}$$

Convert to moles of electrons.

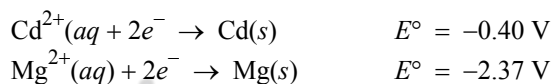
$$? \text{ mol } e^- = (1.80 \times 10^4 \cancel{\text{C}}) \times \frac{1 \text{ mol } e^-}{96500 \cancel{\text{C}}} = 0.187 \text{ mol } e^-$$

We now know the number of moles of electrons ($0.187 \text{ mol } e^-$) needed to produce 0.0466 mol of Pt metal. We can calculate the number of moles of electrons needed to produce 1 mole of Pt metal.

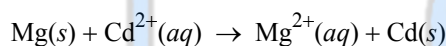
$$\frac{0.187 \text{ mol } e^-}{0.0466 \text{ mol Pt}} = 4.01 \text{ mol } e^-/\text{mol Pt}$$

Since we need 4 moles of electrons to reduce 1 mole of Pt ions, the charge on the Pt ions must be **+4**.

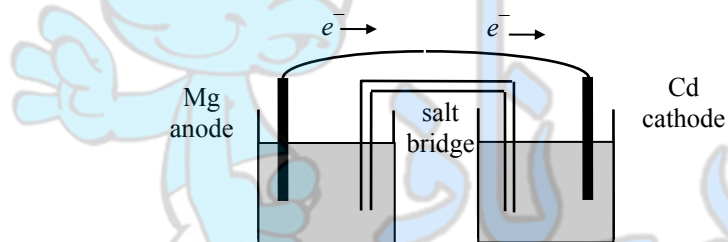
19.91 Using the standard reduction potentials found in Table 19.1



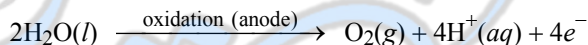
Thus Cd^{2+} will oxidize Mg so that the magnesium half-reaction occurs at the anode.



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.40 \text{ V} - (-2.37 \text{ V}) = \mathbf{1.97 \text{ V}}$$



19.92 The half-reaction for the oxidation of water to oxygen is:



Knowing that one mole of any gas at STP occupies a volume of 22.41 L , we find the number of moles of oxygen.

$$4.26 \cancel{\text{ L}} \text{ O}_2 \times \frac{1 \text{ mol}}{22.41 \cancel{\text{ L}}} = 0.190 \text{ mol O}_2$$

Since four electrons are required to form one oxygen molecule, the number of electrons must be:

$$0.190 \cancel{\text{ mol}} \text{ O}_2 \times \frac{4 \cancel{\text{ mol}} e^-}{1 \cancel{\text{ mol}} \text{ O}_2} \times \frac{6.022 \times 10^{23} e^-}{1 \cancel{\text{ mol}}} = 4.58 \times 10^{23} e^-$$

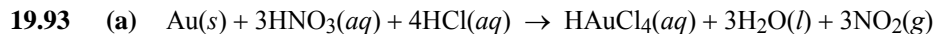
The amount of charge passing through the solution is:

$$6.00 \cancel{\text{ A}} \times \frac{1 \text{ C}}{1 \cancel{\text{ A}} \cdot \cancel{\text{ s}}} \times \frac{3600 \cancel{\text{ s}}}{1 \cancel{\text{ h}}} \times 3.40 \cancel{\text{ h}} = 7.34 \times 10^4 \text{ C}$$

We find the electron charge by dividing the amount of charge by the number of electrons.

$$\frac{7.34 \times 10^4 \text{ C}}{4.58 \times 10^{23} e^-} = \mathbf{1.60 \times 10^{-19} \text{ C/e}^-}$$

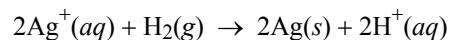
In actual fact, this sort of calculation can be used to find Avogadro's number, not the electron charge. The latter can be measured independently, and one can use this charge together with electrolytic data like the above to calculate the number of objects in one mole. See also Problem 19.80.



(b) To increase the acidity and to form the stable complex ion, AuCl_4^- .

19.94 Cells of higher voltage require very reactive oxidizing and reducing agents, which are difficult to handle. (From Table 19.1 of the text, we see that 5.92 V is the theoretical limit of a cell made up of Li^+/Li and F_2/F^- electrodes under standard-state conditions.) Batteries made up of several cells in series are easier to use.

19.95 The overall cell reaction is:



We write the Nernst equation for this system.

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = 0.080 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

The measured voltage is 0.589 V, and we can find the silver ion concentration as follows:

$$0.589 \text{ V} = 0.80 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{[\text{Ag}^+]^2}$$

$$\ln \frac{1}{[\text{Ag}^+]^2} = 16.42$$

$$\frac{1}{[\text{Ag}^+]^2} = 1.4 \times 10^7$$

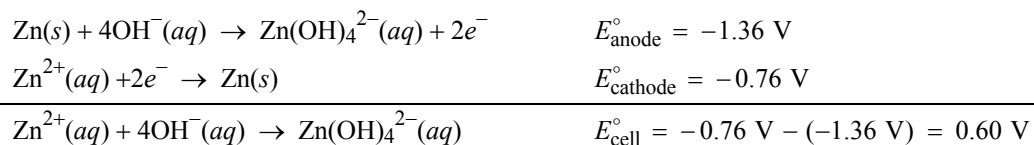
$$[\text{Ag}^+] = 2.7 \times 10^{-4} \text{ M}$$

Knowing the silver ion concentration, we can calculate the oxalate ion concentration and the solubility product constant.

$$[\text{C}_2\text{O}_4^{2-}] = \frac{1}{2}[\text{Ag}^+] = 1.35 \times 10^{-4} \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{2-}] = (2.7 \times 10^{-4})^2(1.35 \times 10^{-4}) = 9.8 \times 10^{-12}$$

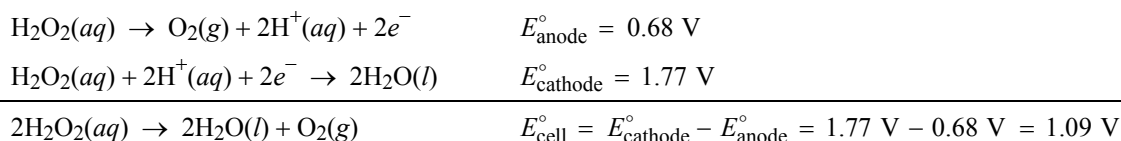
19.96 The half-reactions are:



$$E^\circ_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \ln K_f$$

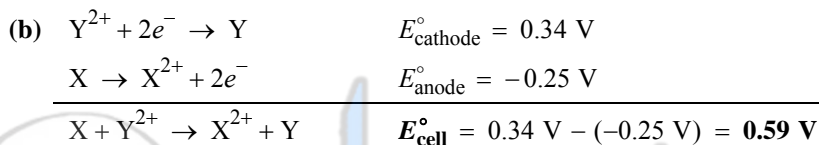
$$K_f = e^{\frac{nE^\circ}{0.0257}} = e^{\frac{(2)(0.60)}{0.0257}} = 2 \times 10^{20}$$

19.97 The half reactions are:

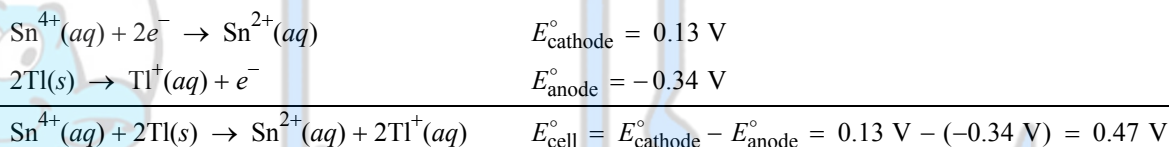


Thus, products are favored at equilibrium. H_2O_2 is not stable (it disproportionates).

19.98 (a) Since electrons flow from X to SHE, E° for X must be negative. Thus E° for Y must be positive.



19.99 (a) The half reactions are:



$$\begin{array}{l}
 \text{(b)} \quad E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K \\
 0.47 \text{ V} = \frac{(8.314)(298)}{(2)(96500)} \ln K \\
 K = \mathbf{8 \times 10^{15}}
 \end{array}$$

$$\text{(c)} \quad E = E^\circ - \frac{0.0257}{2} \ln \frac{(1.0)(10.0)^2}{(1.0)} = (0.47 - 0.0592) \text{ V} = \mathbf{0.41 \text{ V}}$$

19.100 (a) Gold does not tarnish in air because the reduction potential for oxygen is insufficient to result in the oxidation of gold.

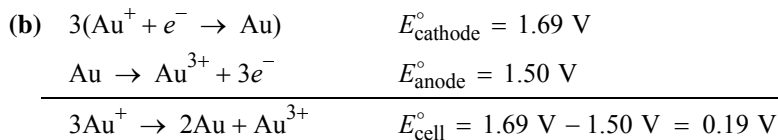


That is, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} < 0$, for either oxidation by O_2 to Au^+ or Au^{3+} .

$$E^\circ_{\text{cell}} = 1.23 \text{ V} - 1.50 \text{ V} < 0$$

or

$$E^\circ_{\text{cell}} = 1.23 \text{ V} - 1.69 \text{ V} < 0$$

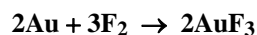


Calculating ΔG ,

$$\Delta G^\circ = -nFE^\circ = -(3)(96,500 \text{ J/V}\cdot\text{mol})(0.19 \text{ V}) = -55.0 \text{ kJ/mol}$$

For spontaneous electrochemical equations, ΔG° must be negative. Thus, **the disproportionation occurs spontaneously.**

(c) Since the most stable oxidation state for gold is Au^{3+} , the predicted reaction is:



19.101 It is mercury ion in solution that is extremely hazardous. Since mercury metal does not react with hydrochloric acid (the acid in gastric juice), it does not dissolve and passes through the human body unchanged. Nitric acid (not part of human gastric juices) dissolves mercury metal (see Problem 19.113); if nitric acid were secreted by the stomach, ingestion of mercury metal would be fatal.

19.102 The balanced equation is: $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

Calculate the amount of iron(II) in the original solution using the mole ratio from the balanced equation.

$$23.0 \text{ mL} \times \frac{0.0200 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol KMnO}_4} = 0.00230 \text{ mol Fe}^{2+}$$

The concentration of iron(II) must be:

$$[\text{Fe}^{2+}] = \frac{0.00230 \text{ mol}}{0.0250 \text{ L}} = \mathbf{0.0920 \text{ M}}$$

The total iron concentration can be found by simple proportion because the same sample volume (25.0 mL) and the same KMnO_4 solution were used.

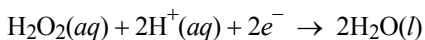
$$[\text{Fe}]_{\text{total}} = \frac{40.0 \text{ mL KMnO}_4}{23.0 \text{ mL KMnO}_4} \times 0.0920 \text{ M} = 0.160 \text{ M}$$

$$[\text{Fe}^{3+}] = [\text{Fe}]_{\text{total}} - [\text{Fe}^{2+}] = \mathbf{0.0680 \text{ M}}$$

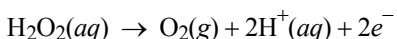
Why are the two titrations with permanganate necessary in this problem?

19.103 Viewed externally, the anode looks negative because of the flow of the electrons (from $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$) toward the cathode. In solution, anions move toward the anode because they are attracted by the Zn^{2+} ions surrounding the anode.

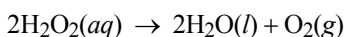
19.104 From Table 19.1 of the text.



$$E^\circ_{\text{cathode}} = 1.77 \text{ V}$$



$$E^\circ_{\text{anode}} = 0.68 \text{ V}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.77 \text{ V} - (0.68 \text{ V}) = \mathbf{1.09 \text{ V}}$$

Because E° is positive, the decomposition is **spontaneous**.

19.105 (a) The overall reaction is: $\text{Pb} + \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

$$\text{Initial mass of H}_2\text{SO}_4: 724 \text{ mL} \times \frac{1.29 \text{ g}}{1 \text{ mL}} \times 0.380 = 355 \text{ g}$$

$$\text{Final mass of H}_2\text{SO}_4: 724 \text{ mL} \times \frac{1.19 \text{ g}}{1 \text{ mL}} \times 0.260 = 224 \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ reacted} = 355 \text{ g} - 224 \text{ g} = 131 \text{ g}$$

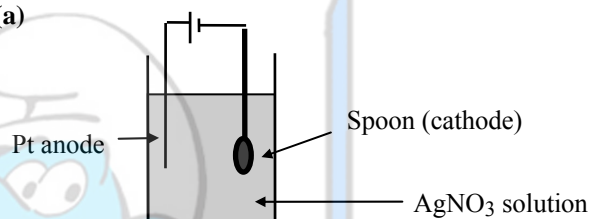
$$\text{Moles of H}_2\text{SO}_4 \text{ reacted} = 131 \cancel{\text{g}} \times \frac{1 \text{ mol}}{98.09 \cancel{\text{g}}} = 1.34 \text{ mol}$$

$$Q = 1.34 \cancel{\text{mol H}_2\text{SO}_4} \times \frac{2 \cancel{\text{mol e}^-}}{2 \cancel{\text{mol H}_2\text{SO}_4}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol e}^-}} = 1.29 \times 10^5 \text{ C}$$

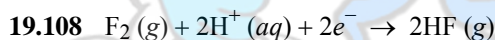
$$(b) \quad t = \frac{Q}{I} = \frac{1.29 \times 10^5 \text{ C}}{22.4 \text{ A}} = 5.76 \times 10^3 \text{ s} = 1.60 \text{ h}$$

19.106 (a) unchanged (b) unchanged (c) squared (d) doubled (e) doubled

19.107 (a)



$$(b) \quad t = \frac{Q}{I} = \frac{\left(0.884 \cancel{\text{g}} \times \frac{1 \text{ mol}}{107.9 \cancel{\text{g}}}\right) \left(\frac{96500 \text{ C}}{1 \cancel{\text{mol}}}\right)}{18.5 \times 10^{-3} \text{ A}} = 4.27 \times 10^4 \text{ s} = 11.9 \text{ h}$$



$$E = E^\circ - \frac{RT}{2F} \ln \frac{P_{\text{HF}}^2}{P_{\text{F}_2} [\text{H}^+]^2}$$

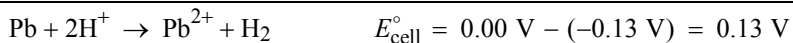
With increasing $[\text{H}^+]$, E will be larger. F_2 will become a **stronger oxidizing agent**.

19.109 **Advantages:**

- (a) No start-up problems, (b) much quieter, (c) no pollution (smog),
- (d) more energy efficient in the sense that when the car is not moving (for example at a traffic light), no electricity is consumed.

Disadvantages:

- (a) Driving range is more limited than automobiles,
- (b) total mass of batteries is appreciable,
- (c) production of electricity needed to charge the batteries leads to pollution.



$$\text{pH} = 1.60$$

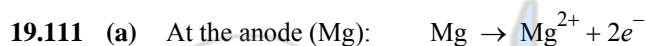
$$[\text{H}^+] = 10^{-1.60} = 0.025 \text{ M}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Pb}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$0 = 0.13 - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.035)P_{\text{H}_2}}{0.025^2}$$

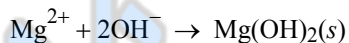
$$\frac{0.26}{0.0257} = \ln \frac{(0.035)P_{\text{H}_2}}{0.025^2}$$

$$P_{\text{H}_2} = 4.4 \times 10^2 \text{ atm}$$

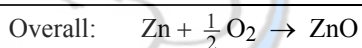
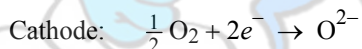
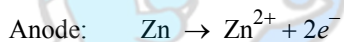


(b) The solution does not turn blue.

(c) After all the HCl has been neutralized, the white precipitate is:



19.112 (a) The half-reactions are:



To calculate the standard emf, we first need to calculate ΔG° for the reaction. From Appendix 3 of the text we write:

$$\Delta G^\circ = \Delta G_f^\circ(\text{ZnO}) - [\Delta G_f^\circ(\text{Zn}) + \frac{1}{2} \Delta G_f^\circ(\text{O}_2)]$$

$$\Delta G^\circ = -318.2 \text{ kJ/mol} - [0 + 0]$$

$$\Delta G^\circ = -318.2 \text{ kJ/mol}$$

$$\Delta G^\circ = -nFE^\circ$$

$$-318.2 \times 10^3 \text{ J/mol} = -(2)(96,500 \text{ J/V}\cdot\text{mol})E^\circ$$

$$E^\circ = 1.65 \text{ V}$$

(b) We use the following equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = 1.65 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{P_{\text{O}_2}}$$

$$E = 1.65 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{0.21}$$

$$E = 1.65 \text{ V} - 0.020 \text{ V}$$

$$E = 1.63 \text{ V}$$

- (c) Since the free energy change represents the maximum work that can be extracted from the overall reaction, the maximum amount of energy that can be obtained from this reaction is the free energy change. To calculate the energy density, we multiply the free energy change by the number of moles of Zn present in 1 kg of Zn.

$$\text{energy density} = \frac{318.2 \text{ kJ}}{1 \text{ mol Zn}} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{1000 \text{ g Zn}}{1 \text{ kg Zn}} = 4.87 \times 10^3 \text{ kJ/kg Zn}$$

- (d) One ampere is 1 C/s. The charge drawn every second is given by nF .

$$\text{charge} = nF$$

$$2.1 \times 10^5 \text{ C} = n(96,500 \text{ C/mol } e^-)$$

$$n = 2.2 \text{ mol } e^-$$

From the overall balanced reaction, we see that 4 moles of electrons will reduce 1 mole of O_2 ; therefore, the number of moles of O_2 reduced by 2.2 moles of electrons is:

$$\text{mol O}_2 = 2.2 \text{ mol } e^- \times \frac{1 \text{ mol O}_2}{4 \text{ mol } e^-} = 0.55 \text{ mol O}_2$$

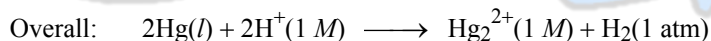
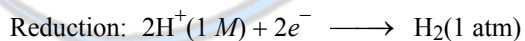
The volume of oxygen at 1.0 atm partial pressure can be obtained by using the ideal gas equation.

$$V_{\text{O}_2} = \frac{nRT}{P} = \frac{(0.55 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})}{(1.0 \text{ atm})} = 13 \text{ L}$$

Since air is 21 percent oxygen by volume, the volume of air required every second is:

$$V_{\text{air}} = 13 \text{ L O}_2 \times \frac{100\% \text{ air}}{21\% \text{ O}_2} = 62 \text{ L of air}$$

- 19.113 (a)** HCl: First, we write the half-reactions.



The standard emf, E° , is given by

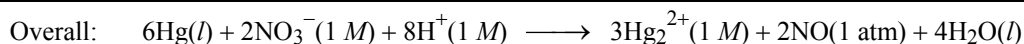
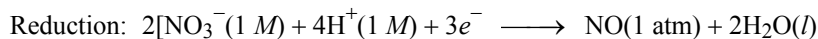
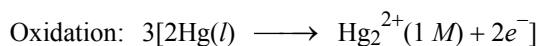
$$E^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$E^\circ = 0 - 0.85 \text{ V}$$

$$E^\circ = -0.85 \text{ V}$$

(We omit the subscript “cell” because this reaction is not carried out in an electrochemical cell.) Since E° is negative, we conclude that mercury is not oxidized by hydrochloric acid under standard-state conditions.

- (b) HNO_3 : The reactions are:



Thus,

$$E^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E^{\circ} = 0.96\text{V} - 0.85\text{V}$$

$$E^{\circ} = \mathbf{0.11\text{V}}$$

Since E° is positive, products are favored at equilibrium under standard-state conditions.

The test tube on the left contains HNO_3 and Hg. HNO_3 can oxidize Hg and the product NO reacts with oxygen to form the brown gas NO_2 .

19.114 We can calculate $\Delta G_{\text{rxn}}^{\circ}$ using the following equation.

$$\Delta G_{\text{rxn}}^{\circ} = \Sigma n\Delta G_{\text{f}}^{\circ}(\text{products}) - \Sigma m\Delta G_{\text{f}}^{\circ}(\text{reactants})$$

$$\Delta G_{\text{rxn}}^{\circ} = 0 + 0 - [(1)(-293.8 \text{ kJ/mol}) + 0] = 293.8 \text{ kJ/mol}$$

Next, we can calculate E° using the equation

$$\Delta G^{\circ} = -nFE^{\circ}$$

We use a more accurate value for Faraday's constant.

$$293.8 \times 10^3 \text{ J/mol} = -(1)(96485.3 \text{ J/V}\cdot\text{mol})E^{\circ}$$

$$E^{\circ} = \mathbf{-3.05 \text{ V}}$$

19.115 (a) First, we calculate the coulombs of electricity that pass through the cell.

$$0.22 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A}\cdot\text{s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times 31.6 \text{ h} = 2.5 \times 10^4 \text{ C}$$

We see that for every mole of Cu formed at the cathode, 2 moles of electrons are needed. The grams of Cu produced at the cathode are:

$$? \text{ g Cu} = (2.5 \times 10^4 \text{ C}) \times \frac{1 \text{ mol } e^{-}}{96,500 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^{-}} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = \mathbf{8.2 \text{ g Cu}}$$

(b) 8.2 g of Cu is 0.13 mole of Cu. The moles of Cu^{2+} in the original solution are:

$$0.218 \text{ L} \times \frac{1 \text{ mol Cu}^{2+}}{1 \text{ L soln}} = 0.218 \text{ mol Cu}^{2+}$$

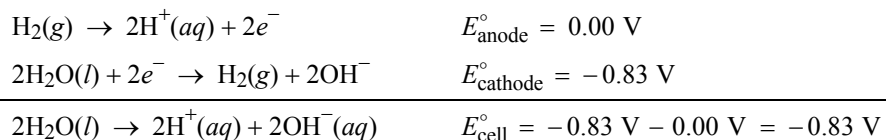
The mole ratio between Cu^{2+} and Cu is 1:1, so the moles of Cu^{2+} remaining in solution are:

$$\text{moles Cu}^{2+} \text{ remaining} = 0.218 \text{ mol} - 0.13 \text{ mol} = 0.088 \text{ mol Cu}^{2+}$$

The concentration of Cu^{2+} remaining is:

$$[\text{Cu}^{2+}] = \frac{0.088 \text{ mol Cu}^{2+}}{0.218 \text{ L soln}} = \mathbf{0.40 \text{ M}}$$

19.116 First, we need to calculate E°_{cell} , then we can calculate K from the cell potential.



We want to calculate K for the reaction: $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$. The cell potential for this reaction will be the same as the above reaction, but the moles of electrons transferred, n , will equal one.

$$E^\circ_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \ln K_w$$

$$\ln K_w = \frac{nE^\circ_{\text{cell}}}{0.0257 \text{ V}}$$

$$K_w = e^{\frac{nE^\circ}{0.0257}}$$

$$K_w = e^{\frac{(1)(-0.83)}{0.0257}} = e^{-32} = 1 \times 10^{-14}$$

19.117 H₂/O₂ Fuel Cell

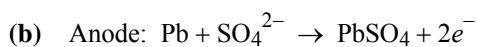
- Pros:
- (1) Almost inexhaustible supplies of H₂ (from H₂O) and O₂ (from air).
 - (2) There is no pollution because the product generated is H₂O.
 - (3) The generation of electricity is not restricted by second law efficiency as in combustion reactions.
 - (4) There is no thermal pollution.

- Cons:
- (1) A large input of energy is required to generate H₂.
 - (2) Storage of hydrogen gas is problematic.
 - (3) Electrocatalysts are expensive.
 - (4) The impact of appreciable leakage of H₂ into the atmosphere is uncertain. How will H₂ affect climate and O₃ in the stratosphere?

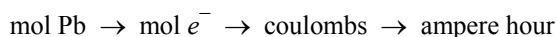
Coal-fired Power Station

- Pros:
- (1) Large deposits of coal.
 - (2) Technology available at acceptable cost. Use of coal and oil are interchangeable.
- Cons:
- (1) The emission pollution to the environment (CO₂, NO_x, SO₂, Hg, etc.) leads to global warming, acid rain, and smog.
 - (2) Combustion reactions cause thermal pollution.
 - (3) The generation of electricity by combustion reactions is restricted by second law efficiency.
 - (4) Mining coal is unsafe and damaging to the environment.

19.118 (a) $1\text{A}\cdot\text{h} = 1\text{A} \times 3600\text{s} = 3600 \text{ C}$



Two moles of electrons are produced by 1 mole of Pb. Recall that the charge of 1 mol e^- is 96,500 C. We can set up the following conversions to calculate the capacity of the battery.



$$406 \cancel{\text{g}}/\text{Pb} \times \frac{1 \cancel{\text{mol}} \text{ Pb}}{207.2 \cancel{\text{g}}/\text{Pb}} \times \frac{2 \cancel{\text{mol}} e^-}{1 \cancel{\text{mol}} \text{ Pb}} \times \frac{96500 \text{ C}}{1 \cancel{\text{mol}} e^-} = (3.74 \times 10^5 \text{ C}) \times \frac{1 \text{ h}}{3600 \text{ s}} = \mathbf{104 \text{ A} \cdot \text{h}}$$

This ampere-hour cannot be fully realized because the concentration of H_2SO_4 keeps decreasing.

(c) $E^\circ_{\text{cell}} = 1.70 \text{ V} - (-0.31 \text{ V}) = \mathbf{2.01 \text{ V}}$ (From Table 19.1 of the text)

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G^\circ = -(2)(96500 \text{ J/V} \cdot \text{mol})(2.01 \cancel{\text{V}}) = \mathbf{-3.88 \times 10^5 \text{ J/mol}}$$

Spontaneous as expected.

19.119 First, we start with Equation (19.3) of the text.

$$\Delta G^\circ = -nFE^\circ$$

Then, we substitute into Equation (18.10) of the text.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-nFE^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$E^\circ = \frac{-\Delta H^\circ + T\Delta S^\circ}{nF}$$

The reaction is: $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$

We use data in Appendix 3 of the text to calculate ΔH° and ΔS° .

$$\Delta H^\circ = \Delta H_f^\circ[\text{Cu}(s)] + \Delta H_f^\circ[\text{Zn}^{2+}(aq)] - \{\Delta H_f^\circ[\text{Zn}(s)] + \Delta H_f^\circ[\text{Cu}^{2+}(aq)]\}$$

$$\Delta H^\circ = 0 + (-152.4 \text{ kJ/mol}) - (0 + 64.39 \text{ kJ/mol}) = -216.8 \text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ[\text{Cu}(s)] + S^\circ[\text{Zn}^{2+}(aq)] - \{S^\circ[\text{Zn}(s)] + S^\circ[\text{Cu}^{2+}(aq)]\}$$

$$\Delta S^\circ = 33.3 \text{ J/K} \cdot \text{mol} + (-106.48 \text{ J/K} \cdot \text{mol}) - (41.6 \text{ J/K} \cdot \text{mol} - 99.6 \text{ J/K} \cdot \text{mol}) = -15.2 \text{ J/K} \cdot \text{mol}$$

At 298 K (25°C),

$$E^\circ = \frac{-\left(\frac{-216.8 \cancel{\text{kJ}}}{1 \cancel{\text{mol}}} \times \frac{1000 \cancel{\text{J}}}{1 \cancel{\text{kJ}}}\right) + (298 \cancel{\text{K}})\left(-15.2 \frac{\cancel{\text{J}}}{\text{K} \cdot \cancel{\text{mol}}}\right)}{(2)(96500 \cancel{\text{J/V} \cdot \text{mol}})} = \mathbf{1.100 \text{ V}} \text{ (carried to 3 decimal places)}$$

At 353 K (80°C),

$$E^\circ = \frac{-\left(\frac{-216.8 \text{ kJ}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right) + (353 \text{ K})\left(-15.2 \frac{\text{J}}{\text{K} \cdot \text{mol}}\right)}{(2)(96500 \text{ J/V} \cdot \text{mol})} = \mathbf{1.095 \text{ V}}$$

This calculation shows that E° is practically independent of temperature. In practice, E° does decrease more noticeably with temperature. The reason is that we have assumed ΔH° and ΔS° to be independent of temperature, which is technically not correct.

19.120 The surface area of an open cylinder is $2\pi rh$. The surface area of the culvert is

$$2\pi(0.900\text{ m})(40.0\text{ m}) \times 2 \text{ (for both sides of the iron sheet)} = 452\text{ m}^2$$

Converting to units of cm^2 ,

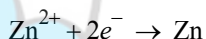
$$452\text{ m}^2 \times \left(\frac{100\text{ cm}}{1\text{ m}}\right)^2 = 4.52 \times 10^6\text{ cm}^2$$

The volume of the Zn layer is

$$0.200\text{ mm} \times \frac{1\text{ cm}}{10\text{ mm}} \times (4.52 \times 10^6\text{ cm}^2) = 9.04 \times 10^4\text{ cm}^3$$

The mass of Zn needed is

$$(9.04 \times 10^4\text{ cm}^3) \times \frac{7.14\text{ g}}{1\text{ cm}^3} = 6.45 \times 10^5\text{ g Zn}$$



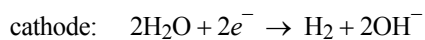
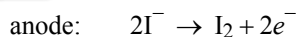
$$Q = (6.45 \times 10^5\text{ g Zn}) \times \frac{1\text{ mol Zn}}{65.39\text{ g Zn}} \times \frac{2\text{ mol } e^-}{1\text{ mol Zn}} \times \frac{96500\text{ C}}{1\text{ mol } e^-} = 1.90 \times 10^9\text{ C}$$

$$1\text{ J} = 1\text{ C} \times 1\text{ V}$$

$$\text{Total energy} = \frac{(1.90 \times 10^9\text{ C})(3.26\text{ V})}{0.95 \leftarrow \text{(efficiency)}} = 6.52 \times 10^9\text{ J}$$

$$\text{Cost} = (6.52 \times 10^9\text{ J}) \times \frac{1\text{ kW}}{1000\text{ J/s}} \times \frac{1\text{ h}}{3600\text{ s}} \times \frac{\$0.12}{1\text{ kWh}} = \text{\$217}$$

19.121 (a) The half-cell reactions are:



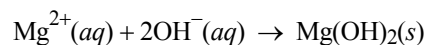
$$n_{\text{H}_2} = \frac{PV}{RT} = \frac{\left(779\text{ mmHg} \times \frac{1\text{ atm}}{760\text{ mmHg}}\right)(1.22\text{ L})}{\left(0.0821\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(299\text{ K})} = 0.05094\text{ mol}$$

$$Q = 0.05094\text{ mol} \times \frac{2\text{ mol } e^-}{1\text{ mol H}_2} \times \frac{96500\text{ C}}{1\text{ mol } e^-} = 9.83 \times 10^3\text{ C}$$

(b) $Q = It$

$$t = \frac{Q}{I} = \frac{9.83 \times 10^3\text{ C}}{7.55\text{ A}} \times \frac{1\text{ A}\cdot\text{s}}{1\text{ C}} = 1302\text{ s} = \text{21.7 min}$$

- (c) The white precipitate is **Mg(OH)₂**.



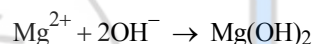
From Table 16.2 of the text, we see that Mg(OH)₂ is insoluble ($K_{\text{sp}} = 1.2 \times 10^{-11}$). From the cathode half-cell reaction,

$$n_{\text{OH}^{-}} = 2n_{\text{H}_2}$$

$$[\text{OH}^{-}] = \frac{(2)(0.05094 \text{ mol})}{0.900 \text{ L}} = 0.113 \text{ M}$$

$$[\text{Mg}^{2+}] = 0.200 \text{ M}$$

We assume that all of the OH[−] ions are converted to Mg(OH)₂ (hydroxide ion is the limiting reagent).



Because the mole ratio between OH[−] and Mg(OH)₂ is 2:1, the moles of Mg(OH)₂ produced is 0.05094 mole.

The mass of Mg(OH)₂ produced is:

$$0.05094 \text{ mol Mg(OH)}_2 \times \frac{58.33 \text{ g Mg(OH)}_2}{1 \text{ mol Mg(OH)}_2} = \mathbf{2.97 \text{ g Mg(OH)}_2}$$

- 19.122** It might appear that because the sum of the first two half-reactions gives Equation (3), E_3° is given by $E_1^{\circ} + E_2^{\circ} = 0.33 \text{ V}$. This is not the case, however, because emf is not an extensive property. We cannot set $E_3^{\circ} = E_1^{\circ} + E_2^{\circ}$. On the other hand, the Gibbs energy is an extensive property, so we can add the separate Gibbs energy changes to obtain the overall Gibbs energy change.

$$\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

Substituting the relationship $\Delta G^{\circ} = -nFE^{\circ}$, we obtain

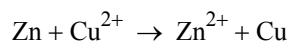
$$n_3FE_3^{\circ} = n_1FE_1^{\circ} + n_2FE_2^{\circ}$$

$$E_3^{\circ} = \frac{n_1E_1^{\circ} + n_2E_2^{\circ}}{n_3}$$

$n_1 = 2$, $n_2 = 1$, and $n_3 = 3$.

$$E_3^{\circ} = \frac{(2)(-0.44 \text{ V}) + (1)(0.77 \text{ V})}{3} = \mathbf{-0.037 \text{ V}}$$

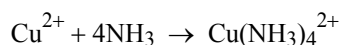
- 19.123 (a)** The reaction is:



Using the Nernst equation:

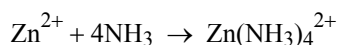
$$E = E^{\circ} - \frac{0.0257}{2} \ln \frac{0.20}{0.20} = \mathbf{1.10 \text{ V}}$$

(i) If NH_3 is added to the CuSO_4 solution:



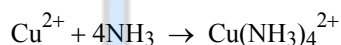
The concentration of copper ions $[\text{Cu}^{2+}]$ decreases, so the \ln term becomes greater than 1 and E decreases.

(ii) If NH_3 is added to the ZnSO_4 solution:



The concentration of zinc ions $[\text{Zn}^{2+}]$ decreases, so the \ln term becomes less than 1 and E increases.

(b) After addition of 25.0 mL of 3.0 M NH_3 ,



Assume that all Cu^{2+} becomes $\text{Cu}(\text{NH}_3)_4^{2+}$:

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 0.10 \text{ M}$$

$$[\text{NH}_3] = \frac{3.0 \text{ M}}{2} - 0.40 \text{ M} = 1.10 \text{ M}$$

$$E = E^\circ - \frac{0.0257}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$0.68 \text{ V} = 1.10 \text{ V} - \frac{0.0257}{2} \ln \frac{0.20}{[\text{Cu}^{2+}]}$$

$$[\text{Cu}^{2+}] = 1.3 \times 10^{-15} \text{ M}$$

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{0.10}{(1.3 \times 10^{-15})(1.1)^4} = 5.3 \times 10^{13}$$

Note: this value differs somewhat from that listed in Table 16.4 of the text.

19.124 First, calculate the standard emf of the cell from the standard reduction potentials in Table 19.1 of the text. Then, calculate the equilibrium constant from the standard emf using Equation (19.5) of the text.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

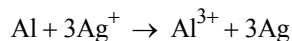
$$\ln K = \frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}$$

$$K = e^{\frac{nE_{\text{cell}}^\circ}{0.0257 \text{ V}}} = e^{\frac{(2)(1.10 \text{ V})}{0.0257 \text{ V}}}$$

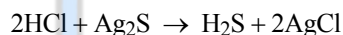
$$K = 2 \times 10^{37}$$

The very large equilibrium constant means that the oxidation of Zn by Cu^{2+} is virtually complete.

- 19.125 (a)** From Table 19.1 of the text, we see that Al can reduce Ag^+ (applying the diagonal rule); $\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$; $\text{Ag}^+ + e^- \rightarrow \text{Ag}$



- (b)** A NaHCO_3 solution is basic. The surplus OH^- ions will convert Al^{3+} ions to $\text{Al}(\text{OH})_3$, which precipitates out of solution. Otherwise, the Al^{3+} ions formed can form Al_2O_3 , which increases the tenacious oxide layer over the aluminum foil, thus preventing further electrochemical reaction. (The Al_2O_3 layer is responsible for preventing aluminum beverage cans from corroding.)
- (c)** Heating the solution speeds up the process and drives air (oxygen) out of solution which minimizes Al_2O_3 formation.
- (d)** HCl reacts with Ag_2S .



The H_2S gas has an unpleasant odor (and in fact is poisonous). Also, this method removes Ag from the spoon as AgCl . The method described in part (a) does not.

- 19.126** The standard free-energy change, ΔG° , can be calculated from the cell potential.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.23 \text{ V} - 0.42 \text{ V} = 0.81 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -(4)(96,500 \text{ J/V}\cdot\text{mol})(0.81 \text{ V})$$

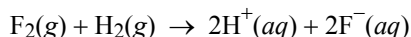
$$\Delta G^\circ = -3.13 \times 10^5 \text{ J/mol} = -313 \text{ kJ/mol}$$

This is the free-energy change for the oxidation of 2 moles of nitrite (NO_2^-)

Looking at Section 18.7 of the text, we find that it takes 31 kJ of free energy to synthesize 1 mole of ATP from ADP. The yield of ATP synthesis per mole of nitrite oxidized is:

$$156.5 \text{ kJ} \times \frac{1 \text{ mol ATP}}{31 \text{ kJ}} = 5.0 \text{ mol ATP}$$

- 19.127** We follow the procedure shown in Problem 19.114.



We can calculate $\Delta G^\circ_{\text{rxn}}$ using the following equation and data in Appendix 3 of the text.

$$\Delta G^\circ_{\text{rxn}} = \sum n\Delta G^\circ_f(\text{products}) - \sum m\Delta G^\circ_f(\text{reactants})$$

$$\Delta G^\circ_{\text{rxn}} = [0 + (2)(-276.48 \text{ kJ/mol})] - [0 + 0] = -552.96 \text{ kJ/mol}$$

Next, we can calculate E° using the equation

$$\Delta G^\circ = -nFE^\circ$$

We use a more accurate value for Faraday's constant.

$$-552.96 \times 10^3 \text{ J/mol} = -(2)(96485.3 \text{ J/V}\cdot\text{mol})E^\circ$$

$$E^\circ = 2.87 \text{ V}$$

- 19.128** The temperature of one compartment of the concentration cell could be changed. E° is a function of T . When one electrode is heated, the two E° values will not cancel. Consequently, there will be a small emf generated.

Answers to Review of Concepts

Section 19.3 (p. 849)

Cu, Ag.

Section 19.4 (p. 852)

It is much easier to determine the equilibrium constant electrochemically. All one has to do is measure the emf of the cell (E°) and then use Equation (19.3) and (18.14) of the text to calculate K . On the other hand, use of Equation (18.14) of the text alone requires measurements of both ΔH° and ΔS° to first determine ΔG° and then K . This is a much longer and tedious process. Keep in mind, however, that most reactions do not lend themselves to electrochemical measurements.

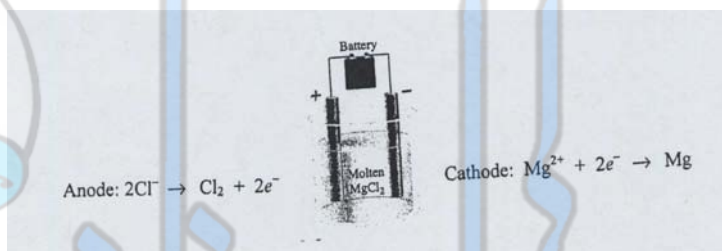
Section 19.5 (p. 855)

2.13 V. (a) 2.14 V. (b) 2.11 V.

Section 19.8 (p. 867)

1.23 V

Section 19.8 (p. 869)



In a galvanic cell, the anode is labeled negative because it supplies electrons to the external circuit. In an electrolytic cell, the anode is labeled positive because electrons are withdrawn from it by the battery. The sign of each electrode in the electrolytic cell is the same as the sign of the battery electrode to which it is attached.