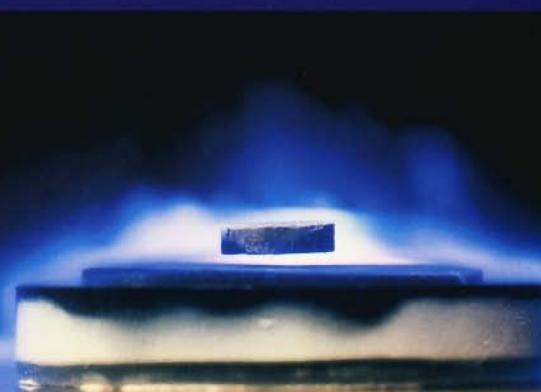
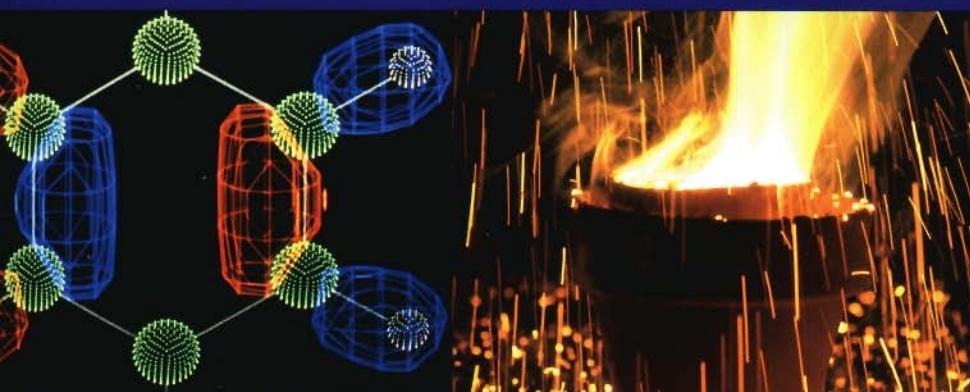


# • SELECTED SOLUTIONS MANUAL

Lucio Gelmini • Robert W. Hilts • Robert K. Wismer

# • GENERAL CHEMISTRY

Principles and Modern Applications



Eighth Edition

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Upper Saddle River, NJ 07458

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Any errors or misinterpretations contained in this manual are solely our responsibility. We have done our best to make this manual error free, but because of its great size and complexity, some errors undoubtedly have gone undetected. Any errors that come to light will, of course, be dealt with during the next round of corrections.

Finally, we would like to extend a very special thanks to the administration of Grant MacEwan College for allowing us to use the college's in-house computing and printing facilities to prepare this manual.

Robert W. Hilts  
Lucio Gelmini

July 2001  
Edmonton, Alberta, Canada

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## **DEDICATION**

This manual is dedicated to the memory of Dr. Grant MacEwan (1902-2000), our college namesake, whose outstanding lifetime achievements and selfless service to the people of Western Canada, continue to be an inspiration to young and old alike.



## FOREWORD

One of the primary benefits that you will obtain from your study of chemistry is the ability to explain a large number of phenomena by learning and applying a relatively small number of fundamental principles. It is very difficult, however, to learn these principles simply by reading about chemistry. To gain a truly deep understanding, you must practice using them, both in the laboratory and by solving problems.

The purpose of this manual is to help you master many of the fundamental chemical principles through the process of problem solving. In this manual you will find solutions to all of the Practice Examples, most of the Review Questions, half of the Exercises questions and selected Feature Problems that are in the companion textbook, General Chemistry: Principles and Modern Applications, by Ralph H. Petrucci, William S. Harwood and F. Geoffrey Herring, 8<sup>th</sup> Edition, Prentice-Hall, Upper Saddle River, NJ. Please note that the answers to all of the Integrative and Advanced Exercises can be found in the Instructors Resource Manual. Below we have listed a few suggestions to help you gain maximum benefit from the manual.

You should attempt to solve a problem only after you have studied the appropriate sections in the textbook. If you try to circumvent this process by attempting to solve the problems without looking in the text, you will find yourself constantly flipping through the pages in the chapter to find the concepts you need to approach the problem. This search will, of course, be quite inefficient because you will not be familiar with the material in the chapter. Worse yet, you might simply look back for a sample question that is similar to the one you are working on. This latter technique does not help you learn how to problem solve; it simply teaches you how to reproduce someone else's solution.

We recommend that you attempt to solve the Practice Exercises, Review Questions, Exercises, Integrative and Advanced Exercises and Feature Problems in a quiet place, with a pencil, paper and an electronic calculator at the ready. After you carefully study an Example in the text, you should attempt to solve one of the analogous Practice Examples. If the answer comes easily to you, then proceed through the rest of the chapter with confidence. If, however, you are stumped, you should study the Example again and then try another Practice Example. Chemistry is a vertically organized discipline; it builds on what has come before. If you do not fully understand a concept at the beginning of a chapter, you will often find that you are not able to understand what comes later in the chapter. Next, for each chapter, you should solve all of the Review Questions and a representative sampling of the Exercises, the Integrative and Advanced Exercises and those Feature Problems whose answers are provided in the textbook (Appendix F) so that you are confident that you have mastered the principles covered in the chapter.

Only after you have made a determined effort to solve each problem should you turn to the solutions in the manual. If you simply read the problem, think about it briefly, and then look up its solution, you will have fooled yourself into believing that you would have come up with the solution on your own. If you take this approach, you will never develop the ability to solve problems. There are many different ways to solve problems and, on some of the following pages, alternate methods of solution are presented. Some of the solutions given in the manual differ slightly from those shown in the text. This will help you realize that there is often more than one

way to arrive at a solution (and that final answers calculated by different individuals often differ by one or two in the last significant digit). Your worst mistake would be to continually try to copy the solution style of another person rather than develop your own methodology.

Be aware that the purpose of the exercise is not to get the right answer. The correct answers to these problems are known already! Instead, you are trying to learn how to solve scientific problems so that when you are confronted with new problems (either on an examination, in another course, or in your job) you will know how to approach them.

There is, of course, much more to chemistry than solving mathematical problems. Many of the problems presented in the textbook and solved here are of a qualitative nature. These problems involve correctly defining terms, explaining chemical phenomena, predicting the products of chemical and nuclear reactions, representing chemical entities through names, formulas, sketches and so on. Don't forget to work on this aspect of your chemical education as well.

What if your answer doesn't match the one in the manual? First, be aware that if you answer disagrees with the one given here in only the last digit, you have probably not made a mistake at all; the discrepancy is simply due to you adopting a method of rounding different from ours. In this manual, we have rounded the result at each step in the calculation where an intermediate answer is required. Intermediate answers must be written down after each *addition* or *subtraction* step. Frequently, one or two significant digits are lost after an addition or subtraction step and, in such cases, it would be inappropriate to carry extra digits beyond the maximum allowed on to the next step. When an extra significant figure has been retained until the end of the calculation, the digit has been written as a subscript or has been underlined. Of course, alternatively, you may have made a serious error. If you wrote down the solution in detail, then you can compare it to the solution in the manual and see where you went wrong.

The important point we are trying to stress here is that you should work on problem solving mostly by yourself. Remember, you are the one who is trying to learn chemistry, for your own sake, not your instructor nor the talented students in your class who seem to know all of the answers. If you make mistakes and fix them yourself, you will learn chemistry much better than if someone else simply shows you the right answer. Of course, above all else, you will have the satisfaction of having done it by yourself.

July 2001

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# CHAPTER 1

## MATTER—ITS PROPERTIES AND MEASUREMENT

### PRACTICE EXAMPLES

---

- 1A** Convert the Fahrenheit temperature to Celsius and compare.

${}^{\circ}\text{C} = \left({}^{\circ}\text{F} - 32\right) \frac{5}{9} = \left(103{}^{\circ}\text{F} - 32\right) \frac{5}{9} = 39.4{}^{\circ}\text{C}$ . The temperature of  $41{}^{\circ}\text{C}$  in New Delhi is higher than the predicted high of  $103{}^{\circ}\text{F} = 39.4{}^{\circ}\text{C}$  in Phoenix.

- 1B** We convert the Fahrenheit temperature to

Celsius.  ${}^{\circ}\text{C} = \left({}^{\circ}\text{F} - 32\right) \frac{5}{9} = \left(-15{}^{\circ}\text{F} - 32\right) \frac{5}{9} = -26.1{}^{\circ}\text{C}$ . The antifreeze only protects to  $-22{}^{\circ}\text{C}$  and will not offer protection to temperatures as low as  $-15{}^{\circ}\text{F} = -26.1{}^{\circ}\text{C}$ .

- 2A** The mass is the difference between the mass of the full and empty flask.

$$\text{density} = \frac{291.4 \text{ g} - 108.6 \text{ g}}{125 \text{ mL}} = 1.46 \text{ g / mL}$$

- 2B** The volume of the stone is the difference between the level in the graduated cylinder with the stone present and with it absent.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{28.4 \text{ g rock}}{44.1 \text{ mL rock \& water} - 33.8 \text{ mL water}} = 2.76 \text{ g / mL}$$

- 3A** Use density as a conversion factor.

$$\text{solution mass} = 125 \text{ mL soln} \times \frac{1.081 \text{ g soln}}{1 \text{ mL soln}} = 135 \text{ g soln.}$$

- 3B** ethanol volume =  $50.0 \text{ kg ethanol} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mL ethanol}}{0.789 \text{ g ethanol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 63.4 \text{ L ethanol}$

- 4A** We first use the density to determine the mass of gasohol.

$$\begin{aligned} \text{ethanol mass} &= 25 \text{ L gasohol} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.71 \text{ g gasohol}}{1 \text{ mL gasohol}} \times \frac{10 \text{ g ethanol}}{100 \text{ g gasohol}} \times \frac{1 \text{ kg ethanol}}{1000 \text{ g ethanol}} \\ &= 1.8 \text{ kg ethanol} \end{aligned}$$

- 4B** We use the mass percent to determine the mass of the 25.0-mL sample.

$$\text{rubbing alcohol mass} = 15.0 \text{ g (2-propanol)} \times \frac{100.0 \text{ g rubbing alcohol}}{70.0 \text{ g (2-propanol)}} = 21.4 \text{ g rubbing alcohol}$$

$$\text{rubbing alcohol density} = \frac{21.4 \text{ g}}{25.0 \text{ mL}} = 0.856 \text{ g/mL}$$

**5A** The factor 0.00456 has three significant figures.  $\frac{62.356}{0.000456 \times 6.422 \times 10^3} = 21.3$

**5B** The factor  $1.3 \times 10^{-3}$  determines the number of significant figures.

$$\frac{8.21 \times 10^4 \times 1.3 \times 10^{-3}}{0.00236 \times 4.071 \times 10^{-2}} = 1.1 \times 10^6$$

**6A** The last term has one digit to the right of the decimal.  $0.236 + 128.55 - 102.1 = 26.7$

**6B** This is easier to visualize if the numbers are not in scientific notation.

$$\frac{(1.302 \times 10^3) + 952.7}{(1.57 \times 10^2) - 12.22} = \frac{1302 + 952.7}{157 - 12.22} = \frac{2255}{145} = 15.6$$

## REVIEW QUESTIONS

---

- A **m<sup>3</sup>** is a cubic meter. As a regular solid, it is a cube one meter on a side, in volume very crudely equal to one cubic yard.
  - % **by mass** is read “percent by mass.” It is the mass in grams of a substance present in precisely 100 grams of the sample it is found in.
  - °C is the temperature of a substance expressed on a scale (the Celsius scale) where the freezing point of water has a value of “zero” and the boiling point of water has a value of “one hundred.”
  - Density** is the concentration of the mass of a material. It is calculated as the mass of the material (in grams) divided by its volume (in mL or cm<sup>3</sup>).
  - An **element** is a substance that cannot be altered or decomposed chemically. Each element has a definite name and a specific position on the periodic table.
- The seven **SI base units** are those from which all other units are derived. Among them are the meter for length, the kilogram for mass, the kelvin for temperature, the second for time, and the mole for amount of substance.
  - Significant figures** are those digits in a number that are the result of experimental measurement, or are derived from such a measurement.
  - A **natural law** is a summary of experimental results or observations, often expressed in mathematical terms.
- The **mass** of an object is a measure of the amount of material in that object. Its **weight**, on the other hand, is the force that the object exerts due to gravitational attraction.
  - An **extensive property** is one that depends on the quantity of material present; an **intensive property** is like a quality; it does not depend on the quantity of material present.

- (c) A **substance** is a pure form of matter; it is either an element or a compound. A **mixture** is a blend of two or more substances, in no particular proportion.
- (d) **Precision** refers to the reproducibility of an experimental measurement; **accuracy** describes the agreement between the measurement and the accepted value of the same property.
- (e) A **hypothesis** is a tentative explanation of a natural law. A **theory** is a hypothesis that has survived the test of repeated experiments.

4. (a)  $1.55 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 1.55 \times 10^3 \text{ g}$  (b)  $642 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.642 \text{ kg}$
- (c)  $2896 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}} = 289.6 \text{ cm}$  (d)  $0.086 \text{ cm} \times \frac{10 \text{ mm}}{1 \text{ cm}} = 0.86 \text{ mm}$
5. (a)  $0.127 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 127 \text{ mL}$  (b)  $15.8 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0158 \text{ L}$
- (c)  $981 \text{ cm}^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.981 \text{ L}$  (d)  $2.65 \text{ m}^3 \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 = 2.65 \times 10^6 \text{ cm}^3$
6. (a)  $68.4 \text{ in.} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} = 174 \text{ cm}$  (b)  $94 \text{ ft} \times \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 29 \text{ m}$
- (c)  $1.42 \text{ lb} \times \frac{453.6 \text{ g}}{1 \text{ lb}} = 644 \text{ g}$  (d)  $248 \text{ lb} \times \frac{0.4536 \text{ kg}}{1 \text{ lb}} = 112 \text{ kg}$
- (e)  $1.85 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{0.9464 \text{ L}}{1 \text{ qt}} = 7.00 \text{ L}$  (f)  $3.72 \text{ qt} \times \frac{0.9464 \text{ L}}{1 \text{ qt}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.52 \times 10^3 \text{ mL}$
7. (a)  $1.00 \text{ km}^2 \times \left(\frac{1000 \text{ m}}{1 \text{ km}}\right)^2 = 1.00 \times 10^6 \text{ m}^2$
- (b)  $1.00 \text{ m}^2 \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^2 = 1.00 \times 10^4 \text{ cm}^2$
- (c)  $1.00 \text{ mi}^2 \times \left(\frac{5280 \text{ ft}}{1 \text{ mi}} \times \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \times \frac{1 \text{ m}}{100 \text{ cm}}\right)^2 = 2.59 \times 10^6 \text{ m}^2$
8. The boiling point of water can serve as our reference.  $204^\circ\text{F}$  is below the  $212^\circ\text{F}$  boiling point of water, while  $102^\circ\text{C}$  is above the  $100^\circ\text{C}$  boiling point of water. Thus,  $102^\circ\text{C}$  is the higher temperature.

9. The 80.0 g ethanol seems least massive. The 100.0 mL of benzene, with a density less than 1 g/mL, must have a mass less than 100.0 g (it is actually 87 g). On the other hand, 90.0 mL of carbon disulfide, with a density of 1.26 g/mL, should have a mass somewhat in excess of 100.0 g (it is actually 113 g). Thus, 90.0 mL of carbon disulfide is the most massive.

10. Butyric acid density =  $\frac{\text{mass}}{\text{volume}} = \frac{2088 \text{ g}}{2.18 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.958 \text{ g / mL}$

11. Mercury density =  $\frac{\text{mass}}{\text{volume}} = \frac{5.23 \text{ kg}}{385 \text{ mL}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 13.6 \text{ g / mL}$

12. (a) mass =  $452 \text{ mL} \times \frac{1.11 \text{ g}}{1 \text{ mL}} = 502 \text{ g ethylene glycol}$

(b) mass =  $18.6 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.11 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 20.6 \text{ kg ethylene glycol}$

(c) volume =  $65.0 \text{ g} \times \frac{1 \text{ mL}}{1.11 \text{ g}} = 58.6 \text{ mL ethylene glycol}$

(d) volume =  $23.9 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mL}}{1.11 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 21.5 \text{ L ethylene glycol}$

13. Acetone mass =  $7.50 \text{ L antifreeze} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.9867 \text{ g antifreeze}}{1 \text{ mL antifreeze}} \times \frac{8.50 \text{ g acetone}}{100.0 \text{ g antifreeze}}$   
 $\times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.629 \text{ kg acetone}$

14. Acetic acid mass =  $1.00 \text{ lb vinegar} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{5.4 \text{ g acetic acid}}{100.0 \text{ g vinegar}} = 24 \text{ g acetic acid}$

15. Solution mass =  $1.00 \text{ kg sucrose} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{100.00 \text{ g solution}}{12.62 \text{ g sucrose}} = 7.92 \times 10^3 \text{ g solution}$

16. Fertilizer mass =  $775 \text{ g nitrogen} \times \frac{1 \text{ kg N}}{1000 \text{ g N}} \times \frac{100 \text{ kg fertilizer}}{21 \text{ kg N}} = 3.69 \text{ kg fertilizer}$

17. (a)  $8950 = 8.950 \times 10^3$  (b)  $10,700 = 1.0700 \times 10^4$  (c)  $0.0240 = 2.40 \times 10^{-2}$

(d)  $0.0047 = 4.7 \times 10^{-3}$  (e)  $938.3 = 9.383 \times 10^2$  (f)  $275,482 = 2.75482 \times 10^5$

18. (a)  $3.21 \times 10^{-2} = 0.0321$  (b)  $5.08 \times 10^{-4} = 0.000508$

(c)  $121.9 \times 10^{-5} = 0.001219$  (d)  $16.2 \times 10^{-2} = 0.162$

- 19.** (a) 450 has two or three significant figures; trailing zeros left of the decimal are indeterminate, if no decimal point is shown.  
 (b) 98.6 has three significant figures; non-zero digits are significant.  
 (c) 0.0033 has two significant digits; leading zeros are not significant.  
 (d) 902.10 has five significant digits; trailing zeros to the right of the decimal point are significant, as are zeros surrounded by non-zero digits.  
 (e) 0.02173 has four significant digits; leading zeros are not significant.  
 (f) 7000 has one to four significant figures; trailing zeros left of the decimal are indeterminate, if no decimal point is shown.  
 (g) 7.02 has three significant figures; zeros surrounded by non-zero digits are significant.  
 (h) 67,000,000 may have from two to eight significant figures; there is no way to determine which, if any, of the zeros are significant, without the presence of a decimal point.
- 20.** Each of the following is expressed with four significant figures.  
 (a)  $3984.6 \approx 3985$       (b)  $422.04 \approx 422.0$       (c)  $186,000 = 1.860 \times 10^5$   
 (d)  $33,900 \approx 3.390 \times 10^4$       (e)  $6.321 \times 10^4$  is correct      (f)  $5.0472 \times 10^{-4} \approx 5.047 \times 10^{-4}$
- 21.** (a)  $0.406 \times 0.0023 = 9.3 \times 10^{-4}$       (b)  $0.1357 \times 16.80 \times 0.096 = 2.2 \times 10^{-1}$   
 (c)  $0.458 + 0.12 - 0.037 = 5.4 \times 10^{-1}$       (d)  $32.18 + 0.055 - 1.652 = 3.058 \times 10^1$
- 22.** (a) 
$$\frac{320 \times 24.9}{0.080} = \frac{3.2 \times 10^2 \times 2.49 \times 10^1}{8.0 \times 10^{-2}} = 1.0 \times 10^5$$
  
 (b) 
$$\frac{432.7 \times 6.5 \times 0.002300}{62 \times 0.103} = \frac{4.327 \times 10^2 \times 6.5 \times 2.300 \times 10^{-3}}{6.2 \times 10^1 \times 1.03 \times 10^{-1}} = 1.0$$
  
 (c) 
$$\frac{32.44 + 4.9 - 0.304}{82.94} = \frac{3.244 \times 10^1 + 4.9 - 3.04 \times 10^{-1}}{8.294 \times 10^1} = 4.47 \times 10^{-1}$$
  
 (d) 
$$\frac{8.002 + 0.3040}{13.4 - 0.066 + 1.02} = \frac{8.002 + 3.040 \times 10^{-1}}{1.34 \times 10^1 - 6.6 \times 10^{-2} + 1.02} = 5.79 \times 10^{-1}$$
- 23.** The calculated volume of the block is converted to its mass with the density of iron.

$$\text{Mass} = 52.8 \text{ cm} \times 6.74 \text{ cm} \times 3.73 \text{ cm} \times 7.86 \frac{\text{g}}{\text{cm}^3} = 1.04 \times 10^4 \text{ g iron}$$

- 24.** The calculated volume of the cylinder is converted to its mass with the density of steel.

$$\text{Mass} = V(\text{density}) = \pi r^2 h(d) = 3.14159 (1.88 \text{ cm})^2 18.35 \text{ cm} \times 7.75 \frac{\text{g}}{\text{cm}^3} = 1.58 \times 10^3 \text{ g steel}$$

## EXERCISES

---

### Scientific Method

- 25.** No. The greater the number of experiments that conform to the predictions of the law, the more confidence we have in the law. There is no point at which the law is ever verified with absolute certainty.
- 27.** A given set of conditions, a cause, is expected to produce a certain result, an effect. Although these cause-and-effect relationships may be difficult to establish at times (“God is subtle”), they nevertheless do exist (“he is not malicious”).
- 29.** The experiments should be carefully set up so as to create a controlled situation in which one can make careful observations after altering the experimental parameters, preferably one at a time. The results must be reproducible (to within experimental error) and, as more and more experiments are conducted, a pattern should begin to emerge, from which a comparison to the current theory can be made.

### Properties and Classification of Matter

- 31.** An object displaying a physical property retains its basic chemical identity. Display of a chemical property is accompanied by a change in composition.
- (a) Physical: The iron nail is not changed in any significant way when it is attracted to a magnet. Its basic chemical identity is unchanged.
- (b) Chemical: The liquid lighter fluid is converted into a gas (carbon dioxide) and water vapor, along with the evolution of considerable energy.
- (c) Chemical: The green patina is the result of the combination of water, oxygen, and carbon dioxide with the copper in the bronze to produce basic copper carbonate.
- (d) Physical: Neither the block of wood nor the water has changed its identity.
- 33.** (a) Heterogeneous mixture: We can clearly see air pockets within the solid matrix. On close examination, we can distinguish different kinds of solids by their colors.
- (b) Homogeneous mixture: Modern inks are solutions of dyes in water. Older inks often were heterogeneous mixtures: suspensions carbon black particles(soot) in water.
- (c) Substance: Assuming that no gases or organic chemicals are dissolved in the water.
- (d) Heterogeneous mixture: The pieces of orange pulp can be seen through a microscope. Most “cloudy” liquids are heterogeneous mixtures; the small particles impede the transmission of light.
- 35.** (a) Physical: This is simply a mixture of sand and sugar (i.e. not chemically bonded).
- (b) Chemical: Oxygen needs to be removed from the iron oxide.
- (c) Physical: Seawater is a solution of various substances dissolved in water.
- (d) Physical: The water sand is simply a heterogeneous mixture.

## Exponential Arithmetic

- 37.** (a) 34,000 centimeters/second =  $3.4 \times 10^4$  cm/s  
 (b) six thousand three hundred seventy eight kilometers =  $6378 \text{ km} = 6.378 \times 10^3 \text{ km}$   
 (c) (trillionth =  $1 \times 10^{-12}$ ) hence,  $74 \times 10^{-12} \text{ m}$  or  $7.4 \times 10^{-11} \text{ m}$   
 (d) 
$$\frac{(2.2 \times 10^3) + (4.7 \times 10^2)}{5.8 \times 10^{-3}} = \frac{2.7 \times 10^3}{5.8 \times 10^{-3}} = 4.6 \times 10^5$$

## Significant figures

- 39.** (a) An exact number—24 soda cans in a case.  
 (b) Pouring the milk into the jug is a process that is subject to error; there can be slightly more or slightly less than one gallon of milk in the jug. This is a measured quantity.  
 (c) The distance between any pair of planetary bodies can only be determined through certain measurements, which are subject to error.  
 (d) Measured quantity: the internuclear separation quoted for H<sub>2</sub> is an estimated value derived from experimental data, which contains some inherent error.

- 41.** (a)  $2.44 \times 10^4$  (b)  $1.5 \times 10^3$  (c) 40.0  
 (d)  $2.131 \times 10^3$  (e)  $4.8 \times 10^{-3}$

- 43.** (a) The average speed is obtained by dividing the distance traveled (in miles) by the elapsed time (in hours). First, we need to obtain the elapsed time, in hours.

$$9 \text{ days} \times \frac{24 \text{ h}}{1 \text{ d}} = 216.000 \text{ h} \quad 3 \text{ min} \times \frac{1 \text{ h}}{60 \text{ min}} = 0.050 \text{ h} \quad 44 \text{ s} \times \frac{1 \text{ h}}{3600 \text{ s}} = 0.012 \text{ h}$$

$$\text{Total time} = 216.000 \text{ h} + 0.050 \text{ h} + 0.012 \text{ h} = 216.062 \text{ h}$$

$$\text{average speed} = \frac{25,012 \text{ mi}}{216.062 \text{ h}} = 115.76 \text{ mi/h}$$

- (b) First compute the mass of fuel remaining

$$\text{mass} = 14 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{0.9464 \text{ L}}{1 \text{ qt}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.70 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ lb}}{453.6 \text{ g}} = 82 \text{ lb}$$

Then determine the mass of fuel used, and finally, the fuel consumption. Notice that we know the initial quantity of fuel quite imprecisely, perhaps at best to the nearest 10 lb, certainly (“nearly 9000 lb”) not to the nearest pound.

$$\text{mass of fuel used} = 9000 \text{ lb} - 82 \text{ lb} \approx 8920 \text{ lb}$$

$$\text{fuel consumption} = \frac{25,012 \text{ mi}}{8920 \text{ lb}} = 2.80 \text{ mi/lb}$$

## Units of Measurement

45. Express both masses in the same units for comparison.  $2172 \mu\text{g} \left( \frac{1\text{g}}{10^6 \mu\text{g}} \right) \left( \frac{10^3 \text{ mg}}{1\text{g}} \right) = 2.172 \text{ mg}$ , which is larger than 0.00515 mg.

47. height = 15 hands  $\times \frac{4 \text{ in.}}{1 \text{ hand}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.5 \text{ m}$

49. (a) We use the speed as a conversion factor, but need to convert yards into meters.

$$\text{time} = 100.0 \text{ m} \times \frac{9.3 \text{ s}}{100 \text{ yd}} \times \frac{1 \text{ yd}}{36 \text{ in.}} \times \frac{39.37 \text{ in.}}{1 \text{ m}} = 10. \text{ s} \quad \text{Keep two significant figures.}$$

(b) We need to convert yards to meters.

$$\text{speed} = \frac{100 \text{ yd}}{9.3 \text{ s}} \times \frac{36 \text{ in.}}{1 \text{ yd}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 9.83 \text{ m/s}$$

(c) The speed is used as a conversion factor.

$$\text{time} = 1.45 \text{ km} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ s}}{9.8 \text{ m}} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.5 \text{ min}$$

51. 1 hectare =  $1 \text{ hm}^2 \times \left( \frac{100 \text{ m}}{1 \text{ hm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \times \frac{1 \text{ in.}}{2.54 \text{ cm}} \times \frac{1 \text{ ft}}{12 \text{ in.}} \times \frac{1 \text{ mi}}{5280 \text{ ft}} \right)^2 \times \frac{640 \text{ acres}}{1 \text{ mi}^2}$

$$1 \text{ hectare} = 2.47 \text{ acres}$$

53. pressure =  $\frac{32 \text{ lb}}{1 \text{ in.}^2} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \left( \frac{1 \text{ in.}}{2.54 \text{ cm}} \right)^2 = 2.2 \times 10^3 \text{ g/cm}^2$

$$\text{pressure} = \frac{2.2 \times 10^3 \text{ g}}{1 \text{ cm}^2} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)^2 = 2.2 \times 10^4 \text{ kg/m}^2$$

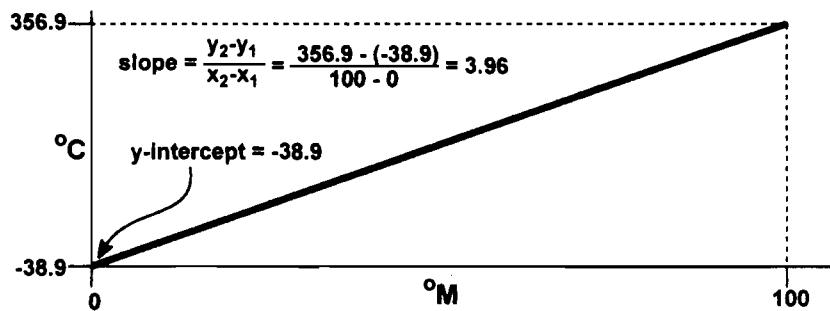
## Temperature Scales

55. high:  ${}^{\circ}\text{C} = \frac{5}{9} ({}^{\circ}\text{F} - 32) = \frac{5}{9} (118{}^{\circ}\text{F} - 32) = 47.8{}^{\circ}\text{C} \approx 48{}^{\circ}\text{C}$

low:  ${}^{\circ}\text{C} = \frac{5}{9} ({}^{\circ}\text{F} - 32) = \frac{5}{9} (17{}^{\circ}\text{F} - 32) = -8.3{}^{\circ}\text{C}$

57. Determine the Celsius temperature that corresponds to the highest Fahrenheit temperature,  $240{}^{\circ}\text{F}$ .  ${}^{\circ}\text{C} = \frac{5}{9} ({}^{\circ}\text{F} - 32) = \frac{5}{9} (240{}^{\circ}\text{F} - 32) = 116{}^{\circ}\text{C}$  Because  $116{}^{\circ}\text{C}$  is above the range of the thermometer, this thermometer cannot be used in this candy making assignment.

- 59. (a)** From the data provided we can write down the following relationship:  $-38.9^{\circ}\text{C} = 0^{\circ}\text{M}$  and  $356.9^{\circ}\text{C} = 100^{\circ}\text{M}$ . To find the mathematical relationship between these two scales, we can treat each relationship as a point on a two-dimensional Cartesian graph (see next page)



Therefore, the equation for the line is  $y = 3.96x - 38.9$ . The algebraic relationship between the two temperature scales is

$$t(^{\circ}\text{C}) = 3.96(^{\circ}\text{M}) - 38.9 \text{ or rearranging, } t(^{\circ}\text{M}) = \frac{t(^{\circ}\text{C}) + 38.9}{3.96}$$

Alternatively, note that the change in temperature in  $^{\circ}\text{C}$  corresponding to a change of  $100^{\circ}\text{M}$  is  $[356.9 - (-38.9)] = 395.8^{\circ}\text{C}$ , hence,  $(100^{\circ}\text{M}/395.8^{\circ}\text{C}) = 1^{\circ}\text{M}/3.96^{\circ}\text{C}$ . This factor must be multiplied by the number of degrees Celsius above zero on the M scale. This number of degrees is  $t(^{\circ}\text{C}) + 38.9$ , which leads to the general equation  $t(^{\circ}\text{M}) = [t(^{\circ}\text{C}) + 38.9]/3.96$ .

The boiling point of water is  $100^{\circ}\text{C}$ , corresponding to  $t(^{\circ}\text{M}) = \frac{100 + 38.9}{3.96} = 35.1^{\circ}\text{M}$

$$(b) \quad t(^{\circ}\text{M}) = \frac{-273.15 + 38.9}{3.96} = -59.2^{\circ}\text{M}$$

## Density

- 61.** The mass of acetone is the difference in masses between empty and filled masses.

$$\text{Density} = \frac{437.5 \text{ lb} - 75.0 \text{ lb}}{55.0 \text{ gal}} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ gal}}{3.785 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.790 \text{ g/mL}$$

- 63.** Determine the mass of each item.

$$(1) \quad \text{mass of iron} = (81.5 \text{ cm} \times 2.1 \text{ cm} \times 1.6 \text{ cm}) \times 7.86 \text{ g/cm}^3 = 2.2 \times 10^3 \text{ g iron}$$

$$(2) \quad \text{mass of aluminum}$$

$$= (12.12 \text{ m} \times 3.62 \text{ m} \times 0.003 \text{ cm}) \times \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)^2 \times 2.70 \text{ g/cm}^3 = 4 \times 10^3 \text{ g aluminum}$$

$$(3) \text{ mass of water} = 4.051 \text{ L} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times 0.998 \text{ g/cm}^3 = 4.04 \times 10^3 \text{ g water}$$

In order of increasing mass, the items are: iron bar < aluminum foil < water. Realize, however, that the rules for significant figures do not allow us to distinguish between the masses of aluminum and water.

- 65.** Total volume of 125 pieces of shot

$$V = 8.9 \text{ mL} - 8.4 \text{ mL} = 0.5 \text{ mL} \quad \frac{\text{mass}}{\text{shot}} = \frac{0.5 \text{ mL}}{125 \text{ shot}} \times \frac{1 \text{ cm}^3}{1 \text{ mL}} \times \frac{8.92 \text{ g}}{1 \text{ cm}^3} = 0.04 \text{ g/shot}$$

- 67.** Here we are asked to calculate the number of liters of whole blood that have to be collected in order to end up with 0.5 kg of red blood cells. Each red blood cell has a mass of

$$9.00 \times 10^{-11} \text{ cm}^3 \times 1.096 \text{ g cm}^{-3} = 9.864 \times 10^{-11} \text{ g}$$

$$\text{red blood cells (mass per mL)} = \frac{9.864 \times 10^{-11} \text{ g}}{1 \text{ cell}} \times \frac{5.4 \times 10^9 \text{ cells}}{1 \text{ mL}} = \frac{0.533 \text{ g red blood cells}}{1 \text{ mL of blood}}$$

For 0.5 kg or  $5 \times 10^2$  g of red blood cells, we require

$$= 5 \times 10^2 \text{ g red blood cells} \times \frac{1 \text{ mL of blood}}{0.533 \text{ g red blood cells}} = 9 \times 10^2 \text{ mL of blood or } 0.9 \text{ L blood}$$

## Percent Composition

- 69.** The percent of students with each grade is obtained by dividing the number of students with that grade by the total number of students.  $\%A = \frac{9 \text{ A's}}{76 \text{ students}} \times 100\% = 12\% A$

$$\%B = \frac{21 \text{ B's}}{76 \text{ students}} \times 100\% = 28\% B$$

$$\%C = \frac{36 \text{ C's}}{76 \text{ students}} \times 100\% = 47\% C$$

$$\%D = \frac{8 \text{ D's}}{76 \text{ students}} \times 100\% = 11\% D$$

$$\%F = \frac{2 \text{ F's}}{76 \text{ students}} \times 100\% = 3\% F$$

Note that the percentages add to 101% due to rounding effects.

- 71.** Use the percent composition as a conversion factor.

$$\text{mass of sucrose} = 2.75 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.118 \text{ g soln}}{1 \text{ mL}} \times \frac{28.0 \text{ g sucrose}}{100 \text{ g soln}} = 8.61 \times 10^2 \text{ g sucrose}$$

## FEATURE PROBLEMS

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89. All of the pennies minted before 1982 weigh more than 3.00 g, while all of those minted after 1982 weigh less than 2.60 g. One might infer that the composition of a penny changed in 1982. In fact, pennies minted prior to 1982 are composed of almost pure copper (about 96% pure). Those minted after 1982 are composed of zinc with a thin copper cladding. Some pennies of each type were minted in 1982.
90. After sitting in a bathtub that was nearly full and observing the water splashing over the side, Archimedes realized that the crown—when submerged in water—would displace a volume of water equal to its volume. Once Archimedes determined the volume in this way and determined the mass of the crown with a balance, he was able to calculate the crown's density. Since the gold-silver alloy has a different density (it is lower) than pure gold, Archimedes could tell that the crown was not pure gold.
91. Notice that the liquid does not fill each of the floating glass balls. The quantity of liquid in each glass ball is sufficient to give each ball a slightly different density. Note that the density of the glass ball is determined by the density of the liquid, the density of the glass (greater than the liquid's density), and the density of the air. Since the density of the liquid in the cylinder varies slightly with temperature—the liquid's volume increases as temperature goes up, but its mass does not change—different balls will be buoyant at different temperatures.
92. The density of the canoe is determined by the density of the concrete and the density of the empty space inside the canoe, where the passengers sit. It is the empty space, (filled with air), that makes the density of the canoe less than that of water ( $1.0 \text{ g/cm}^3$ ). If the concrete canoe fills with water, it will sink to the bottom, unlike a wooden canoe.
93. One needs to convert (lb of force) into (Newtons)  $1 \text{ lb of force} = 1 \text{ slug} \times 1 \text{ ft s}^{-2}$

$$(1 \text{ slug} = 14.59 \text{ kg}). \text{ Therefore, } 1 \text{ lb of force} = \frac{14.59 \text{ kg} \times 1 \text{ ft}}{\text{s}^2}$$
$$= \left( \frac{14.59 \text{ kg} \times 1 \text{ ft}}{\text{s}^2} \right) \left( \frac{12 \text{ in}}{1 \text{ ft}} \right) \left( \frac{2.54 \text{ cm}}{1 \text{ in}} \right) \left( \frac{1 \text{ m}}{100 \text{ cm}} \right) = \frac{4.45 \text{ kg m}}{\text{s}^2} = 4.45 \text{ Newtons}$$

From this result it is clear that  $1 \text{ lb of force} = 4.45 \text{ Newtons}$ .

# CHAPTER 2

## ATOMS AND THE ATOMIC THEORY

### PRACTICE EXAMPLES

- 1A** The total mass must be the same before and after reaction.

$$\text{mass before reaction} = 0.382\text{g magnesium} + 2.652\text{g nitrogen} = 3.034\text{g}$$

$$\text{mass after reaction} = \text{magnesium nitride mass} + 2.505\text{g nitrogen} = 3.034\text{g}$$

$$\text{magnesium nitride mass} = 3.034\text{g} - 2.505\text{g} = 0.529\text{g magnesium nitride}$$

- 1B** Again, the total mass is the same before and after the reaction.

$$\text{mass before reaction} = 7.12\text{g magnesium} + 1.80\text{g bromine} = 8.92\text{g}$$

$$\text{mass after reaction} = 2.07\text{g magnesium bromide} + \text{magnesium mass} = 8.92\text{g}$$

$$\text{magnesium mass} = 8.92\text{g} - 2.07\text{g} = 6.85\text{g magnesium}$$

- 2A** In Example 2-2 we are told that 0.100 g magnesium produces 0.166 g magnesium oxide.

$$\text{mass of Mg} = 0.500\text{g MgO} \times \frac{0.100\text{g Mg}}{0.166\text{g MgO}} = 0.301\text{g Mg}$$

- 2B** In Example 2-2 we are told that 0.100 g Mg forms 0.166 g MgO. With this information, we can determine the mass of magnesium needed to form 2.00 g magnesium oxide.

$$\text{mass of Mg} = 2.00\text{g MgO} \times \frac{0.100\text{g Mg}}{0.166\text{g MgO}} = 1.20\text{g Mg}$$

The remainder of the 2.00 g of magnesium oxide is the mass of oxygen

$$\text{mass of oxygen} = 2.00\text{g magnesium oxide} - 1.20\text{g magnesium} = 0.80\text{ g oxygen}$$

- 3A** The number of protons and electrons are equal, and thus the species has no charge. The mass number is the sum of the atomic number and the number of neutrons:

$$47\text{p} + 61\text{n} = A = 108.$$

The atomic number 47 is that of the element silver. Thus the symbol is  $^{108}_{47}\text{Ag}$ .

- 3B** The element sulfur has an atomic number of 16 and thus has 16 protons. A charge of 2- indicates two more electrons than protons; there are  $16 + 2 = 18$  electrons. The number of neutrons is the mass number minus the number of protons; there are  $35 - 16 = 19$  neutrons.

- 4A** We know that the mass of  $^{16}\text{O} = 15.9949\text{ u}$  and that mass of  $^{16}\text{O} = 1.06632 \times \text{mass of } ^{15}\text{N}$ . We combine these two equations and solve the resulting expression.

$$15.9949\text{u} = 1.06632 \times \text{mass of } ^{15}\text{N} \quad \therefore \text{mass of } ^{15}\text{N} = \frac{15.9949\text{u}}{1.06632} = 15.0001\text{u}$$

**4B** We know the isotopic mass of  $^{12}\text{C}$  is 12 u. Thus, the mass ratio is found by substitution.

$$\frac{^{202}\text{Hg}}{^{12}\text{C}} = \frac{201.970617}{12\text{u}} = 16.8308848$$

Note that the number of significant figures in the result is determined by the precision of the mass of  $^{202}\text{Hg}$ , because the mass of  $^{12}\text{C}$  is established by definition as an exact number.

**5A** The average atomic mass of boron is 10.811, which is closer to 11.009305 than to 10.012937. Thus, boron-11 is the isotope present in greater abundance.

**5B** We let  $x$  be the fractional abundance of lithium-6.

$$6.941\text{u} = [x \times 6.01513\text{u}] + [(1-x) \times 7.01601\text{u}] = 6.01513x\text{u} + 7.01601\text{u} - 7.01601x\text{u}$$

$$6.941\text{u} - 7.01601\text{u} = 6.01513x\text{u} - 7.01601x\text{u} = -1.00088x\text{u}$$

$$x = \frac{6.941\text{u} - 7.01601\text{u}}{-1.00088\text{u}} = 0.075 \quad \text{Percent abundances: 7.5\% lithium-6, 92.5\% lithium-7}$$

**6A** We assume that atoms lose or gain relatively few electrons to become ions. Thus, elements that will form cations will be on the left-hand side of the periodic table, while elements that will form anions will be on the right-hand side. The number of electrons “lost” when a cation forms is the periodic group number; the number of electrons added when an anion forms is eight minus the group number.

Li is in group 1(1A); it should form a cation by losing one electron:  $\text{Li}^+$ .

S is in group 6(6A); it should form an anion by adding two electrons:  $\text{S}^{2-}$ .

Ra is in group 2(2A); it should form a cation by losing two electrons:  $\text{Ra}^{2+}$ .

F and I are both group 17(7A); they should form anions by gaining an electron:  $\text{F}^-$  and  $\text{I}^-$ .

Al is in group 13(3A); it should form a cation by losing three electrons:  $\text{Al}^{3+}$ .

**6B** Main group elements are in the “A” families, while transition elements are in the “B” families. Metals, nonmetals, metalloids, and noble gases are color coded in the periodic table inside the front cover.

Na is a main-group metal in group 1(1A).

Re is a transition metal in group 7

S is a main-group nonmetal in group 16(6A).

I is a main-group nonmetal in group 17.

Kr is a noble gas in group 18(8A).

Mg is a main-group metal in group 2.

U is an inner transition metal, an actinide.

Si is a main-group metalloid in group 14.

B is a nonmetal in group 13(3A).

Al is a main-group metal in group 13.

As is a main-group metalloid in group 15(5A).

H is a main-group nonmetal in group 1.

**7A** Avogadro's number serves as a conversion factor.

$$\text{no. Au atoms} = 5.07 \times 10^{-3} \text{ mol Au} \times \frac{6.022 \times 10^{23} \text{ Au atoms}}{1 \text{ mol Au}} = 3.05 \times 10^{21} \text{ Au atoms}$$

**7B** Of all lead atoms, 24.1% are lead-206, or  $241^{206}\text{Pb}$  atoms in every 1000 lead atoms

$$^{206}\text{Pb atoms} = 8.27 \times 10^{-3} \text{ mol Pb} \times \frac{6.022 \times 10^{23} \text{ Pb atoms}}{1 \text{ mol Pb}} \times \frac{241^{206}\text{Pb atoms}}{1000 \text{ Pb atoms}} = 1.20 \times 10^{21}^{206}\text{Pb atoms}$$

**8A** This is similar to Practice Examples 2-8A and 2-8B.

$$\text{Cu mass} = 2.35 \times 10^{24} \text{ Cu atoms} \times \frac{1 \text{ mol Cu}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{63.546 \text{ g Cu}}{1 \text{ mol Cu}} = 248 \text{ g Cu}$$

**8B** Atoms of He =  $22.6 \text{ g He} \times \frac{1 \text{ mol He}}{4.0026 \text{ g He}} \times \frac{6.022 \times 10^{23} \text{ He atoms}}{1 \text{ mol He}} = 3.40 \times 10^{24} \text{ He atoms}$

**9A** Both the density and the molar mass of Pb serve as conversion factors.

$$\text{atoms of Pb} = 0.105 \text{ cm}^3 \text{ Pb} \times \frac{11.34 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ Pb atoms}}{1 \text{ mol Pb}} = 3.46 \times 10^{21} \text{ Pb atoms}$$

**9B** First we find the number of rhenium atoms in 0.100 mg of the element.

$$0.100 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Re}}{186.207 \text{ g Re}} \times \frac{6.022 \times 10^{23} \text{ Re atoms}}{1 \text{ mol Re}} = 3.23 \times 10^{17} \text{ Re atoms}$$

$$\%^{187}\text{Re} = \frac{2.02 \times 10^{17} \text{ atoms}^{187}\text{Re}}{3.23 \times 10^{17} \text{ Re atoms}} \times 100\% = 62.5\%$$

## REVIEW QUESTIONS

- ${}^A_Z\text{E}$  is the symbol for a nuclide. E represents the symbol of the element; Z is the atomic number, the number of protons in the nucleus; and A is the mass number, the number of protons plus neutrons.
  - A  $\beta$  particle refers to an electron ejected by the nucleus, and is one of the three forms of natural radioactivity.
  - An isotope is one of at least two forms of an atom of an element which have the same number of protons in the nucleus, but different numbers of neutrons.
  - ${}^{16}\text{O}$  is the symbol for the isotope of oxygen that has 16 nucleons in its nucleus: 8 protons (characteristic of the element oxygen) and 8 neutrons.
  - Molar mass is the mass of a quantity of an element (or a compound) that contains Avogadro's number  $6.022 \times 10^{23}$  of atoms (or formula units).

2. (a) The law of conservation of mass states that there is no gain or loss of mass during a chemical reaction.
- (b) The atom as described by Rutherford consists of a very small (approximately  $10^{-13}$  cm diameter), positively charged, and massive (more than 99.5% of the mass) nucleus surrounded by a relatively large (approximately  $10^{-8}$  cm diameter), tenuous (less than 0.5% of the mass), and negatively charged cloud of electrons.
- (c) The atomic mass that appears in the periodic table for each element is a weighted average, with contributions from each naturally-occurring isotope of the element, each weighted by the relative abundance of that isotope.
- (d) Radioactivity refers to the spontaneous emission from the nucleus of a photon ( $\gamma$  radiation) or particles ( $\alpha$  or  $\beta$  particles).
3. (a) Cathode rays are beams of electrons that are generated when a large potential difference is applied across two metal plates in a sealed evacuated tube. X-rays are high-energy photons emitted when these cathode rays strike the anode within the glass tube.
- (b) Protons and neutrons are both particles in the nucleus of the atom, and both have a mass of approximately 1 u. However, protons are positively charged, while neutrons have no electric charge.
- (c) The nuclear charge of an atom is a positive charge equal to the number of protons in the nucleus. The ionic charge equals the nuclear charge minus the number of electrons; as a consequence, the ionic charge may be negative.
- (d) A period is a horizontal row in the periodic table. A group is a vertical column, containing elements of similar chemical and physical properties.
- (e) A metal is an element that has a luster, is malleable, and conducts electricity and heat well. Also, metal atoms tend to form cations in chemical reactions. A nonmetal does not conduct heat or electricity well, and solid nonmetals typically are dull and brittle. Nonmetal atoms tend to form anions in chemical reactions.
- (f) Avogadro's constant is equal to the number of particles of any type that are present in a mole.
4. By the law of conservation of mass, all of the magnesium initially present and all of the oxygen that reacted are present in the product. Thus, the mass of oxygen that has reacted is obtained by difference.

$$\text{mass of oxygen} = 0.674\text{g magnesium oxide} - 0.406\text{g magnesium} = 0.268\text{g oxygen}$$

5. Again we use the law of conservation of mass. The mass of the starting materials equals the mass of substances present after the reaction is complete.
- $$\text{mass of potassium} + \text{mass of chlorine} = \text{mass of potassium chloride} + \text{mass of unreacted chlorine}$$
- $$1.205\text{g potassium} + 6.815\text{g chlorine} = \text{mass of potassium chloride} + 3.300\text{g unreacted chlorine}$$
- $$\text{mass of potassium chloride} = (1.205\text{g} + 6.815\text{g}) - 3.300\text{g} = 4.720\text{ g potassium chloride}$$

6. No solid residue is produced when (solid) sulfur completely burns because the product of combustion is sulfur dioxide gas. The law of conservation of mass is satisfied because the mass of the sulfur dioxide equals the sum of the masses of sulfur and oxygen that react.
7. If the two elements combine in the ratio 1:1, there will be one atom of sodium present for each atom of chlorine. To determine the mass percent sodium, we simply convert these atomic quantities to masses (in u) and convert the resulting ratio to a percent.

$$\text{percent Na} = \frac{1 \text{ Na atom} \times \frac{22.99 \text{ u Na}}{1 \text{ Na atom}}}{\left( 1 \text{ Na atom} \times \frac{22.99 \text{ u Na}}{1 \text{ Na atom}} \right) + \left( 1 \text{ Cl atom} \times \frac{35.45 \text{ u Cl}}{1 \text{ Cl atom}} \right)} \times 100\% = 39.34\% \text{ Na}$$

8. (a) The mass of oxygen present in 0.166 g magnesium oxide is the remainder when the 0.100 g magnesium is deducted, or 0.066 g oxygen. Hence, there is 0.066 g oxygen/0.166 g magnesium oxide.
- (b) From the numbers we have already obtained, we see that there is 0.066 g oxygen/0.100 g magnesium, or 0.66 g oxygen/1.00 g magnesium.

$$(c) \% \text{ Mg, by mass} = \frac{0.100 \text{ g Mg}}{0.166 \text{ g MgO}} \times 100\% = 60.2\% \text{ Mg}$$

9. (a) We can determine that carbon dioxide has a fixed composition by finding the % C in each sample. (In the calculations below, abbreviation "cmpd" is short for compound.)

$$\% \text{ C} = \frac{3.62 \text{ g C}}{13.26 \text{ g cmpd}} \times 100\% = 27.3\% \text{ C} \quad \% \text{ C} = \frac{5.91 \text{ g C}}{21.66 \text{ g cmpd}} \times 100\% = 27.3\% \text{ C}$$

$$\% \text{ C} = \frac{7.07 \text{ g C}}{25.91 \text{ g cmpd}} \times 100\% = 27.3\% \text{ C}$$

Since all three samples have the same percent of carbon, these data do establish that carbon dioxide has a fixed composition.

- (b) Carbon dioxide contains only carbon and oxygen. The percent of oxygen in carbon dioxide is obtained by difference.  $\% \text{ O} = 100.0\% - 27.3\% \text{ C} = 72.7\% \text{ O}$

10. By dividing the mass of the oxygen per gram of sulfur in the second sulfur-oxygen compound (compound 2) by the mass of oxygen per gram of sulfur in the first sulfur-oxygen compound (compound 1), we obtain the ratio (right):

$$\frac{\frac{1.497 \text{ g of O}}{1.000 \text{ g of S}} \text{ (comp 2)}}{\frac{0.998 \text{ g of O}}{1.000 \text{ g of S}} \text{ (comp 1)}} = \frac{1.500}{1}$$

To get the simplest whole number ratio we need to multiply both the numerator and the denominator by 2. This gives the simple whole number ratio 3/2. In other words, for a given mass of sulfur, the mass of oxygen in the second compound ( $\text{SO}_3$ ) relative to the mass of oxygen in the first compound ( $\text{SO}_2$ ) is in a ratio of 3:2. These results are entirely consistent with the Law of Multiple Proportions because the same two elements, sulfur and oxygen in this case, have reacted together to give two different compounds that have masses of oxygen that are in the ratio of small positive integers for a fixed amount of sulfur.

11. This question is similar to question 10 in that two elements, phosphorus and chlorine in this case, have combined to give two different compounds. This time, however, different masses have been used for both of the elements in the second reaction. To see if the Law of Multiple Proportions is being followed, the mass of one of the two elements must be set to the same value in both reactions. This can be achieved by dividing the masses of both phosphorus and chlorine in reaction 2 by 2.500:

$$\text{"normalized" mass of phosphorus} = \frac{2.500 \text{ g phosphorus}}{2.500} = 1.000 \text{ g of phosphorus}$$

$$\text{"normalized" mass of chlorine} = \frac{14.308 \text{ g chlorine}}{2.500} = 5.723 \text{ g of chlorine}$$

Now the mass of phosphorus for both reactions is fixed at 1.000 g. Next, we will divide each amount of chlorine by the fixed mass of phosphorus with which they are combined. This gives

$$\frac{\frac{3.433 \text{ g of Cl}}{1.000 \text{ g P}} \text{ (reaction 1)}}{\frac{5.723 \text{ g of Cl}}{1.000 \text{ g P}} \text{ (reaction 2)}} = 0.600 = 6:10 \text{ or } 3:5$$

12. By knowing that all of the 4.15 g of magnesium reacts, producing only magnesium bromide and leaving excess bromine unreacted, we are unable at this point to calculate the mass of magnesium bromide produced. In order to perform this calculation, we need to know how many moles of bromine are combined with each mole of magnesium in the compound.

<u>13.</u>	Name	Symbol	# of protons	# of electrons	# of neutrons	Mass number
	sodium	$^{23}_{11}\text{Na}$	11	11	12	23
	silicon	$^{28}_{14}\text{Si}$	14	14 <sup>a</sup>	14	28
	rubidium	$^{85}_{37}\text{Rb}$	37	37 <sup>a</sup>	48	85
	potassium	$^{40}_{19}\text{K}$	19	19	21	40
	arsenic <sup>a</sup>	$^{75}_{33}\text{As}$	33 <sup>a</sup>	33	42	75
	neon	$^{20}_{10}\text{Ne}^{2+}$	10	8	10	20
	bromine <sup>b</sup>	$^{80}_{35}\text{Br}$	35	35	45	80
	lead <sup>b</sup>	$^{208}_{82}\text{Pb}$	82	82	126	208

<sup>a</sup>This result assumes that a neutral atom is involved.

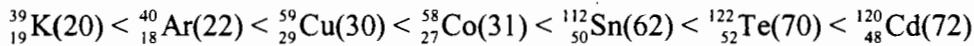
<sup>b</sup>Insufficient data. Does not characterize a specific nuclide; several possibilities exist.

The minimum information needed is the atomic number (or some way to obtain it: the name or the symbol of the element involved), the number of electrons (or some way to obtain it, such as the charge on the species), and the mass number (or the number of neutrons).

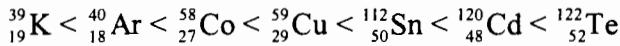
14. (a) Since all of these species are neutral atoms, the number of electrons are the atomic numbers, the subscript numbers. The symbols must be arranged in order of increasing value of these subscripts.



- (b) The number of neutrons is given by the difference between the mass number and the atomic number,  $A - Z$ . This is the difference between superscripted and subscripted values and are provided (in parentheses) after each element in the following list.



- (c) Here the nuclides are arranged by increasing mass number, given by the superscripts.



15. (a) cobalt-60  ${}_{27}^{60}\text{Co}$  (b) phosphorus-32  ${}_{15}^{32}\text{P}$  (c) iodine-131  ${}_{53}^{131}\text{I}$  (d) sulfur-35  ${}_{16}^{35}\text{S}$

16. The nucleus of  ${}_{56}^{138}\text{Ba}$  contains 56 protons and  $(138 - 56) = 82$  neutrons. Thus, the percent of nucleons that are neutrons is given by

$$\% \text{ neutrons} = \frac{82 \text{ neutrons}}{138 \text{ nucleons}} \times 100 = 59\% \text{ neutrons}$$

17. The weighted-average atomic mass of the element iridium is just slightly more than 192 u. The mass of the first isotope is a bit less than 191 u. Hence, the mass of the second isotope must more than 192 u; that isotope must be  ${}^{193}\text{Ir}$ .

18. If we let  $x$  represent the number of protons, then  $x + 2$  is the number of neutrons. The mass number is the sum of the number of protons and the number of neutrons:  
 $38 = x + (x + 2) = 2x + 2$ . We solve this expression for  $x$ , and obtain  $x = 18$ . This is the number of protons of the nuclide and equals the atomic number. Reference to the periodic table indicates that 18 is the atomic number of the element argon.

19. Each isotopic mass must be divided by the isotopic mass of  ${}^{12}\text{C}$ , 12 u, an exact number.

$$(a) {}^{35}\text{Cl} \div {}^{12}\text{C} = 34.96885\text{u} \div 12\text{u} = 2.914071$$

$$(b) {}^{26}\text{Mg} \div {}^{12}\text{C} = 25.98259\text{u} \div 12\text{u} = 2.165216$$

$$(c) {}^{222}\text{Rn} \div {}^{12}\text{C} = 222.0175\text{u} \div 12\text{u} = 18.50146$$

20. We need to work through the mass ratios in sequence to determine the mass of  $^{81}\text{Br}$ .

$$\text{mass of } ^{19}\text{F} = \text{mass of } ^{12}\text{C} \times 1.5832 = 12.00000 \text{ u} \times 1.5832 = 18.998 \text{ u}$$

$$\text{mass of } ^{35}\text{Cl} = \text{mass of } ^{19}\text{F} \times 1.8406 = 18.998 \text{ u} \times 1.8406 = 34.968 \text{ u}$$

$$\text{mass of } ^{81}\text{Br} = \text{mass of } ^{35}\text{Cl} \times 2.3140 = 34.968 \text{ u} \times 2.3140 = 80.917 \text{ u}$$

21. Each of the isotopic masses is multiplied by its fractional abundance. The resulting products are summed to obtain the average atomic mass.

$$\text{contribution from } ^{40}\text{Ar} = 39.9624 \text{ u} \times 0.99600 = 39.803 \text{ u}$$

$$\text{contribution from } ^{36}\text{Ar} = 35.96755 \text{ u} \times 0.00337 = 0.121 \text{ u}$$

$$\text{contribution from } ^{38}\text{Ar} = 37.96272 \text{ u} \times 0.00063 = 0.024 \text{ u}$$

$$\text{average atomic mass of argon} = 39.803 \text{ u} + 0.121 \text{ u} + 0.024 \text{ u} = 39.948 \text{ u}$$

Of course, this calculation can be performed in one step:

$$(39.9624 \text{ u} \times 0.99600) + (35.96755 \text{ u} \times 0.00337) + (37.96272 \text{ u} \times 0.00063) = 39.948 \text{ u}$$

22. (a) In is in group 13(3A) and in the fifth period.

(b) Other elements in group 16(6A) are similar to S: O, Se, Te. Most of the elements in the periodic table are unlike S, but particularly metals such as Na, K, Rb.

(c) The alkali metal in the sixth period is in group 1(1A), Cs.

(d) The halogen (group 17(7A)) in the fifth period is I.

(e) The element with atomic number 18 is Ar, a noble gas. Xe is a noble gas with atomic number (54) greater than 50.

(f) If an element forms an anion with charge 3-, it is in group 15(5A).

(g) If an element forms a cation with charge 2+, it is in group 2(2A)

23. If the seventh period of the periodic table is 32 members long, it will be the same length as the sixth period. Elements in the same family will have atomic numbers 32 units higher.

The noble gas following radon will have atomic number =  $86 + 32 = 118$ . The alkali metal following francium will have atomic number =  $87 + 32 = 119$ .

24. One mole of any element contains  $6.022 \times 10^{23}$  atoms, the Avogadro constant.

$$(a) 12.7 \text{ mol Ca} \times \frac{6.022 \times 10^{23} \text{ Ca atoms}}{1 \text{ mol Ca}} = 7.65 \times 10^{24} \text{ Ca atoms}$$

$$(b) 0.00361 \text{ mol Ne} \times \frac{6.022 \times 10^{23} \text{ Ne atoms}}{1 \text{ mol Ne}} = 2.17 \times 10^{21} \text{ Ne atoms}$$

$$(c) 1.8 \times 10^{-12} \text{ mol Pu} \times \frac{6.022 \times 10^{23} \text{ Pu atoms}}{1 \text{ mol Pu}} = 1.1 \times 10^{12} \text{ Pu atoms}$$

- 25.** In these problems we use the Avogadro constant and the fact that one mole of atoms of an element has a weight in grams equal to its atomic mass.

$$(a) \text{ no. moles Fe} = 2.18 \times 10^{26} \text{ Fe atoms} \times \frac{1 \text{ mol Fe}}{6.022 \times 10^{23} \text{ Fe atoms}} = 362 \text{ mol Fe}$$

$$(b) \text{ mass of Kr, g} = 7.71 \text{ mol Kr} \times \frac{83.80 \text{ g Kr}}{1 \text{ mol Kr}} = 646 \text{ g Kr}$$

$$(c) \text{ Au mass, mg} = 6.15 \times 10^{19} \text{ Au atoms} \times \frac{1 \text{ mol Au}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} \times \frac{1000 \text{ mg}}{1 \text{ g}}$$

$$\text{Au atoms} = 20.1 \text{ mg Au}$$

$$(d) \text{ Fe atoms} = 112 \text{ cm}^3 \text{ Fe} \times \frac{7.86 \text{ g Fe}}{1 \text{ cm}^3 \text{ Fe}} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Fe}}$$

$$\text{Fe atoms} = 9.49 \times 10^{24} \text{ Fe atoms}$$

- 26.** Since the molar mass of nitrogen is 14.0 g/mol, 25.0 g N is almost two moles (1.79 mol N), while  $6.02 \times 10^{23}$  Ni atoms is about one mole, and 52.0 g Cr (52.00 g/mol Cr) is also almost one mole. Finally, 10.0 cm<sup>3</sup> Fe (55.85 g/mol Fe) has a mass of about 79 g, and contains about 1.4 moles of atoms. Thus, 25.0 g N contains the greatest number of atoms.

- 27.** We first determine the number of Pb atoms of all types in 1.57 g of Pb, and then use the percent abundance to determine the number of <sup>204</sup>Pb atoms present.

$$\text{atoms of } {}^{204}\text{Pb} = 215 \text{ mg Pb} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Pb}} \times \frac{14 \text{ }{}^{204}\text{Pb atoms}}{1000 \text{ Pb atoms}}$$

$$= 8.7 \times 10^{18} \text{ atoms } {}^{204}\text{Pb}$$

- 28.** mass of alloy =  $6.50 \times 10^{23} \text{ Cd atoms} \times \frac{1 \text{ mol Cd}}{6.022 \times 10^{23} \text{ Cd atoms}} \times \frac{112.4 \text{ g Cd}}{1 \text{ mol Cd}} \times \frac{100.0 \text{ g alloy}}{8.0 \text{ g Cd}}$
- $$= 1.5 \times 10^3 \text{ g alloy}$$

## EXERCISES

### Law of Conservation of Mass

- 29.** The observations cited do not necessarily violate the law of conservation of mass. The oxide formed when iron rusts is a solid and remains with the solid iron, increasing the mass of the solid by an amount equal to the mass of the oxygen that has combined. The oxide formed when a match burns is a gas and will not remain with the solid product (the ash); the mass of the ash thus is less than that of the match. We would have to collect all reactants and all products and weigh them to determine if the law of conservation of mass is obeyed or violated.

31. We compare the mass before reaction (initial) with that after reaction (final).

$$\text{initial mass} = 10.500 \text{ g calcium hydroxide} + 11.125 \text{ g ammonium chloride} = 21.625 \text{ g}$$

$$\text{final mass} = 14.336 \text{ g solid residue} + (69.605 - 62.316) \text{ g of gases} = 21.625 \text{ g}$$

These data support the law of conservation of mass. Note that the gain in the mass of water is due to the gases that it absorbs.

### Law of Constant Composition

33. In the first experiment, 2.18 g of sodium produces 5.54 g of sodium chloride. In the second experiment, 2.10 g of chlorine produces 3.46 g of sodium chloride. The amount of sodium contained in this second sample of sodium chloride is given by  
 $\text{mass of sodium} = 3.46 \text{ g sodium chloride} - 2.10 \text{ g chlorine} = 1.36 \text{ g sodium}$   
 We now have sufficient information to determine the % Na in each of the samples of sodium chloride.

$$\% \text{Na} = \frac{2.18 \text{ g Na}}{5.54 \text{ g cmpd}} \times 100\% = 39.4\% \text{ Na} \quad \% \text{Na} = \frac{1.36 \text{ g Na}}{3.46 \text{ g cmpd}} \times 100\% = 39.3\% \text{ Na}$$

Thus, the two samples of sodium chloride have the same composition. Recognize that, according to the interpretation of numbers based on significant figures, each percent has an uncertainty of  $\pm 0.1\%$ .

35. The mass of sulfur (0.312 g) needed to produce 0.623 g sulfur dioxide provides the information for the conversion factor.

$$\text{sulfur mass} = 0.842 \text{ g sulfur dioxide} \times \frac{0.312 \text{ g sulfur}}{0.623 \text{ g sulfur dioxide}} = 0.422 \text{ g sulfur}$$

### Law of Multiple Proportions

37. (a) First of all we need to fix the mass of nitrogen in all three compounds at 1.000 g. This can be accomplished by multiplying the masses of hydrogen and nitrogen in compound A by 2 and the amount of hydrogen and nitrogen in compound C by 4/3 (1.333):

$$\begin{aligned} \text{Comp. A: "normalized" mass of nitrogen} &= 0.500 \text{ g N} \times 2 = 1.000 \text{ g N} \\ \text{"normalized" mass of hydrogen} &= 0.108 \text{ g H} \times 2 = 0.216 \text{ g H} \end{aligned}$$

$$\begin{aligned} \text{Comp. C: "normalized" mass of nitrogen} &= 0.750 \text{ g N} \times 1.333 = 1.000 \text{ g N} \\ \text{"normalized" mass of hydrogen} &= 0.108 \text{ g H} \times 1.333 = 0.144 \text{ g H} \end{aligned}$$

Next, we divide the mass of hydrogen in each compound by the smallest mass of hydrogen, namely, 0.0720 g. This gives 3.000 for compound A, 1.000 for compound B and 2.00 for compound C. The ratio of the amounts of hydrogen in the three compounds is 3 (comp A) : 1 (comp B) : 2 (comp C)

These results are consistent with the Law of Multiple Proportions because the masses of hydrogen in the three compounds end up in a ratio of small whole numbers when the mass of nitrogen in all three compounds is normalized to a simple value (1.000 g here).

- (b) The text states that compound B is  $\text{N}_2\text{H}_2$ . This means that, based on the relative amounts of hydrogen calculated in part (a), compound A might be  $\text{N}_2\text{H}_6$  and compound C,  $\text{N}_2\text{H}_4$ . Actually, compound A is  $\text{NH}_3$ , but we have no way of knowing this from the data. Note that the H:N ratio in  $\text{NH}_3$  and  $\text{N}_2\text{H}_6$  are the same, 3H:1N.
39. One oxide of copper has about 20% oxygen by mass. If we assume a 100 gram sample, then ~ 20 grams of the sample is oxygen (~1.25 moles) and 80 grams is copper (~1.26 moles). This would give an empirical formula of  $\text{CuO}$  (copper (II) oxide). The second oxide has less oxygen by mass, hence the empirical formula must have less oxygen or more copper (Cu:O ratio greater than 1). If we keep whole number ratios of atoms, a plausible formula would be  $\text{Cu}_2\text{O}$  (copper (I) oxide), where the mass percent oxygen is  $\approx 11\%$ .

## Fundamental Particles

41. A fundamental particle would be expected to be found in all samples of matter. For instance, cathode rays, which are beams of “free” electrons, have the same properties no matter how they are generated. These properties are independent of the material that was used to construct the cathode ray tube, of the gas that filled the tube when it was constructed (and was subsequently pumped out), and of the method used to generate electricity.

## Fundamental Charges and Mass-to-Charge Ratios

43. We can calculate the charge on each drop, express each in terms of  $10^{-19}$  C, and finally express each in terms of  $e = 1.6 \times 10^{-19}$  C.

$$\text{drop 1: } 1.28 \times 10^{-18} \quad = 12.8 \times 10^{-19} \text{ C} \quad = 8e$$

$$\text{drops 2 \& 3: } 1.28 \times 10^{-18} \div 2 = 0.640 \times 10^{-18} \text{ C} \quad = 6.40 \times 10^{-19} \text{ C} \quad = 4e$$

$$\text{drop 4: } 1.28 \times 10^{-18} \div 8 = 0.160 \times 10^{-18} \text{ C} \quad = 1.60 \times 10^{-19} \text{ C} \quad = 1e$$

$$\text{drop 5: } 1.28 \times 10^{-18} \times 4 = 5.12 \times 10^{-18} \text{ C} \quad = 51.2 \times 10^{-19} \text{ C} \quad = 32e$$

We see that these values are consistent with the charge that Millikan found for that of the electron, and he could have inferred the correct charge from these data, since they are all multiples of  $e$ .

- 45. (a)** Determine the ratio of the mass of a hydrogen atom to that of an electron. We use the mass of a proton plus that of an electron for the mass of a hydrogen atom.

$$\frac{\text{mass of proton} + \text{mass of electron}}{\text{mass of electron}} = \frac{1.0073 \text{ u} + 0.00055 \text{ u}}{0.00055 \text{ u}} = 1.8 \times 10^3$$

$$\text{or} \quad \frac{\text{mass of electron}}{\text{mass of proton} + \text{mass of electron}} = \frac{1}{1.8 \times 10^3} = 5.6 \times 10^{-4}$$

- (b)** The only two mass-to-charge ratios that we can determine from the data in Table 2-1 are those for the proton, a hydrogen ion,  $\text{H}^+$ ; and that for the electron.

$$\text{For the proton :} \quad \frac{\text{mass}}{\text{charge}} = \frac{1.673 \times 10^{-24} \text{ g}}{1.602 \times 10^{-19} \text{ C}} = 1.044 \times 10^{-5} \text{ g/C}$$

$$\text{For the electron :} \quad \frac{\text{mass}}{\text{charge}} = \frac{9.109 \times 10^{-28} \text{ g}}{1.602 \times 10^{-19} \text{ C}} = 5.686 \times 10^{-9} \text{ g/C}$$

The hydrogen ion is the lightest positive ion available. We see that the mass-to-charge ratio for a positive particle is considerably larger than that for an electron.

## Atomic Number, Mass Number, and Isotopes

- 47. (a)** A  $^{108}\text{Pd}$  atom has 46 protons, and 46 electrons. The atom described is neutral, hence, the number of electrons must equal the number of protons. Since there are 108 nucleons in the nucleus, the number of neutrons is 62 (= 108 nucleons – 46 protons).

- (b)** The ratio of the two masses is determined as follows:

$$\frac{^{108}\text{Pd}}{^{12}\text{C}} = \frac{107.90389 \text{ u}}{12 \text{ u}} = 8.9919908$$

- 49.** The mass of  $^{16}\text{O}$  is 15.9949 u. Isotopic mass =  $15.9949 \text{ u} \times 6.68374 = 106.906 \text{ u}$

- 51. (a)** Atoms with equal numbers of protons and neutrons will have mass numbers that are approximately twice the size of their atomic numbers. The following species are approximately suitable (with numbers of protons and neutrons in parentheses).

$^{24}\text{Mg}^{2+}$  (12 p, 12 n),  $^{47}\text{Cr}$  (24 p, 23 n),  $^{60}\text{Co}^{3+}$  (27 p, 33 n), and  $^{35}\text{Cl}^-$  (17 p, 18 n).

Of these four nuclides, only  $^{24}\text{Mg}^{2+}$  has just as many protons as neutrons.

- (b)** A species in which protons have more than 50% of the mass must have a mass number smaller than twice the atomic number. Of these species, only in  $^{47}\text{Cr}$  is more than 50% of the mass contributed by the protons.
- (c)** A species with greater than 50% more neutrons than protons will have a mass number that is at least 2.5 times greater than the atomic number.  $^{226}\text{Th}$  has greater than 50% more neutrons than protons.

## Atomic Mass Units, Atomic Masses

53. It is exceedingly unlikely that another nuclide would have an exact integral mass. The mass of carbon-12 is *defined* as precisely 12 u. Each nuclidic mass is close to integral, but none that we have encountered in this chapter are precisely integral. The reason is that each nuclide is composed of protons, neutrons, and electrons, none of which have integral masses, and there is a small quantity of the mass of each nucleon (nuclear particle) lost in the binding energy holding the nuclides together. It would be highly unlikely that all of these contributions would add up to a precisely integral mass.

55. To determine the average atomic mass, we use the following expression:

$$\text{average atomic mass} = \sum (\text{isotopic mass} \times \text{fractional natural abundance})$$

Each of the three percents given is converted to a fractional abundance by dividing it by 100.

$$\begin{aligned} \text{Mg atomic mass} &= (23.985042 \text{ u} \times 0.7899) + (24.985837 \text{ u} \times 0.1000) + (25.982593 \text{ u} \times 0.1101) \\ &= 18.95 \text{ u} + 2.499 \text{ u} + 2.861 \text{ u} = 24.31 \text{ u} \end{aligned}$$

57. We use the expression for determining the weighted-average atomic mass.

$$107.868 \text{ u} = (106.905092 \text{ u} \times 0.5184) + ({}^{109}\text{Ag} \times 0.4816) = 55.42 \text{ u} + 0.4816 {}^{109}\text{Ag}$$

$$107.868 \text{ u} - 55.42 \text{ u} = 0.4816 {}^{109}\text{Ag} = 52.45 \text{ u} \quad {}^{109}\text{Ag} = \frac{52.45 \text{ u}}{0.4816} = 108.9 \text{ u}$$

59. Since the three percent abundances total 100%, the percent abundance of  ${}^{40}\text{K}$  is found by difference.

$$\% {}^{40}\text{K} = 100.0000\% - 93.2581\% - 6.7302\% = 0.0117\%$$

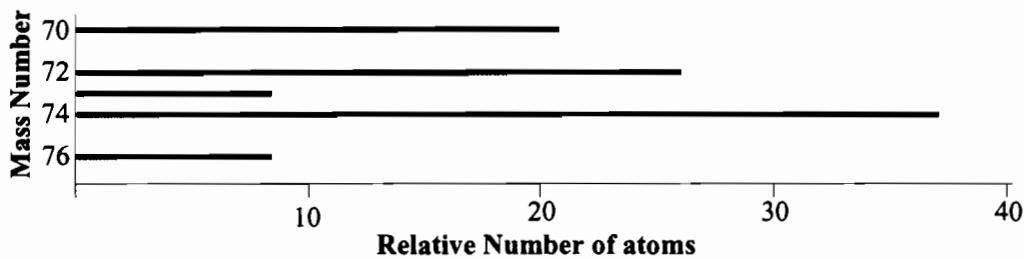
Then the expression for the weighted-average atomic mass is used, with the percent abundances converted to fractional abundances by dividing by 100. The average atomic mass of potassium is 39.0983 u.

$$\begin{aligned} 39.0983 \text{ u} &= (0.932581 \times 38.963707 \text{ u}) + (0.000117 \times 39.963999 \text{ u}) + (0.067302 \times {}^{41}\text{K}) \\ &= 36.3368 \text{ u} + 0.00468 \text{ u} + (0.067302 \times {}^{41}\text{K}) \end{aligned}$$

$$\text{mass of } {}^{41}\text{K} = \frac{39.0983 \text{ u} - (36.3368 \text{ u} + 0.00468 \text{ u})}{0.067302} = 40.962 \text{ u}$$

## Mass spectrometry

61. (a)



- (b) As before, we multiply each isotopic mass by its fractional abundance; after which, we sum these products to obtain the (average) atomic mass for the element.

$$(0.205 \times 70) + (0.274 \times 72) + (0.078 \times 73) + (0.365 \times 74) + (0.078 \times 76)$$

$$14 + 20. + 5.7 + 27 + 5.9 = 72.6 = \text{average atomic mass of germanium}$$

The result is only approximately correct because the isotopic masses are given to only two significant figures. Thus, only a two-significant-figure result can be quoted.

## The Avogadro Constant and the Mole

63. Each of these calculations employs the average atomic mass as a conversion factor.

$$(a) \text{ amount of Rb} = 167.0 \text{ g Rb} \times \frac{1 \text{ mol Rb}}{85.468 \text{ g Rb}} = 1.954 \text{ mol Rb}$$

$$(b) \text{ number of Fe atoms} = 363.2 \text{ kg Fe} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Fe}}{55.847 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ Fe atoms}}{1 \text{ mol Fe}} \\ = 3.916 \times 10^{27} \text{ Fe atoms}$$

$$(c) \text{ Ag mass} = 1.0 \times 10^{12} \text{ Ag atoms} \times \frac{1 \text{ mol Ag}}{6.022 \times 10^{23} \text{ Ag atoms}} \times \frac{107.87 \text{ g Ag}}{1 \text{ mol Ag}} \\ = 1.8 \times 10^{-10} \text{ g Ag}$$

(d) Mass of one fluorine atom: 1 mole F = 18.9984 g. Divide both sides by  $6.022142 \times 10^{23}$  atoms (1 mol F). We find the mass of 1 F atom is  $3.15476 \times 10^{-23}$  grams.

65. We determine the mass of Ag in the piece of jewelry and then the number of Ag atoms.

$$\text{no. Ag atoms} = 38.7 \text{ g sterling} \times \frac{92.5 \text{ g Ag}}{100.0 \text{ g sterling}} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Ag}}$$

$$\text{no. Ag atoms} = 2.00 \times 10^{23} \text{ Ag atoms}$$

**67.** We use the average atomic mass of lead, 207.2 g/mol.

$$(a) \frac{30 \text{ } \mu\text{g Pb}}{1 \text{ dL}} \times \frac{1 \text{ dL}}{0.1 \text{ L}} \times \frac{1 \text{ g Pb}}{10^6 \text{ } \mu\text{g Pb}} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g}} = 1.45 \times 10^{-6} \text{ mol Pb/L}$$

$$(b) \frac{1.45 \times 10^{-6} \text{ mol Pb}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} = 8.7 \times 10^{14} \text{ Pb atoms/mL}$$

**69.** Let's begin by finding the volume of copper metal.

$$\text{Wire diameter (cm)} = 0.03196 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} = 0.08118 \text{ cm}$$

$$\text{The radius in cm is } 0.08118 \text{ cm} \times 1/2 = 0.04059 \text{ cm}$$

$$\text{The volume of Cu(cm}^3\text{)} = (0.04059 \text{ cm})^2 \times (\pi) \times (1.00 \text{ m} \times \frac{100 \text{ cm}}{1 \text{ m}}) = 0.5176 \text{ cm}^3$$

$$\text{So, the mass of Cu} = 0.5176 \text{ cm}^3 \times \frac{8.92 \text{ g Cu}}{1 \text{ cm}^3} = 4.62 \text{ g Cu}$$

$$\text{The number of moles of Cu} = 4.62 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.546 \text{ g Cu}} = 0.0727 \text{ mol Cu}$$

$$\text{Cu atoms in the wire} = 0.0727 \text{ mol Cu} \times \frac{6.022 \times 10^{23} \text{ atoms Cu}}{1 \text{ mol Cu}} = 4.38 \times 10^{22} \text{ atoms}$$

## FEATURE PROBLEMS

**90.** The product mass differs from that of the reactants by  $(5.62 - 2.50 =)$  3.12 grains. In order to determine the percent gain in mass, we need to convert the reactant mass to grains.

$$13 \text{ onces} \times \frac{8 \text{ gros}}{1 \text{ once}} = 104 \text{ gros} \times (104 + 2) \text{ gros} \times \frac{72 \text{ grains}}{1 \text{ gros}} = 7632 \text{ grains}$$

$$\% \text{ mass increase} = \frac{3.12 \text{ grains increase}}{(7632 + 2.50) \text{ grains original}} \times 100\% = 0.0409\% \text{ mass increase}$$

The sensitivity of Lavoisier's balance can be as little as 0.01 grain, which seems to be the limit of the readability of the balance; or it can be as large as 3.12 grains, which assumes that all of the error in the experiment is due to the (in)sensitivity of the balance. Let us convert 0.01 grains to a mass in grams.

$$\text{minimum error} = 0.01 \text{ gr} \times \frac{1 \text{ gros}}{72 \text{ gr}} \times \frac{1 \text{ once}}{8 \text{ gros}} \times \frac{1 \text{ livre}}{16 \text{ once}} \times \frac{30.59 \text{ g}}{1 \text{ livre}} = 3 \times 10^{-5} \text{ g} = 0.03 \text{ mg}$$

$$\text{maximum error} = 3.12 \text{ gr} \times \frac{3 \times 10^{-5} \text{ g}}{0.01 \text{ gr}} = 9 \times 10^{-3} \text{ g} = 9 \text{ mg}$$

The maximum error is close to that of a common modern laboratory balance, which has a sensitivity of 1 mg. The minimum error is approximated by a good quality analytical balance.

91. One way to determine the common factor of which all 13 numbers are multiples is to first divide all of them by the smallest. The ratios thus obtained may either be integers or they may be rational numbers whose decimal equivalents are easy to recognize.

Obs.	1	2	3	4	5	6	7	8	9	10	11	12	13
Quan.	19.66	24.60	29.62	34.47	39.38	44.42	49.41	53.91	59.12	63.68	68.65	78.34	83.22
Ratio	1.000	1.251	1.507	1.753	2.003	2.259	2.513	2.742	3.007	3.239	3.492	3.984	4.233
Mult.	4.000	5.005	6.026	7.013	8.012	9.038	10.05	10.97	12.03	12.96	13.97	15.94	16.93
Int.	4	5	6	7	8	9	10	11	12	13	14	16	17

The row labeled "Mult." is obtained by multiplying the row "ratio" by 4.000. In the row labeled "Int." we give the integer closest to each of these multipliers. It is obvious that each of the 13 measurements is exceedingly close to a common quantity multiplied by an integer.

92. In a 50-year-old chemistry textbook the atomic mass for oxygen would be 16.000 because chemists assigned precisely 16 as the atomic mass of the naturally occurring mixture of oxygen isotopes. This value is slightly higher than the value of 15.9994 in modern chemistry textbooks. Thus, we would expect all other atomic masses to be slightly higher as well in the older textbooks.
93. We begin with the amount of reparations and obtain the volume in cubic kilometers with a series of conversion factors.

$$\begin{aligned} \text{volume} &= \$28.8 \times 10^9 \times \frac{1 \text{ troy oz Au}}{\$21.25} \times \frac{31.103 \text{ g Au}}{1 \text{ troy oz Au}} \times \frac{1 \text{ mol Au}}{196.97 \text{ g Au}} \times \frac{6.022 \times 10^{23} \text{ atoms Au}}{1 \text{ mol Au}} \\ &\times \frac{1 \text{ ton sea water}}{4.67 \times 10^{17} \text{ Au atoms}} \times \frac{2000 \text{ lb}}{1 \text{ ton}} \times \frac{453.6 \text{ g}}{1 \text{ lb sea water}} \times \frac{1 \text{ cm}^3}{1.03 \text{ g}} \times \left( \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{1 \text{ km}}{1000 \text{ m}} \right)^3 \\ \text{volume} &= 2.43 \times 10^5 \text{ km}^3 \end{aligned}$$

94. We start by using the percent natural abundances for  $^{87}\text{Rb}$  and  $^{85}\text{Rb}$  along with the data in the "spiked" mass spectrum to find the total mass of Rb in the sample. Then, we calculate the Rb content in the rock sample in ppm by mass by dividing the mass of Rb by the total mass of the rock sample, and then multiplying the result by  $10^6$  to convert to ppm.

$$^{87}\text{Rb} = 27.83 \% \text{ natural abundance} \quad ^{85}\text{Rb} = 72.17 \% \text{ natural abundance}$$

$$\text{Therefore, } \frac{^{87}\text{Rb(natural)}}{^{85}\text{Rb(natural)}} = \frac{27.83 \%}{72.17 \%} = 0.3856$$

For the  $^{87}\text{Rb}$ (spiked) sample, the  $^{87}\text{Rb}$  peak in the mass spectrum is 1.12 times as tall as the  $^{85}\text{Rb}$  peak. Thus, for this sample  $\frac{^{87}\text{Rb(natural)} + ^{87}\text{Rb(spiked)}}{^{85}\text{Rb(natural)}} = 1.12$

Using this relationship, we can now find the masses of both  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$  in the sample.

$$\text{So, } \frac{^{87}\text{Rb(natural)}}{^{85}\text{Rb(natural)}} = 0.3856; \quad ^{85}\text{Rb(natural)} = \frac{^{87}\text{Rb(natural)}}{0.3856}$$

$$^{87}\text{Rb(natural)} + ^{87}\text{Rb(spiked)} = \frac{1.12 \times ^{87}\text{Rb (natural)}}{0.3856} = 2.905 ^{87}\text{Rb(natural)}$$

$$^{87}\text{Rb(spiked)} = 1.905 ^{87}\text{Rb(natural)}$$

$$\text{and } \frac{^{87}\text{Rb(natural)} + ^{87}\text{Rb(spiked)}}{^{85}\text{Rb(natural)}} = \frac{\frac{^{87}\text{Rb(natural)} + ^{87}\text{Rb(spiked)}}{^{87}\text{Rb(natural)}}}{0.3856} = 1.12$$

Since the mass of  $^{87}\text{Rb}(\text{spike})$  is equal to 29.45  $\mu\text{g}$ , the mass of  $^{87}\text{Rb}(\text{natural})$  must be

$$\frac{29.45 \text{ } \mu\text{g}}{1.905} = 15.46 \text{ } \mu\text{g of } ^{87}\text{Rb(natural)}$$

$$\text{So, the mass of } ^{85}\text{Rb(natural)} = \frac{15.46 \text{ } \mu\text{g of } ^{87}\text{Rb(natural)}}{0.3856} = 40.09 \text{ } \mu\text{g of } ^{85}\text{Rb(natural)}$$

Therefore, the total mass of Rb in the sample = 15.46  $\mu\text{g}$  of  $^{87}\text{Rb}(\text{natural})$  + 40.09  $\mu\text{g}$  of  $^{85}\text{Rb}(\text{natural})$  = 55.55  $\mu\text{g}$  of Rb convert to grams:

$$= 55.55 \text{ } \mu\text{g of Rb} \times \frac{1 \text{ g Rb}}{1 \times 10^6 \text{ } \mu\text{g Rb}} = 5.555 \times 10^{-5} \text{ g Rb}$$

$$\text{Rb content (ppm)} = \frac{5.555 \times 10^{-5} \text{ g Rb}}{0.350 \text{ g of rock}} \times 10^6 = 159 \text{ ppm Rb}$$

# CHAPTER 3

## CHEMICAL COMPOUNDS

### PRACTICE EXAMPLES

**1A** For one conversion factor we need the molar mass of ZnO.

$$M = \left( \frac{1 \text{ mol Zn}}{1 \text{ mol ZnO}} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} \right) + \left( \frac{1 \text{ mol O}}{1 \text{ mol ZnO}} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} \right) = \frac{81.39 \text{ g ZnO}}{1 \text{ mol ZnO}}$$

Then determine the number of ions in 1.0 g of ZnO. Note that each mole of ZnO contains two moles of ions: 1 mole of Zn<sup>2+</sup> ions, and 1 mole of O<sup>2-</sup> ions.

$$\text{? ions} = 1.0 \text{ g ZnO} \times \frac{1 \text{ mol ZnO}}{81.39 \text{ g ZnO}} \times \frac{2 \text{ mol ions}}{1 \text{ mol ZnO}} \times \frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol ions}} = 1.5 \times 10^{22} \text{ ions}$$

**1B** For one conversion factor we need the molar mass of MgCl<sub>2</sub>.

$$M = \left( \frac{1 \text{ mol Mg}}{1 \text{ mol MgCl}_2} \times \frac{24.305 \text{ g Mg}}{1 \text{ mol Mg}} \right) + \left( \frac{2 \text{ mol Cl}}{1 \text{ mol MgCl}_2} \times \frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}} \right) = \frac{95.211 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2}$$

Then convert the number of chloride ions to the mass of MgCl<sub>2</sub>.

$$\begin{aligned} \text{MgCl}_2 \text{ mass} &= 5.0 \times 10^{23} \text{ Cl}^- \text{ ions} \times \frac{1 \text{ f.u. MgCl}_2}{2 \text{ Cl}^- \text{ ions}} \times \frac{1 \text{ mol MgCl}_2}{6.022 \times 10^{23} \text{ f.u.}} \times \frac{95.211 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2} \\ &= 4.0 \times 10^1 \text{ g MgCl}_2 \end{aligned}$$

**2A** The volume of gold is converted to its mass and then to the amount in moles.

$$\begin{aligned} \text{? Au atoms} &= (2.50 \text{ cm})^2 \times (0.100 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}}) \times \frac{19.32 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Au}}{196.97 \text{ g Au}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol Au}} \\ &= 3.69 \times 10^{21} \text{ Au atoms} \end{aligned}$$

**2B** We need the molar mass of ethyl mercaptan for one conversion factor.

$$M = (2 \times 12.011 \text{ g C}) + (6 \times 1.008 \text{ g H}) + (1 \times 32.066 \text{ g S}) = 62.136 \text{ g/mol C}_2\text{H}_6\text{S}$$

$$\begin{aligned} \text{C}_2\text{H}_6\text{S conc.} &= \frac{1.0 \mu\text{L C}_2\text{H}_6\text{S}}{1500 \text{ m}^3} \times \frac{1 \text{ L}}{1 \times 10^6 \mu\text{L}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.84 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol C}_2\text{H}_6\text{S}}{62.136 \text{ g}} \times \frac{10^6 \mu\text{mol}}{1 \text{ mol}} \\ &= 9 \times 10^{-3} \mu\text{mol/m}^3 > 0.9 \times 10^{-3} \mu\text{mol/m}^3 = \text{the detectable limit} \end{aligned}$$

Thus, the vapor will be detectable.

- 3A** The molar mass of halothane is given in Example 3-3 *in the text* as 197.4 g/mol. The rest of the solution uses conversion factors to change units.

$$\begin{aligned} \text{C mass} &= 75.0 \text{ mL } \text{C}_2\text{HBrClF}_3 \times \frac{1.871 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol halothane}}{197.4 \text{ g}} \times \frac{2 \text{ mol C}}{1 \text{ mol } \text{C}_2\text{HBrClF}_3} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} \\ &= 17.1 \text{ g C} \end{aligned}$$

- 3B** Again, the molar mass of halothane is given in Example 3-3 *in the text* as 197.4 g/mol.

$$\begin{aligned} V_{\text{halothane}} &= 100.0 \text{ g Br} \times \frac{1 \text{ mol Br}}{79.904 \text{ g Br}} \times \frac{1 \text{ mol } \text{C}_2\text{HBrClF}_3}{1 \text{ mol Br}} \times \frac{197.4 \text{ g } \text{C}_2\text{HBrClF}_3}{1 \text{ mol } \text{C}_2\text{HBrClF}_3} \times \frac{1 \text{ mL}}{1.871 \text{ g}} \\ &= 132.0 \text{ mL } \text{C}_2\text{HBrClF}_3 \end{aligned}$$

- 4A** The molecular formula of acetic acid is  $\text{C}_2\text{H}_4\text{O}_2$ . Determine the molar mass of acetic acid.

$$\begin{aligned} M &= \left( \frac{2 \text{ mol C}}{1 \text{ mol acid}} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} \right) + \left( \frac{4 \text{ mol H}}{1 \text{ mol acid}} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) + \left( \frac{2 \text{ mol O}}{1 \text{ mol acid}} \times \frac{15.9994 \text{ g O}}{1 \text{ mol O}} \right) \\ M &= \frac{24.022 \text{ g C}}{1 \text{ mol } \text{C}_2\text{H}_4\text{O}_2} + \frac{4.032 \text{ g H}}{1 \text{ mol } \text{C}_2\text{H}_4\text{O}_2} + \frac{31.9988 \text{ g O}}{1 \text{ mol } \text{C}_2\text{H}_4\text{O}_2} = \frac{60.053 \text{ g } \text{C}_2\text{H}_4\text{O}_2}{1 \text{ mol } \text{C}_2\text{H}_4\text{O}_2} \end{aligned}$$

The mass percent for each element is determined by dividing the mass of the element present in a mole of the compound by the molar mass for the compound as a whole, and then multiplying the result by 100%.

$$\% \text{C} = \frac{24.022 \text{ g C}/1 \text{ mol acid}}{60.053 \text{ g acetic acid}/1 \text{ mol acid}} \times 100\% = 40.001\% \text{C}$$

$$\% \text{H} = \frac{4.032 \text{ g H}}{60.053 \text{ g } \text{C}_2\text{H}_4\text{O}_2} \times 100\% = 6.714\% \text{ H} \quad \% \text{O} = \frac{31.9988 \text{ g O}}{60.053 \text{ g } \text{C}_2\text{H}_4\text{O}_2} \times 100\% = 53.284\% \text{ O}$$

Note: As expected, the percentages sum to 100%, within the limits of significant figures.

- 4B** We use the same technique as before: determine the mass of each element in a mole of the compound. Their sum is the molar mass of the compound. The percent composition is determined by comparing the mass of each element with the molar mass of the compound.

$$\begin{aligned} M &= (10 \times 12.011 \text{ g C}) + (16 \times 1.008 \text{ g H}) + (5 \times 14.01 \text{ g N}) + (3 \times 30.97 \text{ g P}) + (13 \times 15.999 \text{ g O}) \\ &= 120.11 \text{ g C} + 16.13 \text{ g H} + 70.05 \text{ g N} + 92.91 \text{ g P} + 207.99 \text{ g O} = 507.19 \text{ g ATP/mol} \end{aligned}$$

$$\% \text{C} = \frac{120.11 \text{ g C}}{507.19 \text{ g ATP}} \times 100\% = 23.681\% \text{C} \quad \% \text{H} = \frac{16.13 \text{ g H}}{507.19 \text{ g ATP}} \times 100\% = 3.180\% \text{ H}$$

$$\% \text{N} = \frac{70.05 \text{ g N}}{507.19 \text{ g ATP}} \times 100\% = 13.81\% \text{ N} \quad \% \text{P} = \frac{92.91 \text{ g P}}{507.19 \text{ g ATP}} \times 100\% = 18.32\% \text{ P}$$

$$\% \text{O} = \frac{207.99 \text{ g O}}{507.19 \text{ g ATP}} \times 100\% = 41.008\% \text{ O} \text{ (NOTE: sums to 99.999%)}$$

- 5A** To answer this question, we start with a 100.00 g sample of the compound. In this way, each elemental mass in grams is numerically equal to its percent. We convert each mass to an amount in moles, and then determine the simplest integer set of molar amounts. This determination begins by dividing all three molar amounts by the smallest.

$$55.37 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 4.610 \text{ mol C} \div 2.305 \rightarrow 2.000 \text{ mol C} \times 3.000 = 6.000 \text{ mol C}$$

$$7.75 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 7.69 \text{ mol H} \div 2.305 \rightarrow 3.34 \text{ mol H} \times 3.000 = 10.02 \text{ mol H}$$

$$36.88 \text{ g O} \times \frac{1 \text{ mol O}}{15.9994 \text{ g O}} = 2.305 \text{ mol O} \div 2.305 \rightarrow 1.000 \text{ mol O} \times 3.000 = 3.000 \text{ mol O}$$

Thus, the empirical formula of the compound is  $\text{C}_6\text{H}_{10}\text{O}_3$ . The empirical molar mass of this compound is:

$$(6 \times 12.01 \text{ g C}) + (10 \times 1.008 \text{ g H}) + (3 \times 16.00 \text{ g O}) = 72.06 \text{ g} + 10.08 \text{ g} + 48.00 \text{ g} = 130.14 \text{ g/mol}$$

The empirical mass is almost precisely one half the reported molar mass, leading to the conclusion that the molecular formula must be twice the empirical formula in order to double the molar mass. Thus, the molecular formula is  $\text{C}_{12}\text{H}_{20}\text{O}_6$ .

- 5B** Once again, we begin with a 100.00 g sample of the compound. In this way, each elemental mass in grams is numerically equal to its percent. We convert each mass to an amount in moles, and then determine the simplest integer set of molar amounts. This determination begins by dividing all three molar amounts by the smallest.

$$39.56 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 3.294 \text{ mol C} \div 3.294 \rightarrow 1.000 \text{ mol C} \times 3.000 = 3.000 \text{ mol C}$$

$$7.74 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 7.68 \text{ mol H} \div 3.294 \rightarrow 2.33 \text{ mol H} \times 3.000 = 6.99 \text{ mol H}$$

$$52.70 \text{ g O} \times \frac{1 \text{ mol O}}{15.9994 \text{ g O}} = 3.294 \text{ mol O} \div 3.294 \rightarrow 1.000 \text{ mol O} \times 3.000 = 3.000 \text{ mol O}$$

Thus, the empirical formula of the compound is  $\text{C}_3\text{H}_7\text{O}_3$ . The empirical molar mass of this compound is:

$$(3 \times 12.01 \text{ g C}) + (7 \times 1.008 \text{ g H}) + (3 \times 16.00 \text{ g O}) = 36.03 \text{ g} + 7.056 \text{ g} + 48.00 \text{ g} = 91.09 \text{ g/mol}$$

The empirical mass is almost precisely one half the reported molar mass, leading to the conclusion that the molecular formula must be twice the empirical formula in order to double the molar mass. Thus, the molecular formula is  $\text{C}_6\text{H}_{14}\text{O}_6$ .

- 6A** We calculate the amount in moles of each element in the sample (determining the mass of oxygen by difference) and transform these molar amounts to the simplest integral amounts, by first dividing all three by the smallest.

$$2.726 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.06194 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.7440 \text{ g C}$$

$$1.116 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.1239 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.1249 \text{ g H}$$

$$(1.152 \text{ g cmpd} - 0.7440 \text{ g C} - 0.1249 \text{ g H}) = 0.283 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0177 \text{ mol O}$$

$0.06194 \text{ mol C} \div 0.0177 \rightarrow 3.50$   
 $0.1239 \text{ mol H} \div 0.0177 \rightarrow 7.00$   
 $0.0177 \text{ mol O} \div 0.0177 \rightarrow 1.00$ 
} All of these amounts in moles are multiplied by 2 to make them integral. Thus, the empirical formula of isobutyl propionate is  $\text{C}_7\text{H}_{14}\text{O}_2$ .

- 6B** Notice that we do not have to obtain the mass of any element in this compound by difference; there is no oxygen present in the compound. We calculate the amount in mole of each element in the sample and transform these molar amounts to the simplest integral amounts, by first dividing all three by the smallest.

$$3.149 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.07155 \text{ mol C} \div 0.01789 = 3.999 \text{ mol C}$$

$$0.645 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.0716 \text{ mol H} \div 0.01789 = 4.00 \text{ mol H}$$

$$1.146 \text{ g SO}_2 \times \frac{1 \text{ mol SO}_2}{64.065 \text{ g SO}_2} \times \frac{1 \text{ mol S}}{1 \text{ mol SO}_2} = 0.01789 \text{ mol S} \div 0.01789 = 1.000 \text{ mol S}$$

Thus, the empirical formula of thiophene is  $\text{C}_4\text{H}_4\text{S}$ .

- 7A** S<sub>8</sub> For an atom of a free element, the oxidation state is 0 (rule 1).

Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> The sum of all the oxidation numbers in the ion is -2 (rule 2). The O.S. of each oxygen is -2 (rule 6). Thus, the total for all seven oxygens is -14. The total for both chromiums must be +12. Thus, each Cr has an O.S. = +6.

Cl<sub>2</sub>O The sum of all oxidation numbers in the compound is 0 (rule 2). The O.S. of oxygen is -2 (rule 6). The total for the two chlorines must be +2. Thus, each chlorine must have O.S. = +1.

KO<sub>2</sub> The sum for all the oxidation numbers in the compound is 0 (rule 2). The O.S. of potassium is +1 (rule 3). The sum of the oxidation numbers of the two oxygens must be -1. Thus, each oxygen must have O.S. = -1/2.

**7B**  $\underline{\text{S}_2\text{O}}_3^{2-}$  The sum of all the oxidation numbers in the ion is  $-2$  (rule 2). The O.S. of oxygen is  $-2$  (rule 6). Thus, the total for three oxygens must be  $-6$ . The total for both sulfurs must be  $+4$ . Thus, each S has an O.S. =  $+2$ .

$\underline{\text{Hg}_2}\text{Cl}_2$  The O.S. of each Cl is  $-1$  (rule 7). The sum of all O.S. is  $0$  (rule 2). Thus, the total for two Hg is  $+2$  and each Hg has O.S. =  $+1$ .

$\text{KMnO}_4$  The O.S. of each O is  $-2$  (rule 6). Thus, the total for 4 oxygens must be  $-8$ . The K has O.S. =  $+1$  (rule 3). The total of all O.S. is  $0$  (rule 2). Thus, the O.S. of Mn is  $+7$ .

$\text{H}_2\underline{\text{CO}}$  The O.S. of each H is  $+1$  (rule 5), producing a total for both hydrogens of  $+2$ . The O.S. of O is  $-2$  (rule 6). Thus, the O.S. of C is  $0$ , because total of all O.S. is  $0$  (rule 2).

**8A** In each case, we determine the formula *with its accompanying charge* of each ion in the compound. We then produce a formula for the compound in which the total positive charge equals the total negative charge.

lithium oxide	$\text{Li}^+$ and $\text{O}^{2-}$	two $\text{Li}^+$ and one $\text{O}^{2-}$	$\text{Li}_2\text{O}$
tin(II) fluoride	$\text{Sn}^{2+}$ and $\text{F}^-$	one $\text{Sn}^{2+}$ and two $\text{F}^-$	$\text{SnF}_2$
lithium nitride	$\text{Li}^+$ and $\text{N}^{3-}$	three $\text{Li}^+$ and one $\text{N}^{3-}$	$\text{Li}_3\text{N}$

**8B** Using a similar procedure as that provided in 8A

aluminum sulfide	$\text{Al}^{3+}$ and $\text{S}^{2-}$	two $\text{Al}^{3+}$ and three $\text{S}^{2-}$	$\text{Al}_2\text{S}_3$
magnesium nitride	$\text{Mg}^{2+}$ and $\text{N}^{3-}$	three $\text{Mg}^{2+}$ and two $\text{N}^{3-}$	$\text{Mg}_3\text{N}_2$
vanadium(III) oxide	$\text{V}^{3+}$ and $\text{O}^{2-}$	two $\text{V}^{3+}$ and three $\text{O}^{2-}$	$\text{V}_2\text{O}_3$

**9A** The name of each of these ionic compounds is the name of the cation followed by that of the anion. Each anion name is a modified (with the ending “ide”) version of the name of the element. Each cation name is the name of the metal, with the oxidation state appended in Roman numerals in parentheses if there is more than one type of cation for that metal.

$\text{CsI}$  cesium iodide

$\text{CaF}_2$  calcium fluoride

$\text{FeO}$  The O.S. of O =  $-2$  (rule 6). Thus, the O.S. of Fe =  $+2$  (rule 2). The cation is iron(II). The name of the compound is iron(II) oxide.

$\text{CrCl}_3$  The O.S. of Cl =  $-1$  (rule 7). Thus, the O.S. of Cr =  $+3$  (rule 2). The cation is chromium (III). The compound is chromium (III) chloride.

**9B** The name of each of these ionic compounds is the name of the cation followed by that of the anion. Each anion name is a modified (with the ending “ide”) version of the name of the element. Each cation name is the name of the metal, with the oxidation state appended in Roman numerals in parentheses if there is more than one type of cation for that metal.



In the next two compounds, the oxidation state of chlorine is  $-1$  (rule 7) and thus the oxidation state of the metal in each cation must be  $+1$  (rule 2).



<b>10A</b>	$\text{SF}_6$	Both S and F are nonmetals. This is a binary molecular compound: sulfur hexafluoride.
	$\text{HNO}_2$	The $\text{NO}_2^-$ ion is the nitrite ion. Its acid is nitrous acid.
	$\text{Ca}(\text{HCO}_3)_2$	$\text{HCO}_3^-$ is the bicarbonate ion or the hydrogen carbonate ion. This compound is calcium bicarbonate or calcium hydrogen carbonate.
	$\text{FeSO}_4$	The $\text{SO}_4^{2-}$ ion is the sulfate ion. The cation is $\text{Fe}^{2+}$ , iron(II). This compound is iron(II) sulfate.

<b>10B</b>	$\text{NH}_4\text{NO}_3$	The cation is $\text{NH}_4^+$ , ammonium ion. The anion is $\text{NO}_3^-$ , nitrate ion. This compound is ammonium nitrate.
	$\text{PCl}_3$	Both P and Cl are nonmetals. This is a binary molecular compound: phosphorus trichloride.
	$\text{HBrO}$	$\text{BrO}^-$ is hypobromite, this is hypobromous acid.
	$\text{AgClO}_4$	The anion is perchlorate ion, $\text{ClO}_4^-$ . The compound is silver perchlorate.
	$\text{Fe}_2(\text{SO}_4)_3$	The $\text{SO}_4^{2-}$ ion is the sulfate ion. The cation is $\text{Fe}^{3+}$ , iron(III). This compound is iron(III) sulfate.

<b>11A</b>	boron trifluoride	Both elements are nonmetals. This is a binary molecular compound: $\text{BF}_3$ ,
	potassium dichromate	Potassium ion is $\text{K}^+$ , and dichromate ion is $\text{Cr}_2\text{O}_7^{2-}$ . This is $\text{K}_2\text{Cr}_2\text{O}_7$ .
	sulfuric acid	The anion is sulphate, $\text{SO}_4^{2-}$ . There must be two $\text{H}^+$ s. This is $\text{H}_2\text{SO}_4$ .
	calcium chloride	The ions are $\text{Ca}^{2+}$ and $\text{Cl}^-$ . There must be one $\text{Ca}^{2+}$ and two $\text{Cl}^-$ s: $\text{CaCl}_2$ .

<b>11B</b>	aluminum nitrate	Aluminum is $\text{Al}^{3+}$ ; the nitrate ion is $\text{NO}_3^-$ . This is $\text{Al}(\text{NO}_3)_3$ .
	tetraphosphorus decoxide	Both elements are nonmetals. This is a binary molecular compound; $\text{P}_4\text{O}_{10}$
	chromium(III) hydroxide	Chromium(III) ion is $\text{Cr}^{3+}$ ; the hydroxide ion is $\text{OH}^-$ . This is $\text{Cr}(\text{OH})_3$ .
	iodic acid	The halogen “ic” acid has the halogen in a $+5$ oxidation state. This is $\text{HIO}_3$ .

- 12A** (a) Not isomers-molecular formulas are different ( $C_8H_{18}$  vs  $C_9H_{20}$ ).  
(b) Molecules are isomers (same formula  $C_7H_{16}$ )

- 12B** (a) Molecules are isomers (same formula  $C_7H_{14}$ )  
(b) Not isomers-molecular formulas are different ( $C_4H_8$  vs  $C_5H_{10}$ ).

- 13A** (a) The carbon to carbon bonds are all single bonds in this hydrocarbon. This compound is an alkane.  
(b) In this compound, there are only single bonds, and a Cl atom has replaced one H atom. This compound is a chloroalkane.  
(c) The presence of the carboxyl group ( $—CO_2H$ ) in this molecule means that the compound is a carboxylic acid.  
(d) There is a carbon to carbon double bond in this hydrocarbon. This is an alkene.

- 13B** (a) The presence of the hydroxyl group ( $—OH$ ) in this molecule means that this compound is an alcohol.  
(b) The presence of the carboxyl group ( $—CO_2H$ ) in this molecule means that the compound is a carboxylic acid. This molecule also contains the hydroxyl group( $—OH$ ).  
(c) The presence of the carboxyl group ( $—CO_2H$ ) in this molecule means that the compound is a carboxylic acid. As well, a Cl atom has replaced one H atom. This compound is a chloroalkane. The compound is a chloro carboxylic acid.  
(d) There is a carbon to carbon double bond in this compound; hence, it is an alkene. There is also one H atom that has been replaced by a Br atom. This compound is also a bromoalkene.

- 14A** (a) The structure is that of an alcohol with the hydroxyl group on the second carbon atom of a three carbon chain. The compound is 2-propanol (commonly isopropyl alcohol).  
(b) The structure is that of an iodoalkane molecule with the I atom on the first carbon of a three-carbon chain. The compound is called 1-iodopropane.  
(c) The carbon chain in this structure is four carbon atoms long with the end C atom in a carboxyl group. There is also a methyl group on the third carbon in the chain. The compound is 3-methylbutanoic acid.  
(d) The structure is that of a three carbon chain that contains a carbon to carbon double bond. This compound is propene.

- 14B** (a) 2-chloropropane (b) 1,4-dichlorobutane (c) 2-methyl propanoic acid

- 15A** (a) pentane:  $CH_3(CH_2)_3CH_3$  (b) ethanoic acid:  $CH_3CO_2H$   
(c) 1-iodooctane:  $ICH_2(CH_2)_6CH_3$  (d) 1-pentanol:  $CH_2(OH)(CH_2)_3CH_3$

- 15B** (a) propene:  $CH_3CHCH_2$  (b) 1-heptanol:  $CH_2(OH)(CH_2)_5CH_3$

(c) chloroacetic acid:  $\text{CH}_2\text{ClCO}_2\text{H}$ (d) hexanoic acid:  $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$ 

## REVIEW QUESTIONS

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1. (a) The formula unit of a compound is a group of atoms that has atoms of the same type and number as are present in the formula of that compound. For example, if “ $\text{Na}_2$ ” appears in the formula of the compound, then there will be two sodium atoms in the formula unit of that compound.  
(b)  $\text{S}_8$  is a molecule of elemental sulfur. Like several other elements (i.e.  $\text{H}_2$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{P}_4$ ), elemental sulfur exists as molecules rather than as isolated atoms.  
(c) An ionic compound is one that is composed of (positively charged) cations and (negatively charged) anions. Most binary ionic compounds are composed of a metal (which becomes the cation) and a nonmetal (which becomes the anion).  
(d) An oxoacid is an acid that contains the element oxygen, in addition to some other element and the element hydrogen.  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HClO}_4$  all are oxoacids, in which the “other element” is S, N, and Cl, respectively.  
(e) A hydrate is a compound that contains water, rather loosely bound. Usually mild heating of the compound can drive off this water of hydration. Addition of water to the anhydrous salt reforms the hydrate (reversible loss/gain of water)
2. (a) A molecule of an element refers to a small independent particle of that element. Usually this is an atom, but in some cases (notably  $\text{H}_2$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{S}_8$ , and  $\text{P}_4$ ) it is a grouping of two or more atoms.  
(b) The structural formula of a compound not only indicates which atoms are present in the formula unit, but also how they are joined together (represents bonding in the molecule)  
(c) The oxidation state of an element in a compound is an indication of how many electrons each atom of that element has lost (positive oxidation state) or gained (negative). Since oxidation state is determined by a set of rules, rather than by experiment, its connection to the number of electrons actually transferred is rather tenuous. It is used in naming compounds and balancing some chemical equations.  
(d) The determination of the carbon–hydrogen–oxygen content of a compound by combustion analysis involves realizing that all of the carbon has formed carbon dioxide, all of the hydrogen has formed water, and the amount of oxygen present in the original compound must be determined by difference.
3. (a) Ionic compounds are made up of positively charged ions (usually metal ions) and negatively charged ions (usually non-metal ions or polyatomic anions) held together by electrostatic forces of attraction. Molecular compounds are made up of discrete units called molecules. Generally they consist of a small number of nonmetal atoms held together by covalent bonds (sharing of electrons).  
(b) An empirical formula indicates the simplest grouping of atoms that has the same ratio of elements as are present in the compound. The molecular formula indicates the

actual number of atoms of each type present in the molecule. The molecular formula is an integral multiple of the empirical formula.

- (c) A systematic name is based on the elements present in a compound, indicating its composition. The trivial or common name is simply a label for the substance.
- (d) A binary acid consists of hydrogen and one other element. A ternary acid consists of hydrogen, the other element, and the element oxygen: three elements in all.
4. (a) The atomic mass of oxygen is the mass of one (average) atom, 15.9994 u.
- (b) Molecular mass of oxygen is the mass of one (average) molecule of  $O_2$ , 31.9988 u.
- (c) The molar mass of molecular oxygen is the mass of one mole of oxygen molecules, 31.9988 g. The molar mass of atomic oxygen is the mass of one mole of oxygen atoms, 15.9994 g.
5. (a) A nitroglycerine molecule,  $C_3H_5(NO_3)_3$ , contains 3 C atoms, 5 H atoms, 3 N atoms, and  $3 \times 3 = 9$  O atoms, for a total of  $(3 + 5 + 3 + 9) = 20$  atoms.

- (b) Each molecule of  $C_2H_6$  contains 6 H atoms and 2 C atoms, 8 atoms total.

$$\text{Number of atoms} = 0.00102 \text{ mol } C_2H_6 \times \frac{6.022 \times 10^{23} C_2H_6 \text{ molecules}}{1 \text{ mol } C_2H_6} \times \frac{8 \text{ atoms}}{C_2H_6 \text{ molecule}} \\ = 4.91 \times 10^{21} \text{ atoms}$$

$$(c) \text{ number of F atoms} = 12.15 \text{ mol } C_2HBrClF_3 \times \frac{3 \text{ mol F}}{1 \text{ mol } C_2HBrClF_3} \times \frac{6.022 \times 10^{23} \text{ F atoms}}{1 \text{ mol F atoms}} \\ = 2.195 \times 10^{25} \text{ F atoms}$$

6. (a) To convert the amount in moles to mass, we need the molar mass of  $N_2O_4$ .

$$\text{molar mass } N_2O_4 = \left( 2 \text{ mol N} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} \right) + \left( 4 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} \right) = 92.02 \text{ g/mol } N_2O_4$$

$$\text{mass } N_2O_4 = 7.34 \text{ mol } N_2O_4 \times \frac{92.02 \text{ g } N_2O_4}{1 \text{ mol}} = 675 \text{ g } N_2O_4$$

$$(b) \text{ mass of } O_2 = 3.16 \times 10^{24} O_2 \text{ molecules} \times \frac{1 \text{ mol } O_2}{6.022 \times 10^{23} \text{ molecules}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 168 \text{ g } O_2$$

$$(c) \text{ molar mass } CuSO_4 \cdot 5H_2O = 63.5 \text{ g Cu} + 32.1 \text{ g S} + (9 \times 16.0 \text{ g O}) + (10 \times 1.01 \text{ g H}) \\ = 249.7 \text{ g/mol } CuSO_4 \cdot 5H_2O$$

$$\text{mass of } CuSO_4 \cdot 5H_2O = 18.6 \text{ mol} \times \frac{249.7 \text{ g } CuSO_4 \cdot 5H_2O}{1 \text{ mol}} = 4.64 \times 10^3 \text{ g } CuSO_4 \cdot 5H_2O$$

$$(d) \text{ molar mass } C_2H_4(OH)_2 = (2 \times 12.01 \text{ g C}) + (6 \times 1.01 \text{ g H}) + (2 \times 16.00 \text{ g O}) = 62.08 \text{ g/mol}$$

$$\text{mass of } \text{C}_2\text{H}_4(\text{OH})_2 = 4.18 \times 10^{24} \text{ molecules} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \times \frac{62.08 \text{ g}}{1 \text{ mol } \text{C}_2\text{H}_4(\text{OH})_2}$$

$$= 431 \text{ g } \text{C}_2\text{H}_4(\text{OH})_2$$

7. (a) amount of  $\text{Br}_2 = 8.08 \times 10^{22} \text{ Br}_2 \text{ molecules} \times \frac{1 \text{ mole } \text{Br}_2}{6.022 \times 10^{23} \text{ Br}_2 \text{ molecules}}$

$$= 0.134 \text{ mol } \text{Br}_2$$

(b) amount of  $\text{Br}_2 = 2.17 \times 10^{24} \text{ Br atoms} \times \frac{1 \text{ Br}_2 \text{ molecule}}{2 \text{ Br atoms}} \times \frac{1 \text{ mole } \text{Br}_2}{6.022 \times 10^{23} \text{ Br}_2 \text{ molecules}}$

$$= 1.80 \text{ mol } \text{Br}_2$$

(c) amount of  $\text{Br}_2 = 11.3 \text{ kg } \text{Br}_2 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } \text{Br}_2}{159.8 \text{ g } \text{Br}_2} = 70.7 \text{ mol } \text{Br}_2$

(d) amount of  $\text{Br}_2 = 2.65 \text{ L } \text{Br}_2 \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{3.10 \text{ g } \text{Br}_2}{1 \text{ mL } \text{Br}_2} \times \frac{1 \text{ mol } \text{Br}_2}{159.8 \text{ g } \text{Br}_2} = 51.4 \text{ mol } \text{Br}_2$

8. (a) molecular mass (mass of one molecule).

$$\text{C}_5\text{H}_{11}\text{NO}_2\text{S} = (5 \times 12.0 \text{ u C}) + (11 \times 1.01 \text{ u H}) + 14.0 \text{ u N} + (2 \times 16.0 \text{ u O}) + 32.1 \text{ u S}$$

$$= 149.2 \text{ u/C}_5\text{H}_{11}\text{NO}_2\text{S molecule}$$

(b) Since there are 11 H atoms in each  $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$  molecule, there are 11 moles of H atoms in each mole of  $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$  molecules

(c) mass C =  $1 \text{ mol } \text{C}_5\text{H}_{11}\text{NO}_2\text{S} \times \frac{5 \text{ mol C}}{1 \text{ mol } \text{C}_5\text{H}_{11}\text{NO}_2\text{S}} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 60.055 \text{ g C}$

(d) no. C atoms =  $9.07 \text{ mol } \text{C}_5\text{H}_{11}\text{NO}_2\text{S} \times \frac{5 \text{ mol C}}{1 \text{ mol } \text{C}_5\text{H}_{11}\text{NO}_2\text{S}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol C}}$

$$= 2.73 \times 10^{25} \text{ C atoms}$$

9. The information obtained in the course of calculating the molar mass is used to determine the mass percent of H in decane.

$$\text{molar mass } \text{C}_{10}\text{H}_{22} = \left( \frac{10 \text{ mol C}}{1 \text{ mol } \text{C}_{10}\text{H}_{22}} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} \right) + \left( \frac{22 \text{ mol H}}{1 \text{ mol } \text{C}_{10}\text{H}_{22}} \times \frac{1.00794 \text{ g H}}{1 \text{ mol H}} \right)$$

$$= \frac{120.11 \text{ g C}}{1 \text{ mol } \text{C}_{10}\text{H}_{22}} + \frac{22.1747 \text{ g H}}{1 \text{ mol } \text{C}_{10}\text{H}_{22}} = \frac{142.28 \text{ g}}{1 \text{ mol } \text{C}_{10}\text{H}_{22}}$$

$$\% \text{H} = \frac{22.1747 \text{ g H/mol decane}}{142.28 \text{ g } \text{C}_{10}\text{H}_{22}/\text{mol decane}} \times 100\% = 15.585\% \text{ H}$$

- 10.** Determine the mass of O in a mol of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  and the molar mass of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ .

$$\text{mass O/mol Cu}_2(\text{OH})_2\text{CO}_3 = \frac{5 \text{ mol O}}{1 \text{ mol Cu}_2(\text{OH})_2\text{CO}_3} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 80.00 \text{ g O/mol Cu}_2(\text{OH})_2\text{CO}_3$$

$$\begin{aligned} \text{molar mass Cu}_2(\text{OH})_2\text{CO}_3 &= (2 \times 63.55 \text{ g Cu}) + (5 \times 16.00 \text{ g O}) + (2 \times 1.01 \text{ g H}) + 12.01 \text{ g C} \\ &= 221.13 \text{ g/mol Cu}_2(\text{OH})_2\text{CO}_3 \end{aligned}$$

$$\text{Percent oxygen in sample} = \frac{80.00 \text{ g}}{221.13 \text{ g}} \times 100\% = 36.18\% \text{ O}$$

- 11.** Determine the mass of a mole of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and then the mass of water in a mole.

$$\begin{aligned} \text{molar mass Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} &= 52.00 \text{ g Cr} + (3 \times 14.01 \text{ g N}) + (18 \times 16.00 \text{ g O}) + (18 \times 1.01 \text{ g H}) \\ &= 400.2 \text{ g/mol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \end{aligned}$$

$$\text{mass H}_2\text{O} = \frac{9 \text{ mol H}_2\text{O}}{1 \text{ mol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 162.2 \text{ g H}_2\text{O/mol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$$

$$\frac{162.2 \text{ g H}_2\text{O/mol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}}{400.2 \text{ g/mol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} \times 100\% = 40.53\% \text{ H}_2\text{O}$$

- 12.** In each case, we first determine the molar mass of the compound, and then the mass of the indicated element in one mole of the compound. Finally, we determine the percent by mass of the indicated element to four significant figures.

$$\begin{aligned} \text{(a) molar mass Pb}(\text{C}_2\text{H}_5)_4 &= 207.2 \text{ g Pb} + (8 \times 12.01 \text{ g C}) + (20 \times 1.008 \text{ g H}) \\ &= 323.4 \text{ g/mol Pb}(\text{C}_2\text{H}_5)_4 \end{aligned}$$

$$\text{mass Pb/mol Pb}(\text{C}_2\text{H}_5)_4 = \frac{1 \text{ mol Pb}}{1 \text{ mol Pb}(\text{C}_2\text{H}_5)_4} \times \frac{207.2 \text{ g Pb}}{1 \text{ mol Pb}} = 207.2 \text{ g Pb/mol Pb}(\text{C}_2\text{H}_5)_4$$

$$\% \text{ Pb} = \frac{207.2 \text{ g Pb}}{323.4 \text{ g Pb}(\text{C}_2\text{H}_5)_4} \times 100\% = 64.07\% \text{ Pb}$$

$$\begin{aligned} \text{(b) molar mass Fe}_4[\text{Fe}(\text{CN})_6]_3 &= (7 \times 55.85 \text{ g Fe}) + (18 \times 12.01 \text{ g C}) + (18 \times 14.01 \text{ g N}) \\ &= 859.3 \text{ g/mol Fe}_4[\text{Fe}(\text{CN})_6]_3 \end{aligned}$$

$$\frac{\text{mass Fe}}{\text{mol Fe}_4[\text{Fe}(\text{CN})_6]_3} = \frac{7 \text{ mol Fe}}{1 \text{ mol Fe}_4[\text{Fe}(\text{CN})_6]_3} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} = 391.0 \text{ g Fe/mol Fe}_4[\text{Fe}(\text{CN})_6]_3$$

$$\% \text{ Fe} = \frac{391.0 \text{ g Fe}}{859.3 \text{ g Fe}_4[\text{Fe}(\text{CN})_6]_3} \times 100\% = 45.50\% \text{ Fe}$$

(c) molar mass  $C_{55}H_{72}MgN_4O_5$

$$= (55 \times 12.011 \text{ g C}) + (72 \times 1.008 \text{ g H}) + (1 \times 24.305 \text{ g Mg}) + (4 \times 14.01 \text{ g N}) + (5 \times 15.999 \text{ g O}) \\ = 893.521 \text{ g/mol } C_{55}H_{72}MgN_4O_5$$

$$\frac{\text{mass Mg}}{\text{mol } C_{55}H_{72}MgN_4O_5} = \frac{1 \text{ mol Mg}}{1 \text{ mol } C_{55}H_{72}MgN_4O_5} \times \frac{24.305 \text{ g Mg}}{1 \text{ mol Mg}} = \frac{24.305 \text{ g Mg}}{\text{mol } C_{55}H_{72}MgN_4O_5}$$

$$\% \text{Mg} = \frac{24.305 \text{ g Mg}}{893.521 \text{ g } C_{55}H_{72}MgN_4O_5} \times 100\% = 2.7201\% \text{ Mg}$$

13. For  $SO_2$  and  $Na_2S$ , a mole of each contains a mole of S and two moles of another element; in the case of  $SO_2$  the other element (oxygen) has a smaller atomic mass than the other element in  $Na_2S$  (Na), causing  $SO_2$  to have a higher mass percent sulfur. For  $S_2Cl_2$  and  $Na_2S_2O_3$ , a mole of each contains two moles of S; for  $S_2Cl_2$  the rest of the mole has a mass of 71.0 g, while for  $Na_2S_2O_3$  it would be  $(2 \times 23) + (3 \times 16) = 94$  g. Sulfur makes up the greater proportion of the mass in  $S_2Cl_2$ , giving it the larger percent of S. Now we compare  $SO_2$  and  $S_2Cl_2$ :  $S_2O_4$  has the same mass proportions as does  $SO_2$  but also has the two moles of S, as does  $S_2Cl_2$ . In  $S_2Cl_2$  the remainder of a mole has a mass of 71.0 g, while in  $S_2O_4$  the remainder of a mole would be  $4 \times 16.0 = 64.0$  g. Thus,  $SO_2$  has the highest percent of S so far. For  $CH_3CH_2SH$  compared to  $SO_2$ , we see that both compounds have one S-atom,  $SO_2$  has two O-atoms (each with a molar mass of  $\sim 16 \text{ g mol}^{-1}$ ) and  $CH_3CH_2SH$  effectively has two  $CH_3$  groups (each  $CH_3$  group with a mass of  $\sim 15 \text{ g mol}^{-1}$ ). Thus,  $CH_3CH_2SH$  has the highest percentage sulfur by mass of the compounds listed.

14. Determine the % oxygen by difference.  $\% O = 100.00\% - 45.27\% C - 9.50\% H = 45.23\% O$

$$\text{no. mol O} = 45.23 \text{ g} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.827 \text{ mol O} \quad \div 2.827 \rightarrow 1.000 \text{ mol O}$$

$$\text{no mol C} = 45.27 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.769 \text{ mol C} \quad \div 2.827 \rightarrow 1.333 \text{ mol C}$$

$$\text{no. mol H} = 9.50 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 9.42 \text{ mol H} \quad \div 2.827 \rightarrow 3.33 \text{ mol H}$$

Multiply all amounts by 3 to obtain integers. Empirical formula is  $C_4H_{10}O_3$ .

15. We base our calculation on 100.0 g of monosodium glutamate.

$$13.6 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 0.592 \text{ mol Na} \quad \div 0.592 \rightarrow 1.00 \text{ mol Na}$$

$$35.5 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.96 \text{ mol C} \quad \div 0.592 \rightarrow 5.00 \text{ mol C}$$

$$4.8 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 4.8 \text{ mol H} \quad \div 0.592 \rightarrow 8.1 \text{ mol H}$$

$$8.3 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.59 \text{ mol N} \quad \div 0.592 \rightarrow 1.0 \text{ mol N}$$

$$37.8 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.36 \text{ mol O} \quad \div 0.592 \rightarrow 3.99 \text{ mol O}$$

Empirical formula :  $\text{NaC}_5\text{H}_8\text{NO}_4$

16. First determine the empirical formula. Begin by determining the percent oxygen by difference.  $\% \text{O} = 100\% - 57.83\% \text{C} - 3.64\% \text{H} = 38.53\% \text{O}$

$$\text{no. mol O} = 38.53 \text{ g} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.408 \text{ mol O} \quad \div 2.408 \rightarrow 1.000 \text{ mol O}$$

$$\text{no. mol C} = 57.83 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.815 \text{ mol C} \quad \div 2.408 \rightarrow 2.000 \text{ mol C}$$

$$\text{no. mol H} = 3.64 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 3.61 \text{ mol H} \quad \div 2.408 \rightarrow 1.50 \text{ mol H}$$

Empirical formula is  $\text{C}_4\text{H}_3\text{O}_2$ .

The empirical molecular mass =  $(4 \times 12.0 \text{ u C}) + (3 \times 1.0 \text{ u H}) + (2 \times 16.0 \text{ u O}) = 83.0 \text{ u}$

This empirical molecular mass is one-half of the measured molecular mass. Thus, the molecular formula of terephthalic acid is twice the empirical formula:  $\text{C}_8\text{H}_6\text{O}_4$

17. (a) First determine the masses of carbon and hydrogen in the original sample.

$$\text{mass C} = 6.029 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g}} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.1370 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 1.646 \text{ g C}$$

$$\text{mass H} = 1.709 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.1897 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.1912 \text{ g H}$$

Then the percents of the two elements in the compound are computed.

$$\% \text{C} = \frac{1.646 \text{ g C}}{2.174 \text{ g cmpd}} \times 100\% = 75.71\% \text{ C} \quad \% \text{ H} = \frac{0.1912 \text{ g H}}{2.174 \text{ g cmpd}} \times 100\% = 8.795\% \text{ H}$$

The % O is determined by difference.

$$\% \text{O} = 100\% - 75.71\% \text{ C} - 8.795\% \text{ H} = 15.50\% \text{ O}$$

- (b) In part (a), we determined the number of moles of C and H in the original sample of the compound. We can determine the mass of oxygen in that sample by difference, and then the number of moles of oxygen in that sample. We divide each of these numbers of moles by the smallest number to determine the empirical formula.

$$\text{mass O} = 2.174 \text{ g cmpd} - 1.646 \text{ g C} - 0.1912 \text{ g H} = 0.337 \text{ g O}$$

$$\text{mol O} = 0.337 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0211 \text{ mol O} \quad \div 0.02111 \rightarrow 1.00 \text{ mol O}$$

$$0.1897 \text{ mol H} \quad \div 0.02111 \rightarrow 8.99 \text{ mol H}$$

$$0.1370 \text{ mol C} \quad \div 0.02111 \rightarrow 6.49 \text{ mol C}$$

Multiply all amounts by 2 to obtain integers; the empirical formula of ibuprofen is  $\text{C}_{13}\text{H}_{18}\text{O}_2$ .

18. The element chromium has an atomic mass of 52.0 u. Thus, there can only be one chromium atom per formula unit of the compound. (Two atoms of chromium have a mass of 104 u, more than the formula mass of the compound.) Three of the four remaining atoms in the formula unit must be oxygen. Thus, the oxide is  $\text{CrO}_3$ , chromium(VI) oxide.
19.  $\text{SO}_3$  (40.05% S) and  $\text{S}_2\text{O}$  (80.0 % S) (2 O atoms ~ 1 S atom in terms of atomic masses)
- 20.
- |                      |                        |                      |                      |
|----------------------|------------------------|----------------------|----------------------|
| (a) $\text{Pb}^{2+}$ | lead(II) ion           | (b) $\text{Co}^{3+}$ | cobalt(III) ion      |
| (c) $\text{Ba}^{2+}$ | barium ion             | (d) $\text{Cr}^{2+}$ | chromium(II) ion     |
| (e) $\text{IO}_4^-$  | periodate ion          | (f) $\text{ClO}_2^-$ | chlorite ion         |
| (g) $\text{Au}^{3+}$ | gold(III) ion          | (h) $\text{HSO}_3^-$ | hydrogen sulfite ion |
| (i) $\text{HCO}_3^-$ | hydrogen carbonate ion | (j) $\text{CN}^-$    | cyanide ion          |
- 21.
- |                    |                          |                            |                      |
|--------------------|--------------------------|----------------------------|----------------------|
| (a) $\text{KBr}$   | potassium bromide        | (b) $\text{SrCl}_2$        | strontium chloride   |
| (c) $\text{ClF}_3$ | chlorine trifluoride     | (d) $\text{N}_2\text{O}_4$ | dinitrogen tetroxide |
| (e) $\text{PCl}_5$ | phosphorus pentachloride |                            |                      |
- 22.
- |                                  |                   |                    |                   |
|----------------------------------|-------------------|--------------------|-------------------|
| (a) $\text{KCN}$                 | potassium cyanide | (b) $\text{HClO}$  | hypochlorous acid |
| (c) $(\text{NH}_4)_2\text{SO}_4$ | ammonium sulfate  | (d) $\text{KIO}_3$ | potassium iodate  |

- 23.** The desired oxidation state is given first, followed by the method used to assign the oxidation state.
- (a)  $\text{Zn} = 0$       Oxidation state (O.S.) of an uncombined, neutral element is 0.
- (b)  $\text{S} = -2$  in  $\text{BaS}$       The O.S. of Ba in its compounds is +2.  
Oxidation states in a compound must sum to zero.
- (c)  $\text{N} = +4$  in  $\text{NO}_2$       The O.S. of O in its compounds is -2 (in most cases).
- (d)  $\text{N} = +3$  in  $\text{HNO}_2$       The O.S. of H in molecular compounds is +1; that of O is -2.
- (e)  $\text{V} = +4$  in  $\text{VO}^{2+}$       The O.S. of O in its compounds is -2. O.S. in a polyatomic ion must sum to the charge on that ion.
- (f)  $\text{P} = +5$  in  $\text{H}_2\text{PO}_4^-$       The O.S. of H in its compounds is +1; that of O is -2.  
O.S. in a polyatomic ion must sum to the charge on that ion.
- 24.**
- |   |                       |   |                            |
|---|-----------------------|---|----------------------------|
| (a) $\text{MgBr}_2$                               | magnesium bromide     | (b) $\text{BaO}$                          | barium oxide               |
| (c) $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ | mercury(II) acetate   | (d) $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ | iron(III) oxalate          |
| (e) $\text{Sr}(\text{ClO}_4)_2$                   | strontium perchlorate | (f) $\text{KHSO}_4$                       | potassium hydrogen sulfate |
| (g) $\text{NCl}_3$                                | nitrogen trichloride  | (h) $\text{BrF}_5$                        | bromine pentafluoride      |
- 25.**
- |                           |                   |                             |                |
|---------------------------|-------------------|-----------------------------|----------------|
| (a) $\text{HClO}_2$       | chlorous acid     | (b) $\text{H}_2\text{SO}_3$ | sulfurous acid |
| (c) $\text{H}_2\text{Se}$ | hydroselenic acid | (d) $\text{HNO}_2$          | nitrous acid   |
- 26.**
- |                             |                 |                             |               |
|-----------------------------|-----------------|-----------------------------|---------------|
| (a) $\text{HI}$ (aq)        | hydroiodic acid | (b) $\text{HNO}_3$          | nitric acid   |
| (c) $\text{H}_3\text{PO}_4$ | phosphoric acid | (d) $\text{H}_2\text{SO}_4$ | sulfuric acid |
- 27.** Answer is (b), 2-butanol is the most appropriate name for this molecule. It has a four carbon atom chain with a hydroxyl group on the carbon second from the end.
- 28.** Answer (c), butanoic acid is the most appropriate name for this molecule. It has a four carbon atom chain with an acid group on the 1<sup>st</sup> carbon (terminal carbon atom)

## EXERCISES

### Representing Molecules

- 29.**
- |  |                                       |                               |
|--|---------------------------------------|-------------------------------|
| (a) $\text{H}_2\text{O}_2$                       | (b) $\text{CH}_3\text{CH}_2\text{Cl}$ | (c) $\text{P}_4\text{O}_{10}$ |
| (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ | (e) $\text{HCO}_2\text{H}$            |                               |
- 31.**
- |                                       |  |                            |
|---------------------------------------|--|----------------------------|
| (b) $\text{CH}_3\text{CH}_2\text{Cl}$ | (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ | (e) $\text{HCO}_2\text{H}$ |
|---------------------------------------|--|----------------------------|

## The Avogadro Constant and the Mole

33. The greatest number of S atoms is contained in the compound with the greatest number of moles of S. The solid sulfur contains  $8 \times 0.12 \text{ mol} = 0.96 \text{ mol S atoms}$ . There are  $0.50 \times 2 \text{ mol S atoms}$  in 0.50 mol  $\text{S}_2\text{O}$ . There is slightly greater than 1 mole (64.1 g) of  $\text{SO}_2$  in 65 g, and thus a bit more than 1 mole of S atoms. The molar mass of thiophene is:  $(4 \text{ mol C} \times 12.0 \text{ g C}) + (4 \text{ mol H} \times 1.0 \text{ g H}) + (1 \text{ mol S} \times 32.1 \text{ g S}) = 84.1 \text{ g}$ ; 75 mL has a mass of 79.8 g and thus contains less than 1 mole of S. So, 65 g  $\text{SO}_2$  has the greatest number of S atoms.

35. (a)  $\text{P mass} = 6.25 \times 10^{-2} \text{ mol P}_4 \times \frac{4 \text{ mol P}}{1 \text{ mol P}_4} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} = 7.74 \text{ g P}$

- (b) First we need the molar mass of  $\text{C}_{18}\text{H}_{36}\text{O}_2$ , stearic acid:

$$\begin{aligned} \text{molar mass} &= (18 \text{ mol C} \times 12.01 \text{ g C}) + (36 \text{ mol H} \times 1.01 \text{ g H}) + (2 \text{ mol O} \times 16.00 \text{ g O}) \\ &= 284.5 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{Stearic acid mass} &= 4.03 \times 10^{24} \text{ molecules} \times \frac{1 \text{ mole}}{6.022 \times 10^{23} \text{ molecules}} \times \frac{284.5 \text{ g}}{1 \text{ mole } \text{C}_{18}\text{H}_{36}\text{O}_2} \\ &= 1.90 \times 10^3 \text{ g stearic acid.} \end{aligned}$$

- (c) molar mass =  $(6 \text{ mol C} \times 12.01 \text{ g C}) + (14 \text{ mol H} \times 1.01 \text{ g H}) + (2 \text{ mol N} \times 14.00 \text{ g N}) + (2 \text{ mol O} \times 16.00 \text{ g O}) = 146.2 \text{ g/mol}$

$$\text{lysine mass} = 1.15 \text{ mol N} \times \frac{1 \text{ mol } \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2}{2 \text{ mol N}} \times \frac{146.2 \text{ g lysine}}{1 \text{ mol lysine}} = 84.1 \text{ g lysine}$$

37. (a)  $\text{moles S}_8 = 0.568 \text{ mm}^3 \times \frac{1 \text{ cm}^3}{1000 \text{ mm}^3} \times \frac{2.07 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol S}}{32.07 \text{ g}} \times \frac{1 \text{ mol S}_8}{8 \text{ mol S}} = 4.58 \times 10^{-6} \text{ mol S}_8$

(b)  $\text{no. S atoms} = 4.58 \times 10^{-6} \text{ mol S}_8 \times \frac{8 \text{ mol S}}{1 \text{ mol S}_8} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol S}} = 2.21 \times 10^{19} \text{ S atoms}$

## Chemical Formulas

39. For glucose (blood sugar),  $\text{C}_6\text{H}_{12}\text{O}_6$ ,

- (a) FALSE

The percentages by mass of C and O are *different* than in CO. For one thing, CO contains no hydrogen.

**(b) TRUE**

In dihydroxyacetone,  $(\text{CH}_2\text{OH})_2\text{CO}$  or  $\text{C}_3\text{H}_6\text{O}_3$ , the ratio of C : H : O = 3 : 6 : 3 or alternatively 1 : 2 : 1. In glucose, this ratio is C : H : O = 6 : 12 : 6 or alternatively 1 : 2 : 1. Thus, the ratios are the *same*.

**(c) FALSE**

The proportions, by number of atoms, of C and O are the same in glucose. Since, however, C and O have different molar masses, their proportions by mass must be *different*.

**(d) FALSE**

Each mole of glucose contains  $(12 \times 1.01) = 12.1$  g H. But each mole also contains 72.0 g C and 96.0 g O. Thus, the highest percentage, by mass, is that of O. The highest percentage, by number of atoms, is that of H.

**41. (a)** A formula unit of  $\text{C}_2\text{HBrClF}_3$  contains:

2 C atoms      1 H atom      1 Br atom      1 Cl atom      3 F atoms

For a total of  $2+1+1+1+3 = 8$  atoms

**(b)** 
$$\frac{\text{no. F atoms}}{\text{no. C atoms}} = \frac{3 \text{ F atoms}}{2 \text{ C atoms}}$$

**(c)** 
$$\frac{\text{mass Br}}{\text{mass F}} = \frac{1 \text{ mol Br}}{3 \text{ mol F}} \times \frac{79.90 \text{ g Br}}{1 \text{ mol Br}} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 1.402 \text{ g Br/g F}$$

**(d)** The element present in greatest mass percent is the one with the greatest mass in one mole. To determine that, we determine molar mass.

$$\begin{aligned} \text{molar mass} &= (2 \text{ mol C} \times 12.01 \text{ g C}) + (1 \text{ mol H} \times 1.008 \text{ g H}) + (1 \text{ mol Br} \times 79.90 \text{ g Br}) \\ &\quad + (1 \text{ mol Cl} \times 35.45 \text{ g Cl}) + (3 \text{ mol F} \times 19.00 \text{ g F}) \\ &= 24.02 \text{ g C} + 1.008 \text{ g H} + 79.90 \text{ g Br} + 35.45 \text{ g Cl} + 57.00 \text{ g F} = 197.38 \text{ g/mol} \end{aligned}$$

Bromine is present in greatest mass percent.

**(e)** compound mass =  $1.00 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} \times \frac{1 \text{ mol cmpd}}{3 \text{ mol F}} \times \frac{197.38 \text{ g cmpd}}{1 \text{ mol cmpd}} = 3.46 \text{ g cmpd}$

## Percent Composition of Compounds

**43.** The information obtained in the course of calculating the molar mass is used to determine the mass percent of each element in stearic acid,  $\text{C}_{18}\text{H}_{36}\text{O}_2$ , abbreviated as SA below. Molar mass  $\text{C}_8\text{H}_{18} = M$

$$M = \left( \frac{18 \text{ mol C}}{1 \text{ mol SA}} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} \right) + \left( \frac{36 \text{ mol H}}{1 \text{ mol SA}} \times \frac{1.00794 \text{ g H}}{1 \text{ mol H}} \right) + \left( \frac{2 \text{ mol O}}{1 \text{ mol SA}} \times \frac{15.9994 \text{ g O}}{1 \text{ mol O}} \right)$$

$$M = \frac{216.20 \text{ g C}}{1 \text{ mol SA}} + \frac{36.2858 \text{ g H}}{1 \text{ mol SA}} + \frac{31.9988 \text{ g O}}{1 \text{ mol SA}} = \frac{284.48 \text{ g}}{1 \text{ mol SA}}$$

$$\%C = \frac{216.20 \text{ g C/mol SA}}{284.48 \text{ g C/mol SA}} \times 100\% = 75.998\% \text{ C};$$

$$\%H = \frac{36.2858 \text{ g H/mol SA}}{284.48 \text{ g SA/mol SA}} \times 100\% = 12.755\% \text{ H}$$

$$\%O = \frac{31.9988 \text{ g O/mol SA}}{284.48 \text{ g SA/mol SA}} \times 100\% = 11.248\% \text{ O}$$

45. (a)  $\%Zr = \frac{1 \text{ mol Zr}}{1 \text{ mol ZrSiO}_4} \times \frac{1 \text{ mol ZrSiO}_4}{183.31 \text{ g ZrSiO}_4} \times \frac{91.224 \text{ g Zr}}{1 \text{ mol Zr}} \times 100\% = 49.765\% \text{ Zr}$

(b)  $\%Be = \frac{3 \text{ mol Fe}}{1 \text{ mol Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}} \times \frac{1 \text{ mol Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}}{537.502 \text{ g Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}} \times \frac{9.01218 \text{ g Be}}{1 \text{ mol Be}} \times 100\%$

$$\% \text{ Be} = 5.03004 \% \text{ Be}$$

(c)  $\%Fe = \frac{3 \text{ mol Fe}}{1 \text{ mol Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}} \times \frac{1 \text{ mol Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}{497.753 \text{ g Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}} \times \frac{55.847 \text{ g Fe}}{1 \text{ mol Fe}} \times 100\%$

$$\% \text{ Fe} = 33.659\% \text{ Fe}$$

(d)  $\%S = \frac{1 \text{ mol S}}{1 \text{ mol Na}_4\text{SSi}_3\text{Al}_3\text{O}_{12}} \times \frac{1 \text{ mol Na}_4\text{SSi}_3\text{Al}_3\text{O}_{12}}{481.219 \text{ g Na}_4\text{SSi}_3\text{Al}_3\text{O}_{12}} \times \frac{32.066 \text{ g S}}{1 \text{ mol S}} \times 100\%$

$$\% \text{ S} = 6.6635\% \text{ S}$$

47. Oxide with the largest %Cr will have the largest number of moles of Cr per mole of oxygen.

$$\text{CrO: } \frac{1 \text{ mol Cr}}{1 \text{ mol O}} = 1 \text{ mol Cr/mol O} \quad \text{Cr}_2\text{O}_3: \frac{2 \text{ mol Cr}}{3 \text{ mol O}} = 0.667 \text{ mol Cr/mol O}$$

$$\text{CrO}_2: \frac{1 \text{ mol Cr}}{2 \text{ mol O}} = 0.500 \text{ mol Cr/mol O} \quad \text{CrO}_3: \frac{1 \text{ mol Cr}}{3 \text{ mol O}} = 0.333 \text{ mol Cr/mol O}$$

Arranged in order of increasing %Cr: CrO<sub>3</sub> < CrO<sub>2</sub> < Cr<sub>2</sub>O<sub>3</sub> < CrO

## Chemical Formulas from Percent Composition

49. Convert each percentage into the mass in 100.00 g, and then to the moles of that element.

$$93.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.803 \text{ mol C} \quad \div 6.23 \rightarrow 1.25 \text{ mol C}$$

$$6.29 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 6.23 \text{ mol H} \quad \div 6.23 \rightarrow 1.00 \text{ mol H}$$

Empirical formula is C<sub>5</sub>H<sub>4</sub>, and molar mass [(5 × 12.0 g C)+(4 × 1.0 g H)] = 64.0 g/mol.

Since this empirical molar mass is one-half of the 128 g/mol correct molar mass, the molecular formula must be twice the empirical formula. Molecular formula: C<sub>10</sub>H<sub>8</sub>

**51. (a)**  $74.01\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} = 6.162\text{ mol C} \div 1.298 \rightarrow 4.747\text{ mol C}$

$$5.23\text{ g H} \times \frac{1\text{ mol H}}{1.01\text{ g H}} = 5.18\text{ mol H} \div 1.298 \rightarrow 3.99\text{ mol H}$$

$$20.76\text{ g O} \times \frac{1\text{ mol O}}{16.00\text{ g O}} = 1.298\text{ mol O} \div 1.298 \rightarrow 1.00\text{ mol O}$$

Multiply each of the mole numbers by 4 to obtain an empirical formula of  $\text{C}_{19}\text{H}_{16}\text{O}_4$ .

**(b)**  $30.20\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} = 2.515\text{ mol C} \div 0.6288 \rightarrow 4.000\text{ mol C}$

$$5.07\text{ g H} \times \frac{1\text{ mol H}}{1.01\text{ g H}} = 5.02\text{ mol H} \div 0.6288 \rightarrow 7.98\text{ mol H}$$

$$44.58\text{ g Cl} \times \frac{1\text{ mol Cl}}{35.45\text{ g Cl}} = 1.258\text{ mol Cl} \div 0.6288 \rightarrow 2.001\text{ mol Cl}$$

$$20.16\text{ g S} \times \frac{1\text{ mol S}}{32.06\text{ g S}} = 0.6288\text{ mol S} \div 0.6288 \rightarrow 1.000\text{ mol S}$$

The empirical formula is  $\text{C}_4\text{H}_8\text{Cl}_2\text{S}$ .

- 53.** Determine the mass of oxygen by difference. Then convert all masses to amounts in moles.  
 $\text{oxygen mass} = 100.00\text{ g} - 73.27\text{ g C} - 3.84\text{ g H} - 10.68\text{ g N} = 12.21\text{ g O}$

$$\text{amount C} = 73.27\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} = 6.100\text{ mol C} \div 0.7625 \rightarrow 8.000\text{ mol C}$$

$$\text{amount H} = 3.84\text{ g H} \times \frac{1\text{ mol H}}{1.008\text{ g H}} = 3.81\text{ mol H} \div 0.7625 \rightarrow 5.00\text{ mol H}$$

$$\text{amount N} = 10.68\text{ g N} \times \frac{1\text{ mol N}}{14.007\text{ g N}} = 0.7625\text{ mol N} \div 0.7625 \rightarrow 1.000\text{ mol N}$$

$$\text{amount O} = 12.21\text{ g O} \times \frac{1\text{ mol O}}{15.999\text{ g O}} = 0.7632\text{ mol O} \div 0.7625 \rightarrow 1.001\text{ mol O}$$

The empirical formula is  $\text{C}_8\text{H}_5\text{NO}$ , which has an empirical mass of

$$(8\text{ mol C} \times 12.0\text{ u C}) + (5\text{ mol H} \times 1.0\text{ u H}) + (1\text{ mol N} \times 14.0\text{ u N}) + (1\text{ mol O} \times 16.0\text{ u O}) = 131\text{ u.}$$

This is almost exactly half the molecular mass of 262.3 u.

Thus, the molecular formula is twice the empirical formula and is  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ .

- 55.** In each 100 g of the compound there are 65 g of F and 35 g of X. The number of moles of X is given by no. mol X =  $65\text{ g F} \times \frac{1\text{ mol F}}{19.0\text{ g F}} \times \frac{1\text{ mol X}}{3\text{ mol F}} = 1.14\text{ mol X}$

Thus, the molar mass of X =  $\frac{35\text{ g X}}{1.14\text{ mol X}} = 31\text{ g/mol X}$ , and the atomic mass is 31 u.

The element is most likely P.

- 57.** Each chlorophyll molecule contains one Mg atom, which makes up 2.72 % of the total mass for the molecule. Thus, 2.72 % of the molecular mass is Mg (24.305 g mol<sup>-1</sup>).

Consequently, the molar mass for chlorophyll =  $\frac{100\text{ % (total mass)}}{2.72\text{ % (by mass Mg)}} \times 24.305\text{ g mol}^{-1}$   
 $= 894\text{ g mol}^{-1}$  is the molecular mass of chlorophyll

Alternatively

Consider 100 g of chlorophyll, 2.72 g is Mg. However, 1 mole of Mg in 1 mole of chlorophyll.

$$\frac{100\text{ g chlorophyll}}{2.72\text{ g Mg}} \times \frac{24.305\text{ g Mg}}{1\text{ mol Mg}} \times \frac{1\text{ mol Mg}}{1\text{ mol chlorophyll}} = 894\text{ g mol}^{-1}$$

Therefore, the molecular mass of chlorophyll is 894 u

## Combustion Analysis

- 59.** (a) Determine the mass of carbon and of hydrogen present in the sample. A hydrocarbon only contains the two elements hydrogen and carbon.

$$0.8661\text{ g CO}_2 \times \frac{1\text{ mol CO}_2}{44.010\text{ g CO}_2} \times \frac{1\text{ mol C}}{1\text{ mol CO}_2} = 0.01968\text{ mol C} \times \frac{12.011\text{ g C}}{1\text{ mol C}} = 0.2364\text{ g C}$$

$$0.2216\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.015\text{ g H}_2\text{O}} \times \frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}} = 0.02460\text{ mol H} \times \frac{1.0079\text{ g H}}{1\text{ mol H}} = 0.02479\text{ g H}$$

Then the % C and % H are found.

$$\% \text{ C} = \frac{0.2364\text{ g C}}{0.2612\text{ g cmpd}} \times 100\% = 90.51\% \text{ C} \quad \% \text{ H} = \frac{0.02479\text{ g H}}{0.2612\text{ g cmpd}} \times 100\% = 9.491\% \text{ H}$$

- (b) Use the moles of C and H from part (a), and divide both by the smallest.  $0.01968\text{ mol C} \div 0.01968 = 1.000\text{ mol C}$ ;  $0.02460\text{ mol H} \div 0.01968 = 1.250\text{ mol H}$ . The empirical formula is obtained by multiplying these mole numbers by 4. It is C<sub>4</sub>H<sub>5</sub>.

- (c) The empirical formula C<sub>4</sub>H<sub>5</sub> has an empirical molar mass of  $[(4 \times 12.0\text{ g C}) + (5 \times 1.0\text{ g H})] = 53.0\text{ g/mol}$ . This value is 1/2 of the actual molar mass.

The molecular formula is twice the empirical formula. Molecular formula: C<sub>8</sub>H<sub>10</sub>.

- 61.** First determine the mass of carbon and hydrogen present in the sample.

$$0.741\text{ g CO}_2 \times \frac{1\text{ mol CO}_2}{44.01\text{ g CO}_2} \times \frac{1\text{ mol C}}{1\text{ mol CO}_2} = 0.0168\text{ mol C} \times \frac{12.01\text{ g C}}{1\text{ mol C}} = 0.202\text{ g C}$$

$$0.605\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} \times \frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}} = 0.0671\text{ mol H} \times \frac{1.008\text{ g H}}{1\text{ mol H}} = 0.0677\text{ g H}$$

From which we can calculate the mass of N in the sample.

$$0.235 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.014 \text{ g N}_2} \times \frac{2 \text{ mol N}}{1 \text{ mol N}_2} \times \frac{14.007 \text{ g N}}{1 \text{ mol N}} = 0.235 \text{ g N}$$

We may alternatively determine the mass of N by difference:

$$505 \text{ g cmpd} - 0.202 \text{ g C} - 0.0677 \text{ g H} = 0.235 \text{ g N}$$

Then, we can calculate the relative number of moles of each element.

$$\left. \begin{array}{l} 0.235 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.0168 \text{ mol N} \quad \div 0.0168 \rightarrow 1.00 \text{ mol N} \\ 0.0168 \text{ mol C} \quad \div 0.0168 \rightarrow 1.00 \text{ mol C} \\ 0.0671 \text{ mol H} \quad \div 0.0168 \rightarrow 3.99 \text{ mol H} \end{array} \right\} \text{Thus, the empirical formula is CH}_4\text{N}$$

- 63.** Each mole of  $\text{CO}_2$  is produced from a mole of C. Therefore, the compound with the largest number of moles of C per mole of the compound will produce the largest amount of  $\text{CO}_2$  and, thus, also the largest mass of  $\text{CO}_2$ . Of the compounds listed —  $\text{CH}_4$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_{10}\text{H}_8$ , and  $\text{C}_6\text{H}_5\text{OH}$ ,  $\text{C}_{10}\text{H}_8$  has the largest number of moles of C per mole of the compound and will produce the greatest mass of  $\text{CO}_2$  per mole on complete combustion.

**65.** mass  $\text{CO}_2 = 1.562 \text{ g C}_7\text{H}_{16} \times \frac{1 \text{ mol C}_7\text{H}_{16}}{100.20 \text{ g C}_7\text{H}_{16}} \times \frac{7 \text{ mol C}}{1 \text{ mol C}_7\text{H}_{16}} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol C}} \times \frac{44.011 \text{ g CO}_2}{1 \text{ mol CO}_2}$   
 $= 4.803 \text{ g CO}_2$

$$\text{mass H}_2\text{O} = 1.562 \text{ g C}_7\text{H}_{16} \times \frac{1 \text{ mol C}_7\text{H}_{16}}{100.20 \text{ g C}_7\text{H}_{16}} \times \frac{16 \text{ mol H}}{1 \text{ mol C}_7\text{H}_{16}} \times \frac{1 \text{ mol H}_2\text{O}}{2 \text{ mol H}} \times \frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}$$
  
 $= 2.247 \text{ g H}_2\text{O}$

## Oxidation States

- 67.** The oxidation state (O.S.) is given first, followed by the explanation for its assignment.

- (a) C = -4 in  $\text{CH}_4$  H has an oxidation state of +1 in its non-metal compounds (Remember that the sum of the oxidation states in a compound equals 0.)
- (b) S = +4 in  $\text{SF}_4$  F has O.S. = -1 in its compounds.
- (c) O = -1 in  $\text{Na}_2\text{O}_2$  Na has O.S. = +1 in its compounds.
- (d) C = 0 in  $\text{C}_2\text{H}_3\text{O}_2^-$  H has O.S. = +1 in its non-metal compounds; that of O = -2 (usually). (Remember that the sum of the oxidation states in a polyatomic ion equals the charge on that ion.)
- (e) Fe = +6 in  $\text{FeO}_4^{2-}$  O has O.S. = -2 in most of its compounds (especially metal containing compounds).

- 69.** The O.S. of oxygen is  $-2$  in its compounds.  $\text{Cr}^{3+}$  and  $\text{O}^{2-} \rightarrow \text{Cr}_2\text{O}_3$ , chromium(III) oxide.  $\text{Cr}^{4+}$  and  $\text{O}^{2-} \rightarrow \text{CrO}_2$ , chromium (IV) oxide.  $\text{Cr}^{6+}$  and  $\text{O}^{2-} \rightarrow \text{CrO}_3$ , chromium(VI) oxide.

## Nomenclature

- 71.**
- |                                 |                              |                                   |                             |
|---------------------------------|------------------------------|-----------------------------------|-----------------------------|
| (a) $\text{SrO}$                | strontium oxide              | (b) $\text{ZnS}$                  | zinc sulfide                |
| (c) $\text{K}_2\text{CrO}_4$    | potassium chromate           | (d) $\text{Cs}_2\text{SO}_4$      | cesium sulfate              |
| (e) $\text{Cr}_2\text{O}_3$     | chromium(III) oxide          | (f) $\text{Fe}_2(\text{SO}_4)_3$  | iron(III) sulfate           |
| (g) $\text{Mg}(\text{HCO}_3)_2$ | magnesium hydrogen carbonate | (h) $(\text{NH}_4)_2\text{HPO}_4$ | ammonium hydrogen phosphate |
| (i) $\text{Ca}(\text{HSO}_3)_2$ | calcium hydrogen sulfite     | (j) $\text{Cu}(\text{OH})_2$      | copper(II) hydroxide        |
| (k) $\text{HNO}_3$              | nitric acid                  | (l) $\text{KClO}_4$               | potassium perchlorate       |
| (m) $\text{HBrO}_3$             | bromic acid                  | (n) $\text{H}_3\text{PO}_3$       | phosphorous acid            |
- 73.**
- |                    |                        |                             |                       |
|--------------------|------------------------|-----------------------------|-----------------------|
| (a) $\text{CS}_2$  | carbon disulfide       | (b) $\text{SiF}_4$          | silicon tetrafluoride |
| (c) $\text{ClF}_5$ | chlorine pentafluoride | (d) $\text{N}_2\text{O}_5$  | dinitrogen pentoxide  |
| (e) $\text{SF}_6$  | sulfur hexafluoride    | (f) $\text{I}_2\text{Cl}_6$ | diiodine hexachloride |
- 75.**
- |                                  |                       |  |                                   |
|----------------------------------|-----------------------|--|-----------------------------------|
| (a) $\text{Al}_2(\text{SO}_4)_3$ | aluminum sulfate      | (b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ | ammonium dichromate               |
| (c) $\text{SiF}_4$               | silicon tetrafluoride | (d) $\text{Fe}_2\text{O}_3$                | iron(III) oxide                   |
| (e) $\text{C}_3\text{S}_2$       | tricarbon disulfide   | (f) $\text{Co}(\text{NO}_3)_2$             | cobalt(II) nitrate                |
| (g) $\text{Sr}(\text{NO}_2)_2$   | strontium nitrite     | (h) $\text{HBr}(\text{aq})$                | hydrobromic acid                  |
| (i) $\text{HIO}_3$               | iodic acid            | (j) $\text{PCl}_2\text{F}_3$               | phosphorus dichloride trifluoride |
- 77.**
- |  |  |
|--|--|
| (a) $\text{Ti}^{4+}$ and $\text{Cl}^-$ produce $\text{TiCl}_4$           | (b) $\text{Fe}^{3+}$ and $\text{SO}_4^{2-}$ produce $\text{Fe}_2(\text{SO}_4)_3$ |
| (c) $\text{Cl}^{7+}$ and $\text{O}^{2-}$ produce $\text{Cl}_2\text{O}_7$ | (d) $\text{S}^{7+}$ and $\text{O}^{2-}$ produce $\text{S}_2\text{O}_8^{2-}$      |

## Hydrates

- 79.** The hydrate with the greatest mass percent  $\text{H}_2\text{O}$  is the one that gives the largest result for the number of moles of water in the hydrate's empirical formula, divided by the mass of one mole of the anhydrous salt for the hydrate.

$$\frac{5\text{H}_2\text{O}}{\text{CuSO}_4} = \frac{5\text{ mol H}_2\text{O}}{159.6\text{ g}} = 0.03133 \quad \frac{6\text{H}_2\text{O}}{\text{MgCl}_2} = \frac{6\text{ mol H}_2\text{O}}{95.2\text{ g}} = 0.0630$$

$$\frac{18\text{H}_2\text{O}}{\text{Cr}_2(\text{SO}_4)_3} = \frac{18\text{ mol H}_2\text{O}}{392.3\text{ g}} = 0.04588 \quad \frac{2\text{H}_2\text{O}}{\text{LiC}_2\text{H}_3\text{O}_2} = \frac{2\text{ mol H}_2\text{O}}{66.0\text{ g}} = 0.0303$$

The hydrate with the greatest %  $\text{H}_2\text{O}$  therefore is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

**81.** Molar mass  $\text{CuSO}_4 = 63.5\text{g Cu} + 32.1\text{g S} + (4 \times 16.0\text{g O}) = 159.6\text{g CuSO}_4/\text{mol}$ .

The mass of solid needed to combine with 8.5 g of water depends on the absorption of 5 moles of water by one mole of the solid, based on the formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

$$\begin{aligned}\text{mass CuSO}_4 &= 8.5\text{g H}_2\text{O} \times \frac{1\text{mol H}_2\text{O}}{18.0\text{g H}_2\text{O}} \times \frac{1\text{mol CuSO}_4}{5\text{mol H}_2\text{O}} \times \frac{159.6\text{g CuSO}_4}{1\text{mol CuSO}_4} \\ &= 15\text{g CuSO}_4 \quad \text{required to remove all the water}\end{aligned}$$

**83.** Converting to molar amounts based on 100.0g:

$$20.3\text{ g Cu} \times \frac{1\text{ mol Cu}}{63.55\text{ g Cu}} = 0.319\text{ mol Cu} \div 0.319 \rightarrow 1.00\text{ mol Cu}$$

$$8.95\text{ g Si} \times \frac{1\text{ mol Si}}{28.09\text{ g Si}} = 0.319\text{ mol Si} \div 0.319 \rightarrow 1.00\text{ mol Si}$$

$$36.3\text{ g F} \times \frac{1\text{ mol F}}{19.00\text{ g F}} = 1.91\text{ mol F} \div 0.319 \rightarrow 6.00\text{ mol F}$$

$$34.5\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{g}} = 1.91\text{ mol H}_2\text{O} \div 0.319 \rightarrow 6.00\text{ mol H}_2\text{O}$$

Thus the empirical formula for the hydrate is  $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ .

## Organic Compounds and Organic Nomenclature

**85.** Molecules (a), (b), (c) and (d) are structural isomers. They share a common formula, namely  $\text{C}_5\text{H}_{12}\text{O}$ , but have different molecular structures. Molecule (e) has a different chemical formula ( $\text{C}_6\text{H}_{14}\text{O}$ ) and hence cannot be classified as an isomer.

- |            |  |                                |
|------------|--|--------------------------------|
| <b>87.</b> | (a) $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$                            | (b) $\text{HCO}_2\text{H}$     |
|            | (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ | (d) $\text{ClCH}_2\text{CH}_3$ |

- |            |  |                          |
|------------|--|--------------------------|
| <b>89.</b> | (a) Methanol; $\text{CH}_3\text{OH}$ ;   | Molecular mass = 32.04 u |
|            | (b) 2-chlorohexane; $\text{CH}_3(\text{CH}_2)_3\text{CHClCH}_3$                  | Molecular mass = 120.6 u |
|            | (c) pentanoic acid; $\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$              | Molecular mass = 102.1 u |
|            | (d) 2-methyl-1-propanol; $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ | Molecular mass = 74.12 u |

## FEATURE PROBLEMS

- 108. (a)** “5-10-5” fertilizer contains 5 g N (that is, 5% N), 10 g  $P_2O_5$ , and 5 g  $K_2O$  in 100 g fertilizer. We convert the last two numbers into masses of the two elements.

$$(1) \quad \%P = 10\%P_2O_5 \times \frac{1 \text{ mol } P_2O_5}{141.9 \text{ g } P_2O_5} \times \frac{2 \text{ mol P}}{1 \text{ mol } P_2O_5} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} = 4.4\%P$$

$$(2) \quad \%K = 5\%K_2O \times \frac{1 \text{ mol } K_2O}{94.20 \text{ g } K_2O} \times \frac{2 \text{ mol K}}{1 \text{ mol } K_2O} \times \frac{39.10 \text{ g K}}{1 \text{ mol K}} = 4.2\%K$$

- (b)** First, we determine %P and then convert it to % $P_2O_5$ , given that 10.0%  $P_2O_5$  is equivalent to 4.37% P.

$$(1) \quad \%P_2O_5 = \frac{2 \text{ mol P}}{1 \text{ mol } Ca(H_2PO_4)_2} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} \times \frac{1 \text{ mol } Ca(H_2PO_4)_2}{234.05 \text{ g } Ca(H_2PO_4)_2} \times 100\% \\ \times \frac{10.0\%P_2O_5}{4.37\%P} = 60.6\%P_2O_5$$

$$(2) \quad \%P_2O_5 = \frac{1 \text{ mol P}}{1 \text{ mol } (NH_4)_2HPO_4} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} \times \frac{1 \text{ mol } (NH_4)_2HPO_4}{132.06 \text{ g } (NH_4)_2HPO_4} \times 100\% \\ \times \frac{10.0\%P_2O_5}{4.37\%P} = 53.7\%P_2O_5$$

- 109. (a)** First calculate the mass of water that was present in the hydrate prior to heating.  
 $Mass \ of \ H_2O = 2.574 \text{ g } CuSO_4 \cdot x \ H_2O - 1.647 \text{ g } CuSO_4 = 0.927 \text{ g } H_2O$   
 Next we need to find the number of moles of anhydrous copper(II) sulfate and water that were initially present together in the original hydrate sample.

$$Moles \ of \ H_2O = 0.927 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} = 0.05146 \text{ moles of water}$$

The empirical formula is obtained by dividing the number of moles of water by the number of moles of  $CuSO_4$  ( $x$  = ratio of moles of water to moles of  $CuSO_4$ )

$$x = \frac{0.05146 \text{ moles } H_2O}{0.01032 \text{ moles } CuSO_4} = 4.99 \sim 5 \text{ The empirical formula is } CuSO_4 \cdot 5 \ H_2O.$$

- (b)** Mass of water present in hydrate = 2.574 g - 1.833 g = 0.741 g  $H_2O$

$$moles \ of \ water = 0.741 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} = 0.0411 \text{ moles of water}$$

$$Mass \ of \ CuSO_4 \ present \ in \ hydrate = 1.833 \text{ g } CuSO_4$$

$$moles \ of \ CuSO_4 = 1.833 \text{ g } CuSO_4 \times \frac{1 \text{ mol } CuSO_4}{159.61 \text{ g } CuSO_4} = 0.0115 \text{ mol } CuSO_4$$

The empirical formula is obtained by dividing the number of moles of water by the number of moles of  $\text{CuSO}_4$  ( $x$  = ratio of moles of water to moles of  $\text{CuSO}_4$ )

$$x = \frac{0.0411 \text{ moles H}_2\text{O}}{0.0115 \text{ moles CuSO}_4} = 3.58 \sim 4.$$

Since the hydrate has not been completely dehydrated, there is no problem with obtaining non-integer "garbage" values. The empirical formula is  $\text{CuSO}_4 \bullet 4\text{H}_2\text{O}$ .

- (c) When copper(II) sulfate is strongly heated, it decomposes to give  $\text{SO}_3(\text{g})$  and  $\text{CuO}(\text{s})$ . The black residue formed at  $1000^\circ\text{C}$  in this experiment is probably  $\text{CuO}$ . The empirical formula for copper(II) oxide is  $\text{CuO}$ . Let's calculate the percentages of Cu and O by mass for  $\text{CuO}$ :

$$\text{Mass percent copper} = \frac{63.546 \text{ g Cu}}{79.545 \text{ g CuO}} \times 100 \% = 79.89 \% \text{ by mass Cu}$$

$$\text{Mass percent oxygen} = \frac{15.9994 \text{ g O}}{79.545 \text{ g CuO}} \times 100 \% = 20.11 \% \text{ by mass O}$$

The number of moles of  $\text{CuO}$  formed (by reheating to  $1000^\circ\text{C}$ )

$$= 0.812 \text{ g CuO} \times \frac{1 \text{ mol CuO}}{79.545 \text{ g CuO}} = 0.0102 \text{ moles of CuO}$$

This is very close to the number of moles of anhydrous  $\text{CuSO}_4$  formed at  $400^\circ\text{C}$ . Thus, it would appear that upon heating to  $1000^\circ\text{C}$ , the sample of  $\text{CuSO}_4$  was essentially completely converted to  $\text{CuO}$ .

- 110.** (a) The formula for stearic acid, obtained from the molecular model, is  $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$ . The number of moles of stearic acid in 10.0 grams is

$$= 10.0 \text{ g stearic acid} \times \frac{1 \text{ mol stearic acid}}{284.48 \text{ g stearic acid}} = 3.515 \times 10^{-2} \text{ mol of stearic acid.}$$

The layer of stearic acid is one molecule thick. According to the figure provided with the question, each stearic acid molecule has a cross-sectional area of  $\sim 0.22 \text{ nm}^2$ . In order to find the stearic acid coverage in square meters, we must multiply the total number of stearic acid molecules by the cross-sectional area for an individual stearic acid molecule. The number of stearic acid molecules is:

$$= 3.515 \times 10^{-2} \text{ mol of stearic acid} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol of stearic acid}} = 2.117 \times 10^{22} \text{ molecules}$$

$$\text{Area in m}^2 = 2.117 \times 10^{22} \text{ molecules of stearic acid} \times \frac{0.22 \text{ nm}^2}{\text{molecule}} \times \frac{(1 \text{ m})^2}{(1 \times 10^9 \text{ nm})^2}$$

The area in  $\text{m}^2 = 4657 \text{ m}^2$  or  $4.7 \times 10^3 \text{ m}^2$  (with correct number of sig. fig.)

- (b) The density for stearic acid is  $0.85 \text{ g cm}^{-3}$ . Thus, 0.85 grams of stearic acid occupies  $1 \text{ cm}^3$ . Find the number of moles of stearic acid in 0.85 g of stearic acid

$$= 0.85 \text{ grams of stearic acid} \times \frac{1 \text{ mol stearic acid}}{284.48 \text{ g stearic acid}} = 3.0 \times 10^{-3} \text{ mol of stearic acid}$$

acid. This number of moles of acid occupies  $1 \text{ cm}^3$  of space. So, the number of stearic acid molecules in  $1 \text{ cm}^3$

$$= 3.0 \times 10^{-3} \text{ mol of stearic acid} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol of stearic acid}}$$

$$= 1.8 \times 10^{21} \text{ stearic acid molecules.}$$

Thus, the volume for a single stearic acid molecule in  $\text{nm}^3$

$$= 1 \text{ cm}^3 \times \frac{1}{1.8 \times 10^{21} \text{ molecules stearic acid}} \times \frac{(1.0 \times 10^7 \text{ nm})^3}{(1 \text{ cm})^3} = 0.556 \text{ nm}^3$$

The volume of a rectangular column is simply its area of the base multiplied by its height (i.e.  $V = \text{area of base} (\text{in nm}^2) \times \text{height} (\text{in nm})$ ).

$$\text{So, the average height of a stearic acid molecule} = \frac{0.556 \text{ nm}^3}{0.22 \text{ nm}^2} = 2.5 \text{ nm}$$

- (c) The density for oleic acid =  $0.895 \text{ g mL}^{-1}$ . So, the concentration for oleic acid is

$$= \frac{0.895 \text{ g acid}}{10.00 \text{ mL}} = 0.0895 \text{ g mL}^{-1} \text{ (solution 1)}$$

This solution is then divided by ten, three more times to give a final concentration of  $8.95 \times 10^{-5} \text{ g mL}^{-1}$ . A 0.10 mL sample of this solution contains:

$$= \frac{8.95 \times 10^{-5} \text{ g acid}}{1.00 \text{ mL}} \times 0.10 \text{ mL} = 8.95 \times 10^{-6} \text{ g of acid.}$$

$$\begin{aligned} \text{The number of acid molecules} &= 85 \text{ cm}^2 \times \frac{1}{4.6 \times 10^{-15} \text{ cm}^2 \text{ per molecule}} \\ &= 1.85 \times 10^{16} \text{ oleic acid molecules.} \end{aligned}$$

So,  $8.95 \times 10^{-6} \text{ g of oleic acid}$  corresponds to  $1.85 \times 10^{16} \text{ oleic acid molecules}$ .

The molar mass for oleic acid,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ , is  $282.47 \text{ g mol}^{-1}$ .

The number of moles of oleic acid is

$$= 8.95 \times 10^{-6} \text{ g} \times \frac{1 \text{ mol oleic acid}}{282.47 \text{ g}} = 3.17 \times 10^{-8} \text{ mol}$$

So, Avogadro's number here would be equal to:

$$= \frac{1.85 \times 10^{16} \text{ oleic acid molecules}}{3.17 \times 10^{-8} \text{ oleic acid moles}} = 5.8 \times 10^{23} \text{ molecules per mole of oleic acid.}$$

# CHAPTER 4

## CHEMICAL REACTIONS

### PRACTICE EXAMPLES

---

- 1A (a)** Unbalanced reaction:  $\text{H}_3\text{PO}_4(\text{aq}) + \text{CaO}(\text{s}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- Balance Ca &  $\text{PO}_4^{3-}$ :  $2 \text{H}_3\text{PO}_4(\text{aq}) + 3 \text{CaO}(\text{s}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- Balance H atoms:  $2 \text{H}_3\text{PO}_4(\text{aq}) + 3 \text{CaO}(\text{s}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$
- Self Check:  $6 \text{H} + 2 \text{P} + 11 \text{O} + 3 \text{Ca} \rightarrow 6 \text{H} + 2 \text{P} + 11 \text{O} + 3 \text{Ca}$
- (b)** Unbalanced reaction:  $\text{C}_3\text{H}_8(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- Balance C & H:  $\text{C}_3\text{H}_8(\text{g}) + \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$
- Balance O atoms:  $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$
- Self Check:  $3 \text{C} + 8 \text{H} + 10 \text{O} \rightarrow 3 \text{C} + 8 \text{H} + 10 \text{O}$
- 1B (a)** Unbalanced reaction:  $\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- Balance N and H:  $\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) + 3/2 \text{H}_2\text{O}(\text{g})$
- Balance O atoms:  $\text{NH}_3(\text{g}) + 7/4 \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) + 3/2 \text{H}_2\text{O}(\text{g})$
- Multiply by 4 (whole #):  $4 \text{NH}_3(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$
- Self Check:  $4 \text{N} + 12 \text{H} + 14 \text{O} \rightarrow 4 \text{N} + 12 \text{H} + 14 \text{O}$
- (b)** Unbalanced reaction:  $\text{NO}_2(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- Balance H atoms:  $\text{NO}_2(\text{g}) + 2 \text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$
- Balance O atoms:  $3/2 \text{NO}_2(\text{g}) + 2 \text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$
- Balance N atoms:  $3/2 \text{NO}_2(\text{g}) + 2 \text{NH}_3(\text{g}) \rightarrow 7/4 \text{N}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$
- Multiply by 4 (whole #):  $6 \text{NO}_2(\text{g}) + 8 \text{NH}_3(\text{g}) \rightarrow 7 \text{N}_2(\text{g}) + 12 \text{H}_2\text{O}(\text{g})$
- Self Check:  $14 \text{N} + 24 \text{H} + 12 \text{O} \rightarrow 14 \text{N} + 24 \text{H} + 12 \text{O}$
- 2A** Unbalanced reaction:  $\text{HgS}(\text{s}) + \text{CaO}(\text{s}) \rightarrow \text{CaS}(\text{s}) + \text{CaSO}_4(\text{s}) + \text{Hg}(\text{l})$
- Balance O atoms:  $\text{HgS}(\text{s}) + 4 \text{CaO}(\text{s}) \rightarrow \text{CaS}(\text{s}) + \text{CaSO}_4(\text{s}) + \text{Hg}(\text{l})$
- Balance Ca atoms:  $\text{HgS}(\text{s}) + 4 \text{CaO}(\text{s}) \rightarrow 3 \text{CaS}(\text{s}) + \text{CaSO}_4(\text{s}) + \text{Hg}(\text{l})$
- Balance S atoms:  $4 \text{HgS}(\text{s}) + 4 \text{CaO}(\text{s}) \rightarrow 3 \text{CaS}(\text{s}) + \text{CaSO}_4(\text{s}) + \text{Hg}(\text{l})$
- Balance Hg atoms:  $4 \text{HgS}(\text{s}) + 4 \text{CaO}(\text{s}) \rightarrow 3 \text{CaS}(\text{s}) + \text{CaSO}_4(\text{s}) + 4 \text{Hg}(\text{l})$
- Self Check:  $4 \text{Hg} + 4 \text{S} + 4 \text{O} + 4 \text{Ca} \rightarrow 4 \text{Hg} + 4 \text{S} + 4 \text{O} + 4 \text{Ca}$

<b>2B</b>	Unbalanced reaction:	$C_7H_6O_2S(l) + O_2(g) \rightarrow CO_2(g) + H_2O(l) + SO_2(g)$
	Balance C atoms:	$C_7H_6O_2S(l) + O_2(g) \rightarrow 7 CO_2(g) + H_2O(l) + SO_2(g)$
	Balance S atoms:	$C_7H_6O_2S(l) + O_2(g) \rightarrow 7 CO_2(g) + H_2O(l) + SO_2(g)$
	Balance H atoms:	$C_7H_6O_2S(l) + O_2(g) \rightarrow 7 CO_2(g) + 3 H_2O(l) + SO_2(g)$
	Balance O atoms:	$C_7H_6O_2S(l) + 8.5 O_2(g) \rightarrow 7 CO_2(g) + 3 H_2O(l) + SO_2(g)$
	Multiply by 2 (whole #):	$2 C_7H_6O_2S(l) + 17O_2(g) \rightarrow 14 CO_2(g) + 6 H_2O(l) + 2 SO_2(g)$
	Self Check:	$14 C + 12 H + 2 S + 38 O \rightarrow 14 C + 12 H + 2 S + 38 O$

**3A** The balanced chemical equation provides the factor needed to convert from moles  $KClO_3$  to moles  $O_2$ . Amount  $O_2 = 1.76 \text{ mol } KClO_3 \times \frac{3 \text{ mol } O_2}{2 \text{ mol } KClO_3} = 2.64 \text{ mol } O_2$

**3B** First, find the molar mass of  $Ag_2O$ .

$$(2 \text{ mol } Ag \times 107.87 \text{ g } Ag) + 16.00 \text{ g } O = 231.74 \text{ g } Ag_2O / \text{ mol}$$

$$\text{amount } Ag = 1.00 \text{ kg } Ag_2O \times \frac{1000 \text{ g}}{1.00 \text{ kg}} \times \frac{1 \text{ mol } Ag_2O}{231.74 \text{ g } Ag_2O} \times \frac{2 \text{ mol } Ag}{1 \text{ mol } Ag_2O} = 8.63 \text{ mol } Ag$$

**4A** The balanced chemical equation provides the factor to convert from amount of Mg to amount of  $Mg_3N_2$ . First, we determine the molar mass of  $Mg_3N_2$ .

$$\text{molar mass} = (3 \text{ mol } Mg \times 24.305 \text{ g } Mg) + (2 \text{ mol } N \times 14.007 \text{ g } N) = 100.93 \text{ g } Mg_3N_2$$

$$\text{mass } Mg_3N_2 = 3.82 \text{ g } Mg \times \frac{1 \text{ mol } Mg}{24.31 \text{ g } Mg} \times \frac{1 \text{ mol } Mg_3N_2}{3 \text{ mol } Mg} \times \frac{100.93 \text{ g } Mg_3N_2}{1 \text{ mol } Mg_3N_2} = 5.29 \text{ g } Mg_3N_2$$

**4B** The pivotal conversion is from  $H_2(g)$  to  $CH_3OH(l)$ . For this we use the balanced equation, which requires that we use the amounts in moles of both substances. The solution involves converting to and from amounts, using molar masses.

$$\text{mass } H_2(g) = 1.00 \text{ kg } CH_3OH(l) \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} \times \frac{2 \text{ mol } H_2}{1 \text{ mol } CH_3OH} \times \frac{2.016 \text{ g } H_2}{1 \text{ mol } H_2}$$

$$\text{mass } H_2(g) = 126 \text{ g } H_2$$

**5A** The equation for the cited reaction is:  $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ .

The pivotal conversion is from one substance to another, in moles with the balanced chemical equation providing the conversion factor.

$$\text{mass } H_2(g) = 1.00 \text{ g } O_2(g) \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} \times \frac{2.016 \text{ g } H_2}{1 \text{ mol } H_2} = 0.126 \text{ g } H_2$$

**5B** The equation for the combustion reaction is:  $C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$

$$\text{mass } O_2 = 1.00 \text{ g } C_8H_{18} \times \frac{1 \text{ mol } C_8H_{18}}{114.23 \text{ g } C_8H_{18}} \times \frac{12.5 \text{ mol } O_2}{1 \text{ mol } C_8H_{18}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 3.50 \text{ g } O_2(g)$$

**6A** We must convert mass  $H_2 \rightarrow$  amount of  $H_2 \rightarrow$  amount of Al  $\rightarrow$  mass of Al  $\rightarrow$  mass of alloy  $\rightarrow$  volume of alloy. The calculation is performed as follows: each arrow in the preceding sentence requires a conversion factor.

$$V_{\text{alloy}} = 1.000 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Al}}{3 \text{ mol } H_2} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \times \frac{100.0 \text{ g alloy}}{93.7 \text{ g Al}} \times \frac{1 \text{ cm}^3 \text{ alloy}}{2.85 \text{ g alloy}}$$

$$\text{Volume of alloy} = 3.34 \text{ cm}^3 \text{ alloy}$$

**6B** In the example, 0.207 g  $H_2$  is collected from 1.97 g alloy; the alloy is 6.3% Cu by mass. This information provides the conversion factors we need.

$$\text{mass Cu} = 1.31 \text{ g } H_2 \times \frac{1.97 \text{ g alloy}}{0.207 \text{ g } H_2} \times \frac{6.3 \text{ g Cu}}{100.0 \text{ g alloy}} = 0.79 \text{ g Cu}$$

Notice that we do not have to consider each step separately. We can simply use values produced in the course of the calculation as conversion factors.

**7A** The cited reaction is  $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$ . The  $HCl(aq)$  solution has a density of 1.14 g/mL and contains 28.0% HCl. We need to convert between the substances  $HCl$  and  $H_2$ ; the important conversion factor comes from the balanced chemical equation. The sequence of conversions is: volume of  $HCl(aq) \rightarrow$  mass of  $HCl(aq) \rightarrow$  mass of pure  $HCl \rightarrow$  amount of  $HCl \rightarrow$  amount of  $H_2 \rightarrow$  mass of  $H_2$ . In the calculation below, each arrow in the sequence is replaced by a conversion factor.

$$\text{mass } H_2 = 0.05 \text{ mL } HCl(aq) \times \frac{1.14 \text{ g soln}}{1 \text{ mL soln}} \times \frac{28.0 \text{ g HCl}}{100.0 \text{ g soln}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} \times \frac{3 \text{ mol } H_2}{6 \text{ mol HCl}} \times \frac{2.016 \text{ g } H_2}{1 \text{ mol } H_2}$$

$$\text{mass } H_2 = 4 \times 10^{-4} \text{ g } H_2(g) = 0.4 \text{ mg } H_2(g)$$

**7B** Density is necessary to determine the mass of the vinegar, and then the mass of acetic acid.

$$\text{mass } CO_2(g) = 5.00 \text{ mL vinegar} \times \frac{1.01 \text{ g}}{1 \text{ mL}} \times \frac{0.040 \text{ g acid}}{1 \text{ g vinegar}} \times \frac{1 \text{ mol } HC_2H_3O_2}{60.05 \text{ g } HC_2H_3O_2} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } HC_2H_3O_2} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} \\ = 0.15 \text{ g } CO_2$$

**8A** Determine the amount in moles of acetone and the volume in liters of the solution.

$$\text{molarity of acetone} = \frac{22.3 \text{ g } (CH_3)_2CO \times \frac{1 \text{ mol } (CH_3)_2CO}{58.08 \text{ g } (CH_3)_2CO}}{1.25 \text{ L soln}} = 0.307 \text{ M}$$

- 8B** The molar mass of acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , is 60.05 g/mol. We begin with the quantity of acetic acid in the numerator and that of the solution in the denominator, and transform to the appropriate units for each.

$$\text{molarity} = \frac{15.0 \text{ mL } \text{HC}_2\text{H}_3\text{O}_2}{500.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \times \frac{1.048 \text{ g } \text{HC}_2\text{H}_3\text{O}_2}{1 \text{ mL } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{1 \text{ mol } \text{HC}_2\text{H}_3\text{O}_2}{60.05 \text{ g } \text{HC}_2\text{H}_3\text{O}_2} = 0.524 \text{ M}$$

- 9A** The molar mass of  $\text{NaNO}_3$  is 84.99 g/mol. We recall that "M" stands for "mol /L soln."

$$\text{mass } \text{NaNO}_3 = 125 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{10.8 \text{ mol } \text{NaNO}_3}{1 \text{ L soln}} \times \frac{84.99 \text{ g } \text{NaNO}_3}{1 \text{ mol } \text{NaNO}_3} = 115 \text{ g } \text{NaNO}_3$$

- 9B** We begin by determining the molar mass of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . The amount of solute needed is computed from the concentration and volume of the solution.

$$\begin{aligned} \text{mass } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} &= 355 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.445 \text{ mol } \text{Na}_2\text{SO}_4}{1 \text{ L soln}} \times \frac{1 \text{ mol } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{1 \text{ mol } \text{Na}_2\text{SO}_4} \\ &\quad \times \frac{322.21 \text{ g } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{1 \text{ mol } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}} = 50.9 \text{ g } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \end{aligned}$$

- 10A** The amount of solute in the concentrated solution doesn't change when the solution is diluted. We take advantage of an alternate definition of molarity to answer the question: millimoles of solute/milliliter of solution.

$$\text{amount } \text{K}_2\text{CrO}_4 = 15.00 \text{ mL} \times \frac{0.450 \text{ mmol } \text{K}_2\text{CrO}_4}{1 \text{ mL soln}} = 6.75 \text{ mmol } \text{K}_2\text{CrO}_4$$

$$\text{K}_2\text{CrO}_4 \text{ molarity, dilute solution} = \frac{6.75 \text{ mmol } \text{K}_2\text{CrO}_4}{100.00 \text{ mL soln}} = 0.0675 \text{ M}$$

- 10B** We know the initial concentration (0.105 M) and volume (275 mL) of the solution, along with its final volume (237 mL). The final concentration equals the initial concentration times a ratio of the two volumes.

$$c_f = c_i \times \frac{V_i}{V_f} = 0.105 \text{ M} \times \frac{275 \text{ mL}}{237 \text{ mL}} = 0.122 \text{ M}$$

- 11A** The balanced equation is  $\text{K}_2\text{CrO}_4 \text{ (aq)} + 2 \text{AgNO}_3 \text{ (aq)} \rightarrow \text{Ag}_2\text{CrO}_4 \text{ (s)} + 2 \text{KNO}_3 \text{ (aq)}$ .

The molar mass of  $\text{Ag}_2\text{CrO}_4$  is 331.73 g/mol. The conversions needed are mass

$\text{Ag}_2\text{CrO}_4 \rightarrow \text{amount } \text{Ag}_2\text{CrO}_4 \text{ (moles)} \rightarrow \text{amount } \text{K}_2\text{CrO}_4 \text{ (moles)} \rightarrow \text{volume } \text{K}_2\text{CrO}_4 \text{ (aq)}$ .

$$\begin{aligned} V_{\text{K}_2\text{CrO}_4} &= 1.50 \text{ g } \text{Ag}_2\text{CrO}_4 \times \frac{1 \text{ mol } \text{Ag}_2\text{CrO}_4}{331.73 \text{ g } \text{Ag}_2\text{CrO}_4} \times \frac{1 \text{ mol } \text{K}_2\text{CrO}_4}{1 \text{ mol } \text{Ag}_2\text{CrO}_4} \times \frac{1 \text{ L soln}}{0.250 \text{ mol } \text{K}_2\text{CrO}_4} \\ &\quad \times \frac{1000 \text{ mL solution}}{1 \text{ L solution}} = 18.1 \text{ mL} \end{aligned}$$

**11B** Balanced reaction:  $2 \text{AgNO}_3(\text{aq}) + \text{K}_2\text{CrO}_4(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{s}) + 2 \text{KNO}_3(\text{aq})$

$$\text{moles of K}_2\text{CrO}_4 = C \times V = 0.0855 \text{ M} \times 0.175 \text{ L sol} = 0.01496 \text{ moles K}_2\text{CrO}_4$$

$$\text{moles of AgNO}_3 = 0.01496 \text{ mol K}_2\text{CrO}_4 \times \frac{2 \text{ mol AgNO}_3}{1 \text{ mol K}_2\text{CrO}_4} = 0.0299 \text{ mol AgNO}_3$$

$$V_{\text{AgNO}_3} = \frac{n}{C} = \frac{0.0299 \text{ mol AgNO}_3}{0.150 \frac{\text{mol}}{\text{L}} \text{ AgNO}_3} = 0.1995 \text{ L or } 2.00 \times 10^2 \text{ mL (0.200 L) of AgNO}_3$$

$$\text{Mass of Ag}_2\text{CrO}_4 \text{ formed} = 0.01496 \text{ moles K}_2\text{CrO}_4 \times \frac{1 \text{ mol Ag}_2\text{CrO}_4}{1 \text{ mol K}_2\text{CrO}_4} \times \frac{331.73 \text{ g Ag}_2\text{CrO}_4}{1 \text{ mol Ag}_2\text{CrO}_4}$$

$$\text{Mass of Ag}_2\text{CrO}_4 \text{ formed} = 4.96 \text{ g Ag}_2\text{CrO}_4$$

**12A** Reaction:  $\text{P}_4(\text{s}) + 6 \text{Cl}_2(\text{g}) \rightarrow 4 \text{PCl}_3(\text{l})$ . Determine mass of  $\text{PCl}_3$  formed by each reactant.

$$\text{mass PCl}_3 = 215 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{123.90 \text{ g P}_4} \times \frac{4 \text{ mol PCl}_3}{1 \text{ mol P}_4} \times \frac{137.33 \text{ g PCl}_3}{1 \text{ mol PCl}_3} = 953 \text{ g PCl}_3$$

$$\text{mass PCl}_3 = 725 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.91 \text{ g Cl}_2} \times \frac{4 \text{ mol PCl}_3}{6 \text{ mol Cl}_2} \times \frac{137.33 \text{ g PCl}_3}{1 \text{ mol PCl}_3} = 936 \text{ g PCl}_3$$

Thus, 936 g  $\text{PCl}_3$  are produced; there is not enough  $\text{Cl}_2$  to produce any more.

**12B** Since data are supplied and the answer is requested in kilograms (thousands of grams), we can use kilomoles (thousands of moles) to solve the problem. We calculate the amount in kilomoles of  $\text{POCl}_3$  that would be produced if each of the reactants were completely converted to product. The smallest of these amounts is the one that is actually produced. (This is a limiting reactant question).

$$\text{amount POCl}_3 = 1.00 \text{ kg PCl}_3 \times \frac{1 \text{ kmol PCl}_3}{137.33 \text{ kg PCl}_3} \times \frac{10 \text{ kmol POCl}_3}{6 \text{ kmol PCl}_3} = 0.0121 \text{ kmol POCl}_3$$

$$\text{amount POCl}_3 = 1.00 \text{ kg Cl}_2 \times \frac{1 \text{ kmol Cl}_2}{70.905 \text{ kg Cl}_2} \times \frac{10 \text{ kmol POCl}_3}{6 \text{ kmol Cl}_2} = 0.0235 \text{ kmol POCl}_3$$

$$\text{amount POCl}_3 = 1.00 \text{ kg P}_4\text{O}_{10} \times \frac{1 \text{ kmol P}_4\text{O}_{10}}{283.89 \text{ kg P}_4\text{O}_{10}} \times \frac{10 \text{ kmol POCl}_3}{1 \text{ kmol P}_4\text{O}_{10}} = 0.0352 \text{ kmol POCl}_3$$

Thus, 0.0121 kmol  $\text{POCl}_3$  is produced. We determine the mass of the product.

$$\text{mass POCl}_3 = 0.0121 \text{ kmol POCl}_3 \times \frac{153.33 \text{ kg POCl}_3}{1 \text{ kmol POCl}_3} = 1.86 \text{ kg POCl}_3$$

**13A** The 725 g Cl<sub>2</sub> limits the mass of product formed. The P<sub>4</sub> (s) therefore is the reactant in excess. The quantity of excess reactant is sufficient to form the excess product: 953 g PCl<sub>3</sub> – 936 g PCl<sub>3</sub> = 17 g PCl<sub>3</sub>. We calculate how much P<sub>4</sub> this is, both in the traditional way and by using the initial (215 g P<sub>4</sub>) and final (953 g PCl<sub>3</sub>) values of the previous calculation.

$$\text{mass P}_4 = 17 \text{ g PCl}_3 \times \frac{1 \text{ mol PCl}_3}{137.33 \text{ g PCl}_3} \times \frac{1 \text{ mol P}_4}{4 \text{ mol PCl}_3} \times \frac{123.90 \text{ g P}_4}{1 \text{ mol P}_4} = 3.8 \text{ g P}_4$$

**13B** Find the amount of H<sub>2</sub>O(l) formed by each reactant, to determine the limiting reactant.

$$\text{amount H}_2\text{O} = 12.2 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{2 \text{ mol H}_2\text{O}}{2 \text{ mol H}_2} = 6.05 \text{ mol H}_2\text{O}$$

$$\text{amount H}_2\text{O} = 154 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} = 9.63 \text{ mol H}_2\text{O}$$

Since H<sub>2</sub> is limiting, we compute the mass of O<sub>2</sub> needed to react with all of the H<sub>2</sub>

$$\text{mass O}_2 \text{ reacting} = 6.05 \text{ mol H}_2\text{O produced} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} = 96.8 \text{ g O}_2 \text{ reacting}$$

$$\text{mass O}_2 \text{ remaining} = 154 \text{ g originally present} - 96.8 \text{ g O}_2 \text{ reacting} = 57 \text{ g O}_2 \text{ remaining}$$

**14A (a)** The theoretical yield is the product mass we predict by calculation.

$$\text{mass CH}_2\text{O(g)} = 1.00 \text{ mol CH}_3\text{OH} \times \frac{1 \text{ mol CH}_2\text{O}}{1 \text{ mol CH}_3\text{OH}} \times \frac{30.03 \text{ g CH}_2\text{O}}{1 \text{ mol CH}_2\text{O}} = 30.0 \text{ g CH}_2\text{O}$$

**(b)** The actual yield is what is obtained experimentally: 25.7 g CH<sub>2</sub>O (g).

**(c)** The percent yield is the ratio of actual to theoretical yields, multiplied by 100%:

$$\% \text{ yield} = \frac{25.7 \text{ g CH}_2\text{O produced}}{30.0 \text{ g CH}_2\text{O calculated}} \times 100 \% = 85.6 \% \text{ yield}$$

**14B** Determine the mass of product formed by each reactant.

$$\text{mass PCl}_3 = 25.0 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{123.90 \text{ g P}_4} \times \frac{4 \text{ mol PCl}_3}{1 \text{ mol P}_4} \times \frac{137.33 \text{ g PCl}_3}{1 \text{ mol PCl}_3} = 111 \text{ g PCl}_3$$

$$\text{mass PCl}_3 = 91.5 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.91 \text{ g Cl}_2} \times \frac{4 \text{ mol PCl}_3}{6 \text{ mol Cl}_2} \times \frac{137.33 \text{ g PCl}_3}{1 \text{ mol PCl}_3} = 118 \text{ g PCl}_3$$

The limiting reactant is P<sub>4</sub>, and 111 g PCl<sub>3</sub> should be produced. This is the theoretical yield. The actual yield is 104 g PCl<sub>3</sub>. Thus, the percent yield of the reaction is

$$\frac{104 \text{ g PCl}_3 \text{ produced}}{111 \text{ g PCl}_3 \text{ calculated}} \times 100 \% = 93.7 \% \text{ yield.}$$

**15A** The reaction is  $2 \text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{NH}_2)_2(\text{s}) + \text{H}_2\text{O}(\text{l})$ . We need to distinguish between mass of urea produced (actual yield) and mass of urea predicted (theoretical yield).

$$\text{mass CO}_2 = 50.0 \text{ g CO}(\text{NH}_2)_2 \text{ produced} \times \frac{100.0 \text{ g predicted}}{87.5 \text{ g produced}} \times \frac{1 \text{ mol CO}(\text{NH}_2)_2}{60.1 \text{ g CO}(\text{NH}_2)_2} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CO}(\text{NH}_2)_2}$$

$$\times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} = 41.8 \text{ g CO}_2 \text{ needed}$$

**15B** Care must be taken to use the proper units/label in each conversion factor. Note, you cannot calculate the molar mass of an impure material or mixture.

$$\text{mass C}_6\text{H}_{11}\text{OH} = 45.0 \text{ g C}_6\text{H}_{10} \text{ produced} \times \frac{100.0 \text{ g C}_6\text{H}_{10} \text{ cal'd}}{86.2 \text{ g C}_6\text{H}_{10} \text{ produc'd}} \times \frac{1 \text{ mol C}_6\text{H}_{10}}{82.1 \text{ g C}_6\text{H}_{10}} \times \frac{1 \text{ mol C}_6\text{H}_{11}\text{OH}}{1 \text{ mol C}_6\text{H}_{10}}$$

$$\times \frac{100.2 \text{ g pure C}_6\text{H}_{11}\text{OH}}{1 \text{ mol C}_6\text{H}_{11}\text{OH}} \times \frac{100.0 \text{ g impure C}_6\text{H}_{11}\text{OH}}{92.3 \text{ g pure C}_6\text{H}_{11}\text{OH}} = 69.0 \text{ g impure C}_6\text{H}_{11}\text{OH}$$

**16A** We can trace the nitrogen through the sequence of reactions. We notice that 4 moles of N (as 4 mol  $\text{NH}_3$ ) are consumed in the first reaction, and 4 moles of N (as 4 mole NO) are produced. In the second reaction, 2 moles of N (as 2 mol NO) is consumed and 2 moles of N (as 2 mol  $\text{NO}_2$ ) are produced. In the last reaction, 3 moles of N (as 3 mol  $\text{NO}_2$ ) are consumed and just 2 moles of N (as 2 mol  $\text{HNO}_3$ ) are produced.

$$\text{mass HNO}_3 = 1.00 \text{ kg NH}_3 \times \frac{1000 \text{ g NH}_3}{1 \text{ kg NH}_3} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{4 \text{ mol NO}}{4 \text{ mol NH}_3} \times \frac{2 \text{ mol NO}_2}{2 \text{ mol NO}}$$

$$\times \frac{2 \text{ mol HNO}_3}{3 \text{ mol NO}_2} \times \frac{63.01 \text{ g HNO}_3}{1 \text{ mol HNO}_3} = 2.47 \times 10^3 \text{ g HNO}_3$$

**16B**  $\text{mass H}_2(\text{Al}) = 0.710 \text{ g alloy} \times \frac{0.700 \text{ g Al}}{1.000 \text{ g alloy}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Al}} \times \frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} = 0.0557 \text{ g}$

$$\text{mass H}_2(\text{Mg}) = 0.710 \text{ g alloy} \times \frac{0.300 \text{ g Mg}}{1.000 \text{ g alloy}} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Mg}} \times \frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} = 0.0177 \text{ g}$$

$$\text{total mass of H}_2 = 0.0557 \text{ g H}_2 \text{ from Al} + 0.0177 \text{ g H}_2 \text{ from Mg} = 0.0734 \text{ g H}_2$$

## REVIEW QUESTIONS

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1. (a) The symbol “ $\xrightarrow{\Delta}$ ” indicates that the mixture is heated to produce the reaction.  
(b) The symbol “(aq)” indicates that the species preceding this symbol is dissolved in aqueous solution, that is, it indicates a solution with water as the solvent.  
(c) The stoichiometric coefficient is the number that appears in a chemical equation immediately before the chemical formula of a species.  
(d) The net “overall” equation is the chemical equation that remains after species that appear on both sides of an equation are “cancelled.” The term also is used to describe an equation that summarizes the overall result of a process consisting of several reactions.
2. (a) One “balances a chemical equation” by inserting stoichiometric coefficients into the formula expression, so that the resulting equation has the same number and type of atoms on each side.  
(b) When one “prepares a solution by dilution” one begins with a more concentrated solution (a homogeneous mixture with a larger concentration of solute) and adds solvent, thus producing a less concentrated (or more dilute) solution.  
(c) One “determines the limiting reactant in a reaction” by discovering which reactant will produce the smallest quantity of product. That reactant will limit the quantity of product that can be formed from the other reactants, and also limit the quantity that will be consumed of the other reactants.
3. (a) A chemical formula is a short-hand representation of a chemical species: atom, ion, or molecule. A chemical equation is a written representation of a chemical reaction; it typically involves two or more species. Whereas a chemical formula is rather analogous to a “word,” chemical equations parallel “sentences.”  
(b) A decomposition reaction is one in which a compound is broken down into simpler substances. In a synthesis reaction two or more substances combine to form a third.  
(c) The solute is the substance that is dispersed in a solution. The solvent is the substance that does the dispersing. Usually, a solution is of the same physical state (solid, liquid, or gas) as the solvent, and the solvent is the component present in the larger amount.  
(d) The actual yield of a chemical reaction is the quantity of product that actually was formed. The percent yield relates the actual yield to the quantity of product that was calculated to be produced, assuming that all reactants produced only one set of products and the reaction continued until one reactant was exhausted.
4. (a)  $\text{Na}_2\text{SO}_4(\text{s}) + 4\text{C}(\text{s}) \rightarrow \text{Na}_2\text{S}(\text{s}) + 4\text{CO}(\text{g})$   
(b)  $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{Cl}_2(\text{g})$   
(c)  $\text{PCl}_5(\text{l}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5\text{HCl}(\text{aq})$   
(d)  $3\text{PbO}(\text{s}) + 2\text{NH}_3(\text{g}) \rightarrow 3\text{Pb}(\text{s}) + \text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$   
(e)  $\text{Mg}_3\text{N}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{Mg}(\text{OH})_2(\text{s}) + 2\text{NH}_3(\text{g})$

5. (a)  $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$   
 (b)  $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$   
 (c)  $2\text{C}_2\text{H}_6\text{(g)} + 7\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}$   
 (d)  $\text{Ag}_2\text{SO}_4\text{(aq)} + \text{BaI}_2\text{(aq)} \rightarrow \text{BaSO}_4\text{(s)} + 2\text{AgI(s)}$
6. (a)  $\text{C}_7\text{H}_{16}\text{(l)} + 11\text{O}_2\text{(g)} \rightarrow 7\text{CO}_2\text{(g)} + 8\text{H}_2\text{O(l)}$   
 (b)  $\text{C}_4\text{H}_9\text{OH(l)} + 6\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 5\text{H}_2\text{O(l)}$   
 (c)  $2\text{HI(aq)} + \text{Na}_2\text{CO}_3\text{(aq)} \rightarrow 2\text{NaI(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$   
 (d)  $3\text{NaOH(aq)} + \text{FeCl}_3\text{(aq)} \rightarrow \text{Fe(OH)}_3\text{(s)} + 3\text{NaCl(aq)}$
7. Expression (c) is incorrect because  $\text{KClO}$  is potassium hypochlorite, but the stated product is potassium chloride,  $\text{KCl}$ . Expression (a) and (b) are incorrect because  $\text{O(g)}$  is not normally produced in chemical reactions;  $\text{O}_2\text{(g)}$  is more thermodynamically stable  
 The correct equation is  $2\text{KClO}_3\text{(s)} \rightarrow 2\text{KCl(s)} + 3\text{O}_2\text{(g)}$ .
8. For the reaction  $2\text{H}_2\text{S(g)} + \text{SO}_2\text{(g)} \rightarrow 3\text{S(s)} + 2\text{H}_2\text{O(l)}$
- (1) FALSE 3 moles of S are produced per *two* moles of  $\text{H}_2\text{S}$ .  
 (2) FALSE 3 *moles* of S are produced for every *mole* of  $\text{SO}_2$  consumed.  
 (3) TRUE 1 mole of  $\text{H}_2\text{O}$  is produced per mole of  $\text{H}_2\text{S}$  consumed.  
 (4) TRUE Two-thirds of the S produced *does* come from the  $\text{H}_2\text{S}$ .  
 (5) FALSE There are *five* moles of products and *three* moles of reactants.
9. The conversion factor is obtained from the balanced chemical equation.  
 $\text{moles FeCl}_3 = 7.26 \text{ mol Cl}_2 \times \frac{2 \text{ mol FeCl}_3}{3 \text{ mol Cl}_2} = 4.84 \text{ mol FeCl}_3$
10. The pivotal conversion factor, from the balanced equation, enables one to relate the amounts of  $\text{O}_2$  and  $\text{KClO}_3$ .  
 $\text{mass O}_2 = 43.4 \text{ g KClO}_3 \times \frac{1 \text{ mol KClO}_3}{122.5 \text{ g KClO}_3} \times \frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} = 17.0 \text{ g O}_2$
11. Each calculation uses the stoichiometric coefficients from the balanced chemical equation and the molar mass of the reactant.  
 $\text{mass Cl}_2 = 0.337 \text{ mol PCl}_3 \times \frac{6 \text{ mol Cl}_2}{4 \text{ mol PCl}_3} \times \frac{70.91 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 35.8 \text{ g Cl}_2$   
 $\text{mass P}_4 = 0.337 \text{ mol PCl}_3 \times \frac{1 \text{ mol P}_4}{4 \text{ mol PCl}_3} \times \frac{123.9 \text{ g P}_4}{1 \text{ mol P}_4} = 10.4 \text{ g P}_4$

12. (a) amount O<sub>2</sub> = 156 g CO<sub>2</sub> ×  $\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{3 \text{ mol O}_2}{2 \text{ mol CO}_2} = 5.32 \text{ mol O}_2$
- (b) mass KO<sub>2</sub> = 100.0 g CO<sub>2</sub> ×  $\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{4 \text{ mol KO}_2}{2 \text{ mol CO}_2} \times \frac{71.10 \text{ g KO}_2}{1 \text{ mol KO}_2} = 323.1 \text{ g KO}_2$
- (c) no. O<sub>2</sub> molecules = 1.00 mg KO<sub>2</sub> ×  $\frac{1 \text{ g KO}_2}{1000 \text{ mg}} \times \frac{1 \text{ mol KO}_2}{71.10 \text{ g KO}_2} \times \frac{3 \text{ mol O}_2}{4 \text{ mol KO}_2}$   
 $\times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol O}_2} = 6.35 \times 10^{18} \text{ O}_2 \text{ molecules}$
13. (a) CH<sub>3</sub>OH molarity =  $\frac{2.92 \text{ mol CH}_3\text{OH}}{7.16 \text{ L}} = 0.408 \text{ M}$
- (b) C<sub>2</sub>H<sub>5</sub>OH molarity =  $\frac{7.69 \text{ mmol C}_2\text{H}_5\text{OH}}{50.00 \text{ mL}} = 0.154 \text{ M}$
- (c) CO(NH<sub>2</sub>)<sub>2</sub> molarity =  $\frac{25.2 \text{ g CO(NH}_2)_2}{275 \text{ mL}} \times \frac{1 \text{ mol CO(NH}_2)_2}{60.06 \text{ g CO(NH}_2)_2} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.53 \text{ M}$
- (d) molarity =  $\frac{18.5 \text{ mL C}_3\text{H}_5(\text{OH})_3}{375 \text{ mL soln}} \times \frac{1.26 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol C}_3\text{H}_5(\text{OH})_3}{92.09 \text{ g C}_3\text{H}_5(\text{OH})_3} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.675 \text{ M}$
14. (a) mol NaI =  $2.55 \times 10^3 \text{ L} \times \frac{0.125 \text{ mol NaI}}{1 \text{ L soln}} = 319 \text{ mol NaI}$
- (b) mass Na<sub>2</sub>CO<sub>3</sub> =  $475 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.398 \text{ mol Na}_2\text{CO}_3}{1 \text{ L}} \times \frac{106.0 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3}$   
 $= 20.0 \text{ g Na}_2\text{CO}_3$
- (c) mg CaCl<sub>2</sub> =  $1.00 \text{ mL} \times \frac{0.148 \text{ mmol CaCl}_2}{1 \text{ mL}} \times \frac{111.0 \text{ mg CaCl}_2}{1 \text{ mmol CaCl}_2} = 16.4 \text{ mg CaCl}_2$
15. A 1.00 M KCl solution contains 1 mol KCl per liter of solution. The molar mass of KCl is 74.6 g. Thus, a 1.00 M KCl solution contains 74.6 g KCl per liter of solution. "1.00 L containing 100 g" is incorrect; 1.00 L should contain 74.6 g. "500 mL containing 74.6 g" also is incorrect; 74.6 g should be contained in 1000 mL. "a solution containing 7.46 mg KCl/mL" is incorrect; there should be 74.6 mg. 5.00 L of 1.00 M KCl contains five times the mass of solute as does 1.00 L of this solution, 373 g. The last description is correct.
16. Volume of concentrated AgNO<sub>3</sub> solution

$$V_{\text{AgNO}_3} = 250.0 \text{ mL dilute soln} \times \frac{0.423 \text{ mmol AgNO}_3}{1 \text{ mL dilute soln}} \times \frac{1 \text{ mL conc. soln.}}{0.650 \text{ mmol AgNO}_3}$$

$$V_{\text{AgNO}_3} = 163 \text{ mL AgNO}_3$$

17. The same amount in moles of  $K_2SO_4$  is present in both solutions. That amount is given in the numerator of the following expression.

$$K_2SO_4 \text{ molarity} = \frac{135 \text{ mL} \times \frac{0.188 \text{ mmol } K_2SO_4}{1 \text{ mL}}}{105 \text{ mL}} = 0.242 \text{ M}$$

18. The balanced chemical equation provides a conversion factor between the two compounds.

$$\text{mass } CuCO_3 = 415 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.275 \text{ mol } Cu(NO_3)_2}{1 \text{ L}} \times \frac{1 \text{ mol } CuCO_3}{1 \text{ mol } Cu(NO_3)_2} \times \frac{123.6 \text{ g } CuCO_3}{1 \text{ mol } CuCO_3}$$

$$\text{mass } CuCO_3 = 14.1 \text{ g } CuCO_3$$

19. After determining the amount of  $CaCO_3$  (100.09 g/mol), we find the volume of HCl.

$$\text{volume HCl(aq)} = 1.75 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.09 \text{ g}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } CaCO_3} \times \frac{1 \text{ L soln}}{2.35 \text{ mol HCl}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 14.9 \text{ mL HCl(aq) solution}$$

20. In this situation, since 2 mol  $H_2O$  are required per mol  $CaH_2$ , 1.52 mol  $H_2O$  is the limiting reactant. Thus, the amount in moles of  $H_2$  can be computed as follows.

$$\text{amount } H_2 = 1.52 \text{ mol } H_2O \times \frac{2 \text{ mol } H_2}{2 \text{ mol } H_2O} = 1.52 \text{ mol } H_2$$

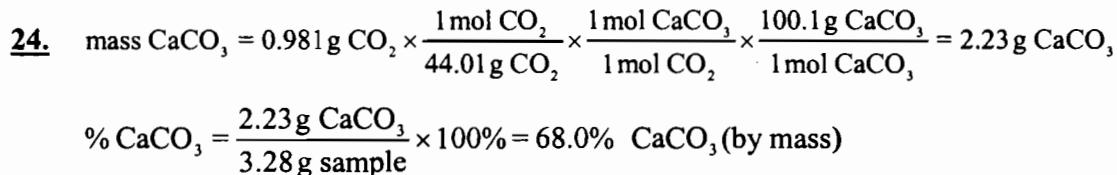
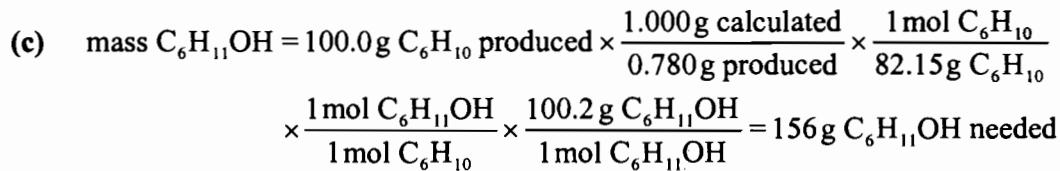
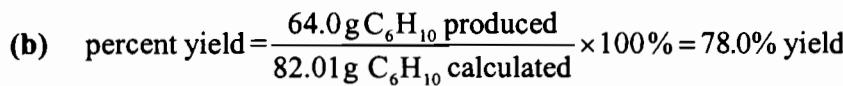
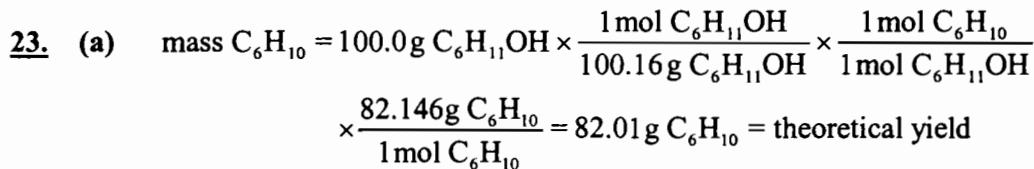
21. Determine the number of moles of NO produced by each reactant. The one producing the smaller amount of NO is the limiting reactant.

$$\text{mol NO} = 0.696 \text{ mol Cu} \times \frac{2 \text{ mol NO}}{3 \text{ mol Cu}} = 0.464 \text{ mol NO}$$

$$\text{mol NO} = 136 \text{ mL } HNO_3 \text{ (aq)} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{6.0 \text{ mol } HNO_3}{1 \text{ L}} \times \frac{2 \text{ mol NO}}{8 \text{ mol } HNO_3} = 0.204 \text{ mol NO}$$

Since  $HNO_3$  (aq) is the limiting reactant, it will be completely consumed, leaving some Cu unreacted.

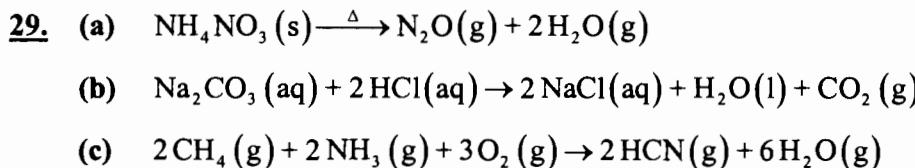
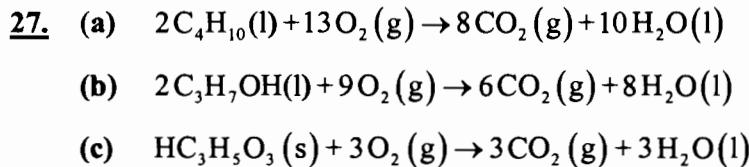
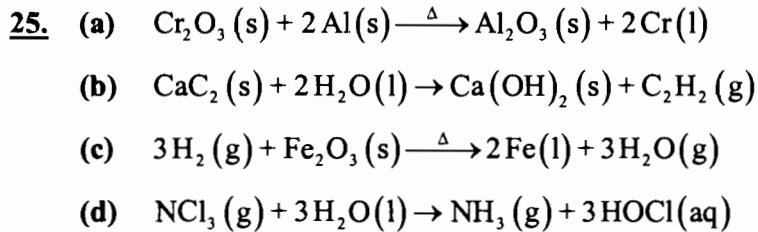
22. (a) Since the stoichiometry indicates that 1 mole  $CCl_2F_2$  is produced per mole  $CCl_4$ , the use of 1.80 mole  $CCl_4$  will produce 1.80 mole  $CCl_2F_2$ . This is the theoretical yield of the reaction.
- (b) The actual yield of the reaction is the amount actually produced, 1.55 mol  $CCl_2F_2$ .
- (c)  $\% \text{ yield} = \frac{1.55 \text{ mol } CCl_2F_2 \text{ obtained}}{1.80 \text{ mol } CCl_2F_2 \text{ calculated}} \times 100\% = 86.1\% \text{ yield}$



## EXERCISES

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### Writing and Balancing Chemical Equations



- 31.** Unbalanced reaction:  $\text{N}_2\text{H}_4(\text{g}) + \text{N}_2\text{O}_4(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$
- Balance H atoms:  $\text{N}_2\text{H}_4(\text{g}) + \text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$
- Balance O atoms:  $\text{N}_2\text{H}_4(\text{g}) + 1/2 \text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$
- Balance N atoms:  $\text{N}_2\text{H}_4(\text{g}) + 1/2 \text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + 3/2 \text{N}_2(\text{g})$
- Multiply by 2 (whole #)  $2 \text{N}_2\text{H}_4(\text{g}) + \text{N}_2\text{O}_4(\text{g}) \rightarrow 4 \text{H}_2\text{O}(\text{g}) + 3 \text{N}_2(\text{g})$
- Self Check:  $6 \text{N} + 8 \text{H} + 4 \text{O} \rightarrow 6 \text{N} + 8 \text{H} + 4 \text{O}$

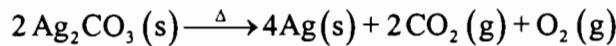
## Stoichiometry of Chemical Reactions

**33. (a)**  $\text{mol O}_2 = 32.8 \text{ g KClO}_3 \times \frac{1 \text{ mol KClO}_3}{122.6 \text{ g KClO}_3} \times \frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} = 0.401 \text{ mol O}_2$

**(b)**  $\text{mass KClO}_3 = 50.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} = 128 \text{ g KClO}_3$

**(c)**  $\text{mass KCl} = 28.3 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{2 \text{ mol KCl}}{3 \text{ mol O}_2} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = 44.0 \text{ g KCl}$

- 35.** Balance the given equation, and then solve the problem.



$$\text{mass Ag}_2\text{CO}_3 = 75.1 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.87 \text{ g Ag}} \times \frac{2 \text{ mol Ag}_2\text{CO}_3}{4 \text{ mol Ag}} \times \frac{275.75 \text{ g Ag}_2\text{CO}_3}{1 \text{ mol Ag}_2\text{CO}_3} = 96.0 \text{ g Ag}_2\text{CO}_3$$

- 37.** The balanced equation is  $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) \xrightarrow{\Delta} 2\text{Fe}(\text{l}) + 3\text{CO}(\text{g})$

$$\text{mass Fe}_2\text{O}_3 = 523 \text{ kg Fe} \times \frac{1 \text{ kmol Fe}}{55.85 \text{ kg Fe}} \times \frac{1 \text{ kmol Fe}_2\text{O}_3}{2 \text{ kmol Fe}} \times \frac{159.7 \text{ kg Fe}_2\text{O}_3}{1 \text{ kmol Fe}_2\text{O}_3} = 748 \text{ kg Fe}_2\text{O}_3$$

$$\% \text{Fe}_2\text{O}_3 \text{ in ore} = \frac{748 \text{ kg Fe}_2\text{O}_3}{938 \text{ kg ore}} \times 100\% = 79.7\% \text{ Fe}_2\text{O}_3$$

- 39.**  $2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2(\text{g})$ . First determine the mass of Al in the foil.

$$\text{mass Al} = (10.25 \text{ cm} \times 5.50 \text{ cm} \times 0.601 \text{ mm}) \times \frac{1 \text{ cm}}{10 \text{ mm}} \times \frac{2.70 \text{ g}}{1 \text{ cm}^3} = 9.15 \text{ g Al}$$

$$\text{mass H}_2 = 9.15 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Al}} \times \frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} = 1.03 \text{ g H}_2$$

- 41.** In each balanced reaction, one mole of  $\text{O}_2(\text{g})$  is produced from two moles of solid reactant. Thus, the reaction that produces the most  $\text{O}_2(\text{g})$  per gram of reactant is the one involving the reactant with the smallest molar mass.  $\text{NH}_4\text{NO}_3$  is 80.04 g/mol;  $\text{Ag}_2\text{O}$  is 231.74 g/mol;  $\text{HgO}$  is 216.59 g/mol; and  $\text{Pb}(\text{NO}_3)_2$  is 331.2 g/mol. Thus,  $\text{NH}_4\text{NO}_3$  (reaction 1) produces the most oxygen per gram of reactant.

## Molarity

43. (a)  $[C_{12}H_{22}O_{11}] = \frac{150.0 \text{ g } C_{12}H_{22}O_{11}}{250.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}} = 1.753 \text{ M}$

(b)  $[CO(NH_2)_2] = \frac{98.3 \text{ mg solid}}{5.00 \text{ mL soln}} \times \frac{97.9 \text{ mg } CO(NH_2)_2}{100 \text{ mg solid}} \times \frac{1 \text{ mmol } CO(NH_2)_2}{60.06 \text{ mg } CO(NH_2)_2}$   
 $= 0.320 \text{ M } CO(NH_2)_2$

(c)  $[CH_3OH] = \frac{125.0 \text{ mL } CH_3OH}{15.0 \text{ L soln}} \times \frac{0.792 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} = 0.206 \text{ M}$

45. (a) mass  $C_6H_{12}O_6 = 75.0 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.350 \text{ mol } C_6H_{12}O_6}{1 \text{ L soln}} \times \frac{180.16 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 4.73 \text{ g}$

(b)  $V_{CH_3OH} = 2.25 \text{ L soln} \times \frac{0.485 \text{ mol}}{1 \text{ L}} \times \frac{32.04 \text{ g } CH_3OH}{1 \text{ mol } CH_3OH} \times \frac{1 \text{ mL}}{0.792 \text{ g}} = 44.1 \text{ mL } CH_3OH$

47. We determine the molar concentration of the 46% by mass sucrose solution.

$$[C_{12}H_{22}O_{11}] = \frac{46 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}}}{100 \text{ g soln} \times \frac{1 \text{ mL}}{1.21 \text{ g soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 1.6 \text{ M}$$

The 46% by mass sucrose solution is the more concentrated.

49.  $[KNO_3] = \frac{10.00 \text{ mL conc'd soln} \times \frac{2.05 \text{ mmol } KNO_3}{1 \text{ mL}}}{250.0 \text{ mL}} = 0.0820 \text{ M}$

51. Let us compute how many mL of dilute (<sub>d</sub>) solution we obtain from each mL of concentrated (<sub>c</sub>) solution.  $V_c \times C_c = V_d \times C_d$  becomes  $1.00 \text{ mL} \times 0.250 \text{ M} = x \text{ mL} \times 0.0125 \text{ M}$  and  $x = 20$ . Thus, the ratio of the volume of the volumetric flask to that of the pipet would be 20:1. We could use a 100.0-mL flask and a 5.00-mL pipet, a 1000.0-mL flask and a 50.00-mL pipet, or a 500.0-mL flask and a 25.00-mL pipet. There are many combinations that could be used.

## Chemical Reactions in Solutions

**53. (a)** mass  $\text{Na}_2\text{S} = 27.8 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.163 \text{ mol AgNO}_3}{1 \text{ L soln}} \times \frac{1 \text{ mol Na}_2\text{S}}{2 \text{ mol AgNO}_3}$   
 $\times \frac{78.05 \text{ g Na}_2\text{S}}{1 \text{ mol Na}_2\text{S}} = 0.177 \text{ g Na}_2\text{S}$

**(b)** mass  $\text{Ag}_2\text{S} = 0.177 \text{ g Na}_2\text{S} \times \frac{1 \text{ mol Na}_2\text{S}}{78.05 \text{ g Na}_2\text{S}} \times \frac{1 \text{ mol Ag}_2\text{S}}{1 \text{ mol Na}_2\text{S}} \times \frac{247.80 \text{ g Ag}_2\text{S}}{1 \text{ mol Ag}_2\text{S}} = 0.562 \text{ g Ag}_2\text{S}$

**55. (a)** We know that the Al forms the  $\text{AlCl}_3$ .

$$\text{mol AlCl}_3 = 1.87 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{1 \text{ mol AlCl}_3}{1 \text{ mol Al}} = 0.0693 \text{ mol AlCl}_3$$

**(b)**  $[\text{AlCl}_3] = \frac{0.0693 \text{ mol AlCl}_3}{23.8 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 2.91 \text{ M AlCl}_3$

**57.** The molarity unit can be interpreted as millimoles of solute per milliliter of solution.

$$V_{\text{K}_2\text{CrO}_4} = 415 \text{ mL} \times \frac{0.186 \text{ mmol AgNO}_3}{1 \text{ mL soln}} \times \frac{1 \text{ mmol K}_2\text{CrO}_4}{2 \text{ mmol AgNO}_3} \times \frac{1 \text{ mL K}_2\text{CrO}_4 \text{ (aq)}}{0.650 \text{ mmol K}_2\text{CrO}_4}$$

$$V_{\text{K}_2\text{CrO}_4} = 59.4 \text{ mL K}_2\text{CrO}_4$$

**59.** mass  $\text{Na} = 155 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.175 \text{ mol NaOH}}{1 \text{ L soln}} \times \frac{2 \text{ mol Na}}{2 \text{ mol NaOH}} \times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}}$   
 $= 0.624 \text{ g Na}$

**61.** The mass of oxalic acid enables us to determine the amount of NaOH in the solution.

$$[\text{NaOH}] = \frac{0.3126 \text{ g H}_2\text{C}_2\text{O}_4}{26.21 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \times \frac{1 \text{ mol H}_2\text{C}_2\text{O}_4}{90.04 \text{ g H}_2\text{C}_2\text{O}_4} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{C}_2\text{O}_4} = 0.2649 \text{ M}$$

## Determining the Limiting Reactant

**63.** There are equal numbers of moles of each reactant present, but more  $\text{O}_2$  is needed than  $\text{NH}_3$ . Thus,  $\text{O}_2(\text{g})$  is the limiting reactant, and all of the  $\text{O}_2(\text{g})$  is consumed. The mass of product produced from 1.00 mol  $\text{O}_2(\text{g})$  is then calculated.

$$\text{mass NO(g)} = 1.00 \text{ mol O}_2 \times \frac{4 \text{ mol NO(g)}}{5 \text{ mol O}_2(\text{g})} \times \frac{30.01 \text{ g NO(g)}}{1 \text{ mol NO(g)}} = 24.0 \text{ g NO(g)}$$

65. Determine the amount of  $\text{Na}_2\text{CS}_3$  produced from each of the reactants.

$$\text{amount Na}_2\text{CS}_3 = 92.5 \text{ mL CS}_2 \times \frac{1.26 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol CS}_2}{76.14 \text{ g CS}_2} \times \frac{2 \text{ mol Na}_2\text{CS}_3}{3 \text{ mol CS}_2} = 1.02 \text{ mol Na}_2\text{CS}_3$$

$$\text{amount Na}_2\text{CS}_3 = 2.78 \text{ mol NaOH} \times \frac{2 \text{ mol Na}_2\text{CS}_3}{6 \text{ mol NaOH}} = 0.927 \text{ mol Na}_2\text{CS}_3$$

$$\text{Thus, the mass produced is } 0.927 \text{ mol Na}_2\text{CS}_3 \times \frac{154.2 \text{ g Na}_2\text{CS}_3}{1 \text{ mol Na}_2\text{CS}_3} = 143 \text{ g Na}_2\text{CS}_3$$

67.  $\text{Ca(OH)}_2(s) + 2 \text{NH}_4\text{Cl}(s) \rightarrow \text{CaCl}_2(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{NH}_3(g)$

Compute the amount of  $\text{NH}_3$  formed from each reactant in this limiting reactant problem.

$$\text{amount NH}_3 = 33.0 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \times \frac{2 \text{ mol NH}_3}{2 \text{ mol NH}_4\text{Cl}} = 0.617 \text{ mol NH}_3$$

$$\text{amount NH}_3 = 33.0 \text{ g Ca(OH)}_2 \times \frac{1 \text{ mol Ca(OH)}_2}{74.09 \text{ g Ca(OH)}_2} \times \frac{2 \text{ mol NH}_3}{1 \text{ mol Ca(OH)}_2} = 0.891 \text{ mol NH}_3$$

$$\text{Thus, } 0.617 \text{ mol NH}_3 \text{ is produced. mass NH}_3 = 0.617 \text{ mol NH}_3 \times \frac{17.03 \text{ g NH}_3}{1 \text{ mol NH}_3} = 10.5 \text{ g NH}_3$$

Now we determine the mass of reactant in excess,  $\text{Ca(OH)}_2$ .

$$\text{Ca(OH)}_2 \text{ used} = 0.617 \text{ mol NH}_3 \times \frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol NH}_3} \times \frac{74.09 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} = 22.9 \text{ g Ca(OH)}_2$$

$$\text{excess Ca(OH)}_2 = 33.0 \text{ g Ca(OH)}_2 - 22.9 \text{ g Ca(OH)}_2 = 10.1 \text{ g excess Ca(OH)}_2$$

## Theoretical, Actual, and Percent Yields

69. (a) We first need to solve the limiting reactant problem involved here.

$$\text{mol C}_4\text{H}_9\text{Br} = 15.0 \text{ g C}_4\text{H}_9\text{OH} \times \frac{1 \text{ mol C}_4\text{H}_9\text{OH}}{74.12 \text{ g C}_4\text{H}_9\text{OH}} \times \frac{1 \text{ mol C}_4\text{H}_9\text{Br}}{1 \text{ mol C}_4\text{H}_9\text{OH}} = 0.202 \text{ mol C}_4\text{H}_9\text{Br}$$

$$\begin{aligned} \text{mol C}_4\text{H}_9\text{Br} &= 22.4 \text{ g NaBr} \times \frac{1 \text{ mol NaBr}}{102.9 \text{ g NaBr}} \times \frac{1 \text{ mol C}_4\text{H}_9\text{Br}}{1 \text{ mol NaBr}} \\ &= 0.218 \text{ mol C}_4\text{H}_9\text{Br} \end{aligned}$$

$$\text{mol C}_4\text{H}_9\text{Br} = 32.7 \text{ g H}_2\text{SO}_4 \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4} \times \frac{1 \text{ mol C}_4\text{H}_9\text{Br}}{1 \text{ mol H}_2\text{SO}_4} = 0.333 \text{ mol C}_4\text{H}_9\text{Br}$$

$$\text{Theoretical yield of C}_4\text{H}_9\text{Br} = 0.202 \text{ mol C}_4\text{H}_9\text{Br} \times \frac{137.0 \text{ g C}_4\text{H}_9\text{Br}}{1 \text{ mol C}_4\text{H}_9\text{Br}} = 27.7 \text{ g C}_4\text{H}_9\text{Br}$$

(b) The actual yield is the mass obtained, 17.1 g  $\text{C}_4\text{H}_9\text{Br}$ .

(c) Then, % yield =  $\frac{17.1 \text{ g } \text{C}_4\text{H}_9\text{Br produced}}{27.7 \text{ g } \text{C}_4\text{H}_9\text{Br expected}} \times 100\% = 61.7\% \text{ yield}$

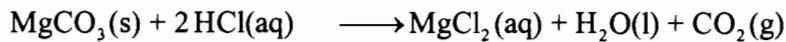
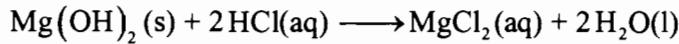
71. Balanced equation:  $3\text{C}_2\text{H}_4\text{O}_2 + \text{PCl}_3 \rightarrow 3\text{C}_2\text{H}_3\text{OCl} + \text{H}_3\text{PO}_3$

$$\text{mass acid} = 75 \text{ g } \text{C}_2\text{H}_3\text{OCl} \times \frac{100.0 \text{ g calculated}}{78.2 \text{ g produced}} \times \frac{1 \text{ mol } \text{C}_2\text{H}_3\text{OCl}}{78.5 \text{ g } \text{C}_2\text{H}_3\text{OCl}} \times \frac{3 \text{ mol } \text{C}_2\text{H}_4\text{O}_2}{3 \text{ mol } \text{C}_2\text{H}_3\text{OCl}} \\ \times \frac{60.1 \text{ g pure } \text{C}_2\text{H}_4\text{O}_2}{1 \text{ mol } \text{C}_2\text{H}_4\text{O}_2} \times \frac{100 \text{ g commercial}}{97 \text{ g pure } \text{C}_2\text{H}_4\text{O}_2} = 76 \text{ g commercial } \text{C}_2\text{H}_4\text{O}_2$$

73. A less-than-100% yield of desired product in synthesis reactions is always the case. This is because of side reactions that yield products other than those desired and because of the loss of material in the various steps of the synthesis procedure. A main criterion for choosing a synthesis reaction is how economically it can be run. In the analysis of a compound, on the other hand, it is essential that all of the material present be detected. Therefore, a 100% yield is required; none of the material present in the sample can be lost during the analysis. Therefore analysis reactions are carefully chosen to meet this criterion; they need not be economical to run.

## Consecutive Reactions, Simultaneous Reactions

75. Determine the amount of HCl needed to react with each component of the mixture.



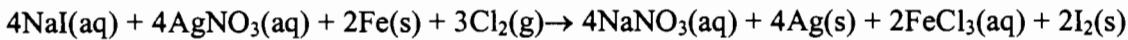
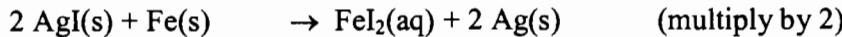
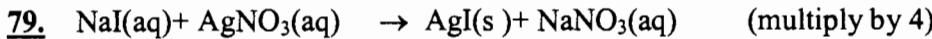
$$\text{mol HCl} = 425 \text{ g mixt.} \times \frac{35.2 \text{ g } \text{MgCO}_3}{100.0 \text{ g mixt.}} \times \frac{1 \text{ mol } \text{MgCO}_3}{84.3 \text{ g } \text{MgCO}_3} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } \text{MgCO}_3} = 3.55 \text{ mol HCl}$$

$$\text{mol HCl} = 425 \text{ g mixt.} \times \frac{64.8 \text{ g } \text{Mg}(\text{OH})_2}{100.0 \text{ g mixt.}} \times \frac{1 \text{ mol } \text{Mg}(\text{OH})_2}{58.3 \text{ g } \text{Mg}(\text{OH})_2} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } \text{MgCO}_3} = 9.45 \text{ mol HCl}$$

$$\text{mass HCl} = (3.55 + 9.45) \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 474 \text{ g HCl}$$

77. The molar ratios given by the stoichiometric coefficients in the balanced chemical equations are used in the solution.

$$\text{amount Cl}_2 = 2.25 \times 10^3 \text{ g } \text{CCl}_2\text{F}_2 \times \frac{1 \text{ mol } \text{CCl}_2\text{F}_2}{120.91 \text{ g } \text{CCl}_2\text{F}_2} \times \frac{1 \text{ mol } \text{CCl}_4}{1 \text{ mol } \text{CCl}_2\text{F}_2} \times \frac{4 \text{ mol Cl}_2}{1 \text{ mol } \text{CCl}_4} \\ = 74.4 \text{ mol Cl}_2$$



For every 4 moles of  $\text{AgNO}_3$ , 2 moles of  $\text{I}_2\text{(s)}$  are produced. The mass of  $\text{AgNO}_3$  required

$$= 1.00 \text{ kg I}_2\text{(s)} \times \frac{1000 \text{ g I}_2\text{(s)}}{1 \text{ kg I}_2\text{(s)}} \times \frac{1 \text{ mol I}_2\text{(s)}}{253.809 \text{ g I}_2\text{(s)}} \times \frac{4 \text{ mol AgNO}_3\text{(s)}}{2 \text{ mol I}_2\text{(s)}} \times \frac{169.873 \text{ g AgNO}_3\text{(s)}}{1 \text{ mol AgNO}_3\text{(s)}}$$

$$= 1338.59 \text{ g AgNO}_3 \text{ per kg of I}_2 \text{ produced or } 1.34 \times 10^3 \text{ g AgNO}_3 \text{ per kg of I}_2$$

## FEATURE PROBLEMS

109. If the sample that was caught is representative of all fish in the lake, there are five marked fish for every 18 fish. Thus, the total number of fish in the lake is determined.

$$\text{total fish} = 100 \text{ marked fish} \times \frac{18 \text{ fish}}{5 \text{ marked fish}} = 360 \text{ fish} \cong 4 \times 10^2 \text{ fish}$$

- 110. (a)** The graph obtained is one of two straight lines, meeting at a peak of about 2.50 g  $\text{Pb}(\text{NO}_3)_2$ , corresponding to about 3.5 g  $\text{PbI}_2$ . Maximum mass of  $\text{PbI}_2$  (calculated)

$$= 2.503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.0 \text{ g KI}} \times \frac{1 \text{ mol PbI}_2}{2 \text{ mol KI}} \times \frac{461.01 \text{ g PbI}_2}{1 \text{ mol PbI}_2} = 3.476 \text{ g PbI}_2$$

- (b)** The total quantity of reactant is limited to 5.000 g. If either reactant is in excess, the amount in excess will be "wasted," because it cannot be used to form product. Thus, we obtain the maximum amount of product when neither reactant is in excess (i.e., when there is a stoichiometric amount of each present). The balanced chemical equation for this reaction,  $2 \text{KI} + \text{Pb}(\text{NO}_3)_2 \rightarrow 2 \text{KNO}_3 + \text{PbI}_2$ , shows that stoichiometric quantities are two moles of KI (166.00 g/mol) for each mole of  $\text{Pb}(\text{NO}_3)_2$  (331.21 g/mol). If we have 5.000 g total, we can let the mass of KI equal  $x$  g, so that the mass of

$$\text{Pb}(\text{NO}_3)_2 = (5.000 - x) \text{ g. Then we have amount KI} = x \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g}} = \frac{x}{166.00}$$

$$\text{amount Pb}(\text{NO}_3)_2 = (5.000 - x) \text{ g Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{331.21 \text{ g}} = \frac{5.000 - x}{331.21}$$

At the point of stoichiometric balance, amount KI = 2 × amount  $\text{Pb}(\text{NO}_3)_2$

$$\frac{x}{166.00} = 2 \times \frac{5.000 - x}{331.21} \text{ OR } 331.21x = 10.00 \times 166.00 - 332.00x$$

$$x = \frac{1660.0}{331.21 + 332.00} = 2.503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = 0.01508 \text{ mol KI}$$

$$5.000 - x = 2.497 \text{ g Pb(NO}_3)_2 \times \frac{1 \text{ mol Pb(NO}_3)_2}{331.21 \text{ g Pb(NO}_3)_2} = 0.007539 \text{ mol Pb(NO}_3)_2$$

$$\text{As a mass ratio we have: } \frac{2.503 \text{ g KI}}{2.497 \text{ g Pb(NO}_3)_2} = \frac{1.002 \text{ g KI}}{1 \text{ g Pb(NO}_3)_2}$$

$$\text{As a molar ratio we have: } \frac{0.01508 \text{ mol KI}}{0.007539 \text{ mol Pb(NO}_3)_2} = \frac{2 \text{ mol KI}}{1 \text{ mol Pb(NO}_3)_2}$$

- (c) The molar ratio just determined in part (b) is the same as the ratio of coefficients for KI and Pb(NO<sub>3</sub>)<sub>2</sub> in the balanced chemical equation. Finally to determine the proportions precisely, we used the balanced chemical equation.

111. (a) For the balanced equation, the order is immaterial; the relative amount of each is important. 20rd + 20bl + 30gr → 1 necklace
- (b) This is similar to a limiting reactant problem. We determine how many necklaces can be made from each quantity of beads.

$$\text{number of necklaces} = 10.0 \text{ kg beads} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ rd bead}}{1.98 \text{ g}} \times \frac{1 \text{ necklace}}{20 \text{ rd beads}} = 252, \text{ necklaces}$$

$$\text{number of necklaces} = 10.0 \text{ kg beads} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ bl bead}}{3.05 \text{ g}} \times \frac{1 \text{ necklace}}{20 \text{ bl beads}} = 163, \text{ necklaces}$$

$$\text{number of necklaces} = 10.0 \text{ kg beads} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ gr bead}}{1.82 \text{ g}} \times \frac{1 \text{ necklace}}{30 \text{ gr beads}} = 183, \text{ necklaces}$$

We have expressed each result with an additional significant figure, written as a subscript, so that we can see the effect of rounding. With the beads available, we can produce 163 necklaces, since we are unable to produce a fraction of a necklace.

- (c) Because the mass of a bead, and the total mass available of each type of bead, both are known to just three significant figures, our results are only known that well. The best we can state is that we can make at least 163 necklaces, because 164 is uncertain by one unit. We should not be surprised if we actually made just 161 necklaces, or if we produced 165 of them. More precise masses would help.

112. The more HCl used, the more impure the sample (compared to NaHCO<sub>3</sub>, twice as much HCl is needed to neutralize Na<sub>2</sub>CO<sub>3</sub>).

Sample from trona: 6.93 g sample forms 11.89 g AgCl or 1.72 g AgCl per gram sample.

Sample derived from manufactured sodium bicarbonate: 6.78 g sample forms 11.77 g AgCl or 1.74 g AgCl per gram sample.

Thus the trona sample is purer (i.e., it has the greater mass percent NaHCO<sub>3</sub> ).

# CHAPTER 5

## INTRODUCTION TO REACTIONS IN AQUEOUS SOLUTIONS

### PRACTICE EXAMPLES

- 1A** In determining total  $[\text{Cl}^-]$ , we recall the definition of molarity: moles of solute per liter of solution.

$$\text{from NaCl, } [\text{Cl}^-] = \frac{0.438 \text{ mol NaCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} = 0.438 \text{ M Cl}^-$$

$$\text{from MgCl}_2, [\text{Cl}^-] = \frac{0.0512 \text{ mol MgCl}_2}{1 \text{ L soln}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol MgCl}_2} = 0.102 \text{ M Cl}^-$$

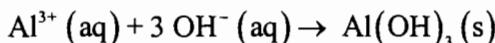
$$[\text{Cl}^-]_{\text{total}} = [\text{Cl}^-]_{\text{from NaCl}} + [\text{Cl}^-]_{\text{from MgCl}_2} = 0.438 \text{ M} + 0.102 \text{ M} = 0.540 \text{ M Cl}^-$$

**1B**  $\frac{1.5 \text{ mg F}^-}{\text{L}} \times \frac{1 \text{ g F}^-}{1000 \text{ mg F}^-} \times \frac{1 \text{ mol F}^-}{18.998 \text{ g F}^-} = 7.9 \times 10^{-5} \text{ M F}^-$

$$\text{(b)} \quad 1.00 \times 10^6 \text{ L} \times \frac{7.9 \times 10^{-5} \text{ mol F}^-}{1 \text{ L}} \times \frac{1 \text{ mol CaF}_2}{2 \text{ mol F}^-} \times \frac{78.075 \text{ g CaF}_2}{1 \text{ mol CaF}_2} \times \frac{1 \text{ kg}}{1000 \text{ g}} \\ = 3.1 \text{ kg CaF}_2$$

- 2A** In each case we use the solubility rules to determine whether either product is insoluble. The ions in each product compound are determined by simply “switching the partners” of the reactant compounds. The designation “(aq)” on each reactant indicates that it is soluble.

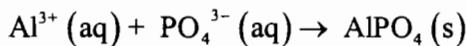
- (a) Possible products are potassium chloride,  $\text{KCl}$ , which is soluble, and aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , which is not. The net ionic equation is:



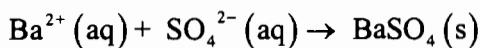
- (b) Possible products are iron(III) sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , and potassium bromide,  $\text{KBr}$ , both of which are soluble. No reaction occurs.

- (c) Possible products are calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , which is soluble, and lead(II) iodide,  $\text{PbI}_2$ , which is insoluble. The net ionic equation is:  $\text{Pb}^{2+} \text{ (aq)} + 2 \text{ I}^- \text{ (aq)} \rightarrow \text{PbI}_2 \text{ (s)}$

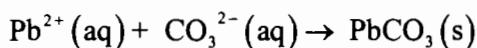
- 2B** (a) Possible products are sodium chloride,  $\text{NaCl}$ , which is soluble, and aluminum phosphate,  $\text{AlPO}_4$ , which is insoluble. The net ionic equation is:



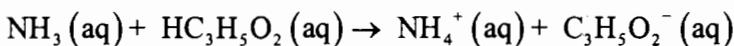
- (b) Possible products are aluminum chloride,  $\text{AlCl}_3$ , which is soluble, and barium sulfate,  $\text{BaSO}_4$ , which is insoluble. The net ionic equation is:



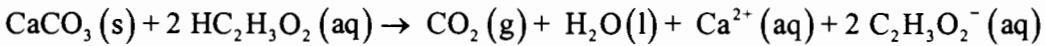
- (c) Possible products are ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , which is soluble, and lead (II) carbonate,  $\text{PbCO}_3$ , which is insoluble. The net ionic equation is:



- 3A** Propionic acid is a weak acid, not dissociated completely in aqueous solution. Ammonia is a weak base. The acid and base react to form a salt solution of ammonium propionate.



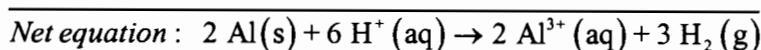
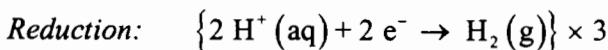
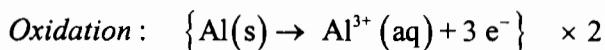
- 3B** Since acetic acid is a weak acid, it is not dissociated completely in aqueous solution (except at infinite dilution); it is misleading to write it in ionic form. The products of this reaction are the gas carbon dioxide, the covalent compound water, and the ionic solute calcium acetate. Only the latter exists as ions in aqueous solution.



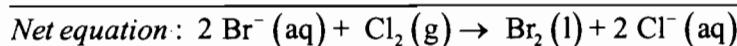
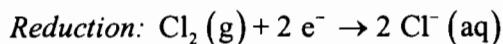
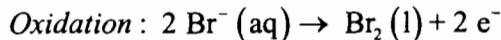
- 4A** (a) This is a metathesis or double displacement reaction. Elements do not change oxidation states during this reaction. It is not an oxidation-reduction reaction.
- (b) The presence of  $\text{O}_2(\text{g})$  as a product indicates that this is an oxidation-reduction reaction. Oxygen is oxidized from O.S. = -2 in  $\text{Pb}(\text{NO}_3)_2(\text{s})$  to O.S. = 0 in  $\text{O}_2(\text{g})$ . Nitrogen is reduced from O.S. = +5 in  $\text{Pb}(\text{NO}_3)_2(\text{s})$  to O.S. = +4 in  $\text{NO}_2(\text{g})$ .

- 4B** We determine the oxidation state (O.S.) of each element on each side of the equation. The O.S. of H is +1 on each side of the equation, and the O.S. of O is -2. For *vanadium*, the O.S. of V is +4 in  $\text{VO}^{2+}$ , and the O.S. of V is +5 in  $\text{VO}_2^+$ ; since the oxidation state of V has increased during the reaction,  $\text{VO}^{2+}$  has been oxidized. For *manganese*, the O.S. of Mn in  $\text{MnO}_4^-$  is +7, and the O.S. of Mn in  $\text{Mn}^{2+}$  is +2; since the oxidation state of Mn has decreased during the reaction,  $\text{MnO}_4^-$  is the species reduced.

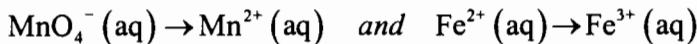
- 5A** Aluminum is oxidized (from an O.S. of 0 to an O.S. of +3), while hydrogen is reduced (from an O.S. of +1 to an O.S. of 0).



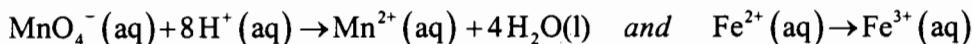
**5B** Bromide is oxidized (from  $-1$  to  $0$ ) while chlorine is reduced (from  $0$  to  $-1$ ).



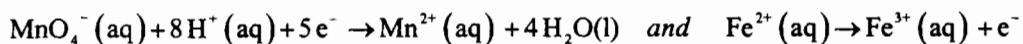
**6A** Step 1: Write the two skeleton half-equations.



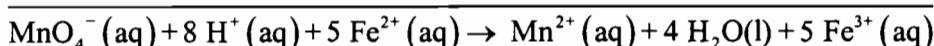
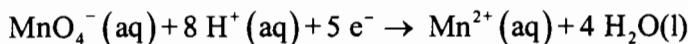
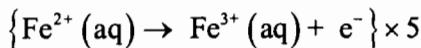
Step 2: Balance each skeleton half-equation for O (with  $\text{H}_2\text{O}$ ) and for H atoms (with  $\text{H}^+$ ).



Step 3: Balance electric charge by adding electrons.

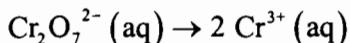


Step 4: Combine the two  $\frac{1}{2}$ -reactions

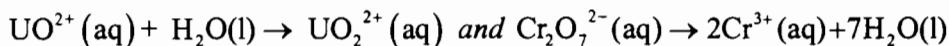


**6B** Step 1: Uranium is oxidized and chromium is reduced in this reaction. The “skeleton” half-equations are:  $\text{UO}^{2+} (\text{aq}) \rightarrow \text{UO}_2^{2+} (\text{aq})$  and  $\text{Cr}_2\text{O}_7^{2-} (\text{aq}) \rightarrow \text{Cr}^{3+} (\text{aq})$

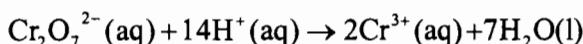
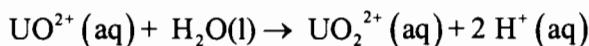
Step 2: First, balance the chromium skeleton half-equation for chromium atoms:



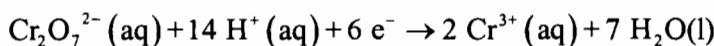
Next, balance oxygen atoms with water molecules in each half-equation:



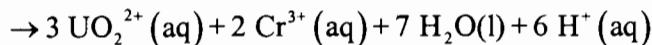
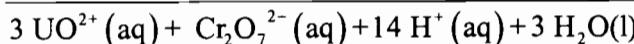
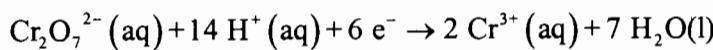
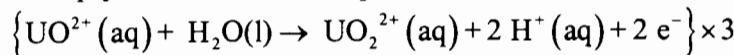
Then, balance hydrogen atoms with hydrogen ions in each half-equation:



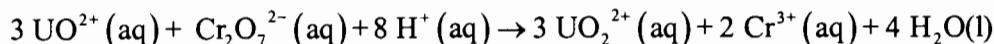
Step 3: Balance the charge of each half-equation with electrons.



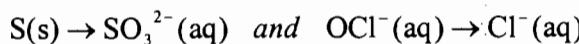
Step 4: Multiply the uranium half-equation by 3 and add the chromium half-equation to it.



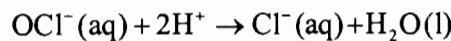
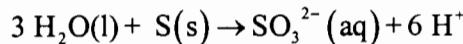
Step 5: SIMPLIFY. Subtract 3 H<sub>2</sub>O (l) and 6 H<sup>+</sup> (aq) from each side of the equation.



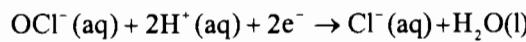
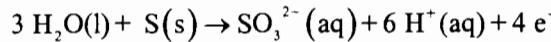
**7A** Step 1: Write the two skeleton half-equations.



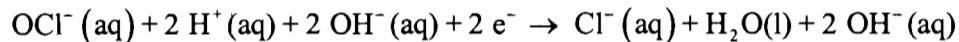
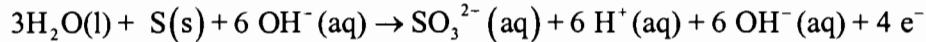
Step 2: Balance each skeleton half-equation for O (with H<sub>2</sub>O) and for H atoms (with H<sup>+</sup>).



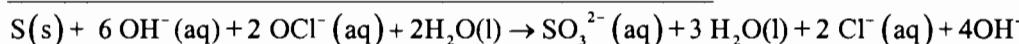
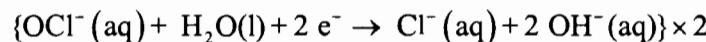
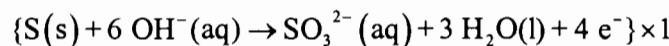
Step 3: Balance electric charge by adding electrons.



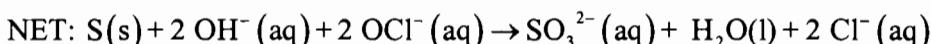
Step 4: Change from an acidic medium to a basic one by adding OH<sup>-</sup> to eliminate H<sup>+</sup>.



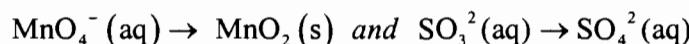
Step 5: Simplify by removing the items present on both sides of each half-equation, and combine the half-equations to obtain the net redox equation.



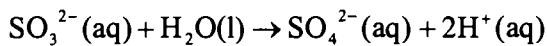
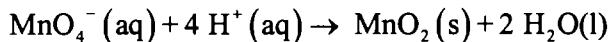
Simplify by removing the species present on both sides.



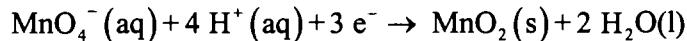
**7B** Step 1: Write the two skeleton half-equations.



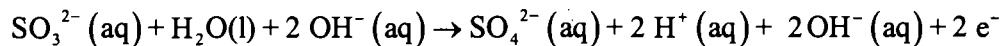
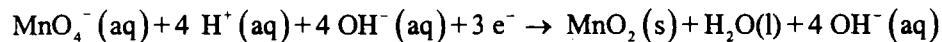
Step 2: Balance each skeleton half-equation for O (with  $\text{H}_2\text{O}$ ) and for H atoms (with  $\text{H}^+$ ).



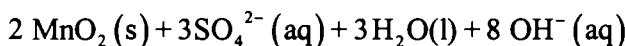
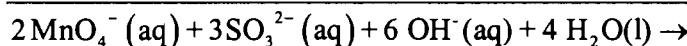
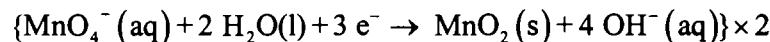
Step 3: Balance electric charge by adding electrons.



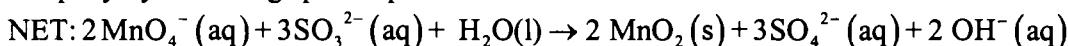
Step 4: Change from an acidic medium to a basic one by adding  $\text{OH}^-$  to eliminate  $\text{H}^+$ .



Step 5: Simplify by removing species present on both sides of each half-equation, and combine the half-equations to obtain the net redox equation.



Simplify by removing species present on both sides.



**8A** Since the oxidation state of H is 0 in  $\text{H}_2 (\text{g})$  and is +1 in both  $\text{NH}_3 (\text{g})$  and  $\text{H}_2\text{O} (\text{g})$ , hydrogen is oxidized. A substance that is oxidized is called the reducing agent. In addition, the oxidation state of N in  $\text{NO}_2 (\text{g})$  is +4, while it is -3 in  $\text{NH}_3$ ; the oxidation state of the element N decreases during this reaction, meaning that  $\text{NO}_2 (\text{g})$  is reduced. The substance that is reduced is called the oxidizing agent.

**8B** In  $[\text{Au}(\text{CN})_2]^- (\text{aq})$ , gold has an oxidation state of +1; Au has been oxidized and, thus, Au(s) (oxidation state = 0), is the reducing agent. In  $\text{OH}^- (\text{aq})$ , oxygen has an oxidation state of -2; O has been reduced and thus,  $\text{O}_2 (\text{g})$  (oxidation state = 0) is the oxidizing agent.

**9A** We first determine the amount of NaOH that reacts with 0.500 g KHP.

$$\begin{aligned} \text{amount NaOH} &= 0.5000 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.22 \text{ g KHP}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol KHP}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \\ &= 0.002448 \text{ mol NaOH} \end{aligned}$$

$$[\text{NaOH}] = \frac{0.002448 \text{ mol NaOH}}{24.03 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.1019 \text{ M}$$

- 9B** The net ionic equation when solid hydroxides react with a strong acid is  $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$ . There are two sources of  $\text{OH}^-$ :  $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$ . We compute the amount of  $\text{OH}^-$  from each source and add the results.

moles of  $\text{OH}^-$  from  $\text{NaOH}$ :

$$= 0.235 \text{ g sample} \times \frac{92.5 \text{ g NaOH}}{100.0 \text{ g sample}} \times \frac{1 \text{ mol NaOH}}{39.997 \text{ g NaOH}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.00543 \text{ mol OH}^-$$

moles of  $\text{OH}^-$  from  $\text{Ca}(\text{OH})_2$ :

$$= 0.235 \text{ g sample} \times \frac{7.5 \text{ g Ca}(\text{OH})_2}{100.0 \text{ g sample}} \times \frac{1 \text{ mol Ca}(\text{OH})_2}{74.093 \text{ g Ba}(\text{OH})_2} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ca}(\text{OH})_2} = 0.00048 \text{ mol OH}^-$$

$$\text{total amount OH}^- = 0.00543 \text{ mol from NaOH} + 0.00048 \text{ mol from Ca}(\text{OH})_2 = 0.00591 \text{ mol OH}^-$$

$$[\text{HCl}] = \frac{0.00591 \text{ mol OH}^-}{45.6 \text{ mL HCl soln}} \times \frac{1 \text{ mol H}^+}{1 \text{ mol OH}^-} \times \frac{1 \text{ mol HCl}}{1 \text{ mol H}^+} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} = 0.130 \text{ M}$$

- 10A** First, determine the mass of iron that has reacted as  $\text{Fe}^{2+}$  with the titrant. The balanced chemical equation provides the essential conversion factor.

$$\text{mass Fe} = 0.04125 \text{ L titrant} \times \frac{0.02140 \text{ mol MnO}_4^-}{1 \text{ L titrant}} \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} \times \frac{55.847 \text{ g Fe}}{1 \text{ mol Fe}^{2+}} = 0.246 \text{ g Fe}$$

$$\text{Then determine the \% Fe in the ore. } \% \text{ Fe} = \frac{0.246 \text{ g Fe}}{0.376 \text{ g ore}} \times 100\% = 65.4\% \text{ Fe}$$

- 10B** The balanced equation provides stoichiometric coefficients used in the solution.

$$\text{amount MnO}_4^- = 0.2482 \text{ g Na}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mol Na}_2\text{C}_2\text{O}_4}{134.00 \text{ g Na}_2\text{C}_2\text{O}_4} \times \frac{1 \text{ mol C}_2\text{O}_4^{2-}}{1 \text{ mol Na}_2\text{C}_2\text{O}_4} \times \frac{2 \text{ mol MnO}_4^-}{5 \text{ mol C}_2\text{O}_4^{2-}}$$

$$= 0.0007409 \text{ mol MnO}_4^-$$

$$[\text{KMnO}_4] = \frac{0.0007409 \text{ mol MnO}_4^-}{23.68 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol KMnO}_4}{1 \text{ mol MnO}_4^-} = 0.03129 \text{ M KMnO}_4$$

## REVIEW QUESTIONS

- The symbol “ $\rightleftharpoons$ ” means that a chemical reaction reaches a point of balance or equilibrium where the rate of the forward reaction equals the rate of the reverse reaction.
  - The square brackets,  $[ ]$ , surrounding the formula of a species, are the symbol for the molarity of that species in solution.

- (c) A “spectator” ion is one that is present in a solution in which a reaction takes place but is not included in the net ionic equation for that reaction because it does not get involved in the reaction.
- (d) A weak acid is a species that produces hydrogen ion in aqueous solution (an acid), but does not dissociate completely into its ions (except at infinite dilutions - a weak electrolyte).
2. (a) In the half-reaction method of balancing redox equations, each species that is oxidized or reduced is the basis for a balanced half-equation. These half-equations then are combined to produce the balanced net ionic equation for the redox reaction.
- (b) A disproportionation reaction is one in which the same species is both oxidized and reduced.
- (c) A titration is the procedure of adding a measured amount of one material to a measured amount of another, in such a way that chemically equivalent amounts of substances are present at the end of the titration. The concentration of substance in one of the two materials is known; the technique permits the determination of the other concentration.
- (d) Standardization of a solution refers to the determination of its concentration by titration.
3. (a) A strong electrolyte is a substance that dissociates completely into its ions when it is dissolved in aqueous solution. A strong acid is a strong electrolyte that produces hydrogen ions and anions when it dissociates.
- (b) An oxidizing agent is a species that causes another species to be oxidized: to lose electrons and thereby have the oxidation state of one of its elements increased. A reducing agent is a species that causes another species to be reduced: to accept electrons and have the oxidation state of one of its elements decreased.
- (c) A precipitation reaction is one in which an insoluble substance is formed when solutions of two soluble substances are mixed. A neutralization reaction is the reaction of an acid with a base; the normal products are water and a salt that has the same cation as the base and the same anion as the acid.
- (d) A half-reaction refers to just the oxidation or just the reduction aspect of a redox reaction. An overall or “net” reaction refers to the entire chemical reaction, with only spectator ions omitted (or it can be the net result of several reactions that, together, make up a process).
4. (a) The best electrical conductor is the solution of the strong electrolyte: 0.10 M NaCl. In each liter of this solution, there are 0.10 mol  $\text{Na}^+$  ions and 0.10 mol  $\text{Cl}^-$  ions.
- (b) The poorest electrical conductor is the solution of the nonelectrolyte: 0.10 M  $\text{C}_2\text{H}_5\text{OH}$ . In this solution, the concentration of ions is almost nonexistent.

- 5.** (a)  $\text{Na}_2\text{SO}_4$  is a *salt* of sodium hydroxide,  $\text{NaOH}$ , and sulfuric acid,  $\text{H}_2\text{SO}_4$ .
- (b)  $\text{Ba}(\text{OH})_2$  is a *strong base*, one of the common strong bases listed in Table 5-1.
- (c)  $\text{Ba}(\text{NO}_3)_2$  is a *salt* of barium hydroxide,  $\text{Ba}(\text{OH})_2$ , and nitric acid,  $\text{HNO}_3$ .
- (d)  $\text{H}_3\text{PO}_4$  is a *weak acid*, (formula begins with hydrogen), but is not listed in Table 5-1.
- (e)  $\text{HBr}$  is a *strong acid*, listed in Table 5-1.
- (f)  $\text{HNO}_2$  is a *weak acid* (formula begins with hydrogen), but it is not listed in Table 5-1.
- (g)  $\text{NH}_3$  is a *weak base*, ammonia.
- (h)  $\text{NH}_4\text{I}$  is a *salt* of ammonia,  $\text{NH}_3$ , and hydroiodic acid,  $\text{HI}$ .
- (i)  $\text{KOH}$  is a *strong base*, one of the common ones listed in Table 5-1.

- 6.** For all these solutes but one— $\text{Al}_2(\text{SO}_4)_3$ —there is one sulfate ion per formula unit. Consequently, the concentration of the compound and the sulfate ion concentration in that compound's aqueous solution will be the same. This makes 0.22 M  $\text{Mg}(\text{SO}_4)$  the solution with the highest  $[\text{SO}_4^{2-}]$  among these four. But there are three sulfate ions per formula unit of  $\text{Al}_2(\text{SO}_4)_3$ . Thus,  $[\text{SO}_4^{2-}]$  in the  $\text{Al}_2(\text{SO}_4)_3$  solution is three times the concentration of the solute, or  $[\text{SO}_4^{2-}] = 3 \times 0.080 \text{ M} = 0.24 \text{ M}$ ; therefore this solution has the highest  $[\text{SO}_4^{2-}]$ .

- 7.** (a)  $[\text{K}^+] = \frac{0.238 \text{ mol KNO}_3}{1 \text{ L soln}} \times \frac{1 \text{ mol K}^+}{1 \text{ mol KNO}_3} = 0.238 \text{ M K}^+$
- (b)  $[\text{NO}_3^-] = \frac{0.167 \text{ mol Ca}(\text{NO}_3)_2}{1 \text{ L soln}} \times \frac{2 \text{ mol NO}_3^-}{1 \text{ mol Ca}(\text{NO}_3)_2} = 0.334 \text{ M NO}_3^-$
- (c)  $[\text{Al}^{3+}] = \frac{0.083 \text{ mol Al}_2(\text{SO}_4)_3}{1 \text{ L soln}} \times \frac{2 \text{ mol Al}^{3+}}{1 \text{ mol Al}_2(\text{SO}_4)_3} = 0.17 \text{ M Al}^{3+}$
- (d)  $[\text{Na}^+] = \frac{0.209 \text{ mol Na}_3\text{PO}_4}{1 \text{ L soln}} \times \frac{3 \text{ mol Na}^+}{1 \text{ mol Na}_3\text{PO}_4} = 0.627 \text{ M Na}^+$

- 8.** The amount of chloride ion in each solution in millimoles is computed.

$$\text{Cl}^- \text{ amount} = 200.0 \text{ mL} \times \frac{0.35 \text{ mmol NaCl}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol Cl}^-}{1 \text{ mmol NaCl}} = 70. \text{ mmol Cl}^-$$

$$\text{Cl}^- \text{ amount} = 500.0 \text{ mL} \times \frac{0.065 \text{ mmol MgCl}_2}{1 \text{ mL soln}} \times \frac{2 \text{ mmol Cl}^-}{1 \text{ mmol MgCl}_2} = 65 \text{ mmol Cl}^-$$

$$\text{Cl}^- \text{ amount} = 1.00 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.068 \text{ mmol HCl}}{1 \text{ mL}} \times \frac{1 \text{ mmol Cl}^-}{1 \text{ mmol HCl}} = 68 \text{ mmol Cl}^-$$

The 200.0 mL of 0.035 M  $\text{NaCl}$  contains the largest amount of  $\text{Cl}^-$ .

9.  $[\text{OH}^-] = \frac{0.132 \text{ g Ba(OH)}_2 \cdot 8\text{H}_2\text{O}}{275 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol Ba(OH)}_2 \cdot 8\text{H}_2\text{O}}{315.5 \text{ g Ba(OH)}_2 \cdot 8\text{H}_2\text{O}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba(OH)}_2 \cdot 8\text{H}_2\text{O}}$   
 $= 3.04 \times 10^{-3} \text{ M OH}^-$

10.  $[\text{K}^+] = \frac{0.126 \text{ mol KCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol K}^+}{1 \text{ mol KCl}} = 0.126 \text{ M K}^+$

$[\text{Mg}^{2+}] = \frac{0.148 \text{ mol MgCl}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol Mg}^{2+}}{1 \text{ mol MgCl}_2} = 0.148 \text{ M Mg}^{2+}$

Now determine the amount of  $\text{Cl}^-$  in 1.00 L of the solution.

$\text{mol Cl}^- = \left( \frac{0.126 \text{ mol KCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol KCl}} \right) + \left( \frac{0.148 \text{ mol MgCl}_2}{1 \text{ L soln}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol MgCl}_2} \right)$   
 $= 0.126 \text{ mol Cl}^- + 0.296 \text{ mol Cl}^- = 0.422 \text{ mol Cl}^-$

$[\text{Cl}^-] = \frac{0.422 \text{ mol Cl}^-}{1 \text{ L soln}} = 0.422 \text{ M Cl}^-$

11. Determine the amount of  $\text{I}^-$  in the solution as it now exists, and the amount of  $\text{I}^-$  in the solution of the desired concentration. The difference in these two amounts is the amount of  $\text{I}^-$  that must be added. Convert this amount to a mass of  $\text{MgI}_2$  in grams.

$\text{moles of I}^- \text{ in final solution} = 250.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1000 \text{ mol I}^-}{1 \text{ L soln}} = 0.02500 \text{ mol I}^-$

$\text{moles of I}^- \text{ in KI solution} = 250.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.0876 \text{ mol KI}}{1 \text{ L soln}} \times \frac{1 \text{ mol I}^-}{1 \text{ mol KI}} = 0.0219 \text{ mol I}^-$

$\text{mass MgI}_2 \text{ required} = (0.02500 - 0.0219) \text{ mol I}^- \times \frac{1 \text{ mol MgI}_2}{2 \text{ mol I}^-} \times \frac{278.11 \text{ g MgI}_2}{1 \text{ mol MgI}_2} \times \frac{1000 \text{ mg}}{1 \text{ g}}$   
 $= 4.3 \times 10^2 \text{ mg MgI}_2$

12. Nitrates, acetates, and alkali metal compounds are water-soluble.  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $\text{NaI}$  are soluble. Most halides are soluble in water;  $\text{CuCl}_2$  is soluble in water. Although most sulfates are soluble in water,  $\text{BaSO}_4(s)$  is not soluble in water. Only a few hydroxides are soluble in water;  $\text{Al}(\text{OH})_3(s)$  is not soluble in water.

13.  $\text{HCl(aq)}$  reacts with active metals and some anions to produce a gas.



$\text{HSO}_3^-$  produces a gas with an acid:



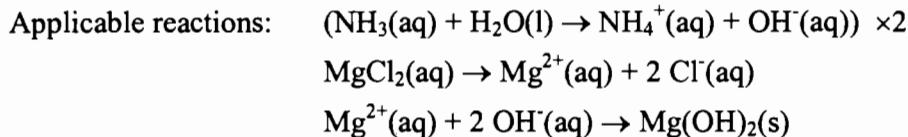
- 14.** In each case, each available cation is paired with the available anions, one at a time, to determine if a compound is produced that is insoluble, based on the solubility rules of Chapter 5. Then a net ionic equation is written to summarize this information.

- (a)  $\text{Pb}^{2+}(\text{aq}) + 2 \text{Br}^-(\text{aq}) \rightarrow \text{PbBr}_2(\text{s})$  (b) No reaction occurs.  
 (c)  $\text{Fe}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$  (d)  $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$   
 (e)  $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$  (f) No reaction;  $\text{CaS}(\text{s})$  is moderately soluble.

- 15.** The type of reaction is given first, followed by the net ionic equation.

- (a) Neutralization:  $\text{OH}^-(\text{aq}) + \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$   
 (b) No reaction occurs. This is the mixing of two acids.  
 (c) Gas evolution:  $\text{FeS}(\text{s}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{S}(\text{g}) + \text{Fe}^{2+}(\text{aq})$   
 (d) Gas evolution:  $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$   
 (e) Redox:  $\text{Mg}(\text{s}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{H}_2(\text{g})$   
 (f) No reaction occurs, based on the information in Table 5-3.

- 16.** Use (b)  $\text{NH}_3(\text{aq})$ :  $\text{NH}_3$  affords  $\text{OH}^-$  ions necessary for the precipitation of  $\text{Mg}(\text{OH})_2$

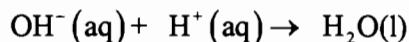


- 17.** The problem is most easily solved with amounts in millimoles.

$$\text{V}_{\text{NaOH}} = 10.00 \text{ mL HCl}(\text{aq}) \times \frac{0.128 \text{ mmol HCl}}{1 \text{ mL HCl}(\text{aq})} \times \frac{1 \text{ mmol H}^+}{1 \text{ mmol HCl}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol H}^+} \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol OH}^-} \times \frac{1 \text{ mL NaOH}(\text{aq})}{0.0962 \text{ mmol NaOH}} = 13.3 \text{ mL NaOH}(\text{aq}) \text{ soln}$$

$$\text{18. } [\text{NaOH}] = \frac{10.00 \text{ mL acid} \times \frac{0.1012 \text{ mmol H}_2\text{SO}_4}{1 \text{ mL acid}} \times \frac{2 \text{ mmol NaOH}}{1 \text{ mmol H}_2\text{SO}_4}}{23.31 \text{ mL base}} = 0.08683 \text{ M}$$

- 19.** The net ionic equation for the reaction of  $\text{KOH}$ , a strong base, with  $\text{HCl}$ , a strong acid, is:



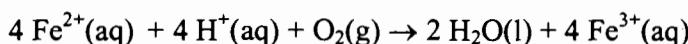
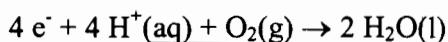
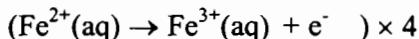
Thus, the reactant that produces the smaller amount of ions is the limiting reactant. More to the point, the difference between the larger number of ions and the smaller number, determines whether the resulting solution is acidic or basic. If the difference is zero, the solution is neutral.

$$\text{amount OH}^- = 23.58 \text{ mL KOH(aq)} \times \frac{0.1278 \text{ mmol KOH}}{1 \text{ mL KOH(aq)}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 3.014 \text{ mmol OH}^-$$

$$\text{amount H}^+ = 25.13 \text{ mL HCl(aq)} \times \frac{0.1264 \text{ mmol HCl}}{1 \text{ mL HCl(aq)}} \times \frac{1 \text{ mmol H}^+}{1 \text{ mmol HCl}} = 3.176 \text{ mmol H}^+$$

excess ion =  $3.176 \text{ mmol H}^+ - 3.014 \text{ mmol OH}^- = 0.162 \text{ mmol H}^+$ . The solution is acidic.

- 20.** The answer is: (a) the missing coefficients are each four.



- 21.** (a) The O.S. of H is +1, that of O is -2, that of C is +4, and that of Mg is +2 on each side of this equation. This is not a redox equation.  
 (b) The O.S. of Cl is 0 on the left and -1 on the right side of this equation. The O.S. of Br is -1 on the left and 0 on the right side of this equation. This is a redox reaction.  
 (c) The O.S. of Ag is 0 on the left and +1 on the right side of this equation. The O.S. of N is +5 on the left and +4 on the right side of this equation. This is a redox reaction.  
 (d) The O.S. of O is -2, that of Ag is +1, and that of Cr is +6 on both sides of this equation. This is not a redox equation.

- 22.** (a) The O.S. of O is -2 on both sides of this reaction. The O.S. of H is 0 on the left and +1 on the right side of this equation; H is oxidized and thus NO must be an oxidizing agent. The O.S. of N is +2 on the left and -3 on the right side of this equation; N is reduced and thus  $\text{H}_2$  must be a reducing agent.  
 (b) The O.S. of O is -2 and that of H is +1 on both sides of this equation. The O.S. of Cu is 0 on the left and +2 on the right side of this equation; Cu is oxidized and thus  $\text{NO}_3^-$  must be an oxidizing agent. The O.S. of N is +5 on the left and +2 on the right side of this equation; N is reduced and thus Cu must be a reducing agent.  
 (c) The O.S. of O is -2 and that of H is +1 on both sides of this equation. The O.S. of Cl is 0 on the left side of this equation; on the right side, the O.S. of Cl is -1 in  $\text{Cl}^-$  and it is +5 in  $\text{ClO}_3^-$ . Cl is both oxidized and reduced and  $\text{Cl}_2$  serves as both an oxidizing agent and as a reducing agent in this disproportionation reaction.

- 23.** (a) Reduction:  $2\text{SO}_3^{2-}(\text{aq}) + 6 \text{ H}^+(\text{aq}) + 4 \text{ e}^- \rightarrow \text{S}_2\text{O}_3^{2-}(\text{aq}) + 3 \text{ H}_2\text{O}(\text{l})$   
 (b) Reduction:  $2\text{NO}_3^-(\text{aq}) + 10 \text{ H}^+(\text{aq}) + 8 \text{ e}^- \rightarrow \text{N}_2\text{O}(\text{g}) + 5 \text{ H}_2\text{O}(\text{l})$   
 (c) Oxidation:  $\text{I}^-(\text{aq}) + 3 \text{ H}_2\text{O}(\text{l}) \rightarrow \text{IO}_3^-(\text{aq}) + 6 \text{ H}^+(\text{aq}) + 6 \text{ e}^-$   
 (d) Oxidation:  $\text{Al}(\text{s}) + 4 \text{ OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq}) + 3 \text{ e}^-$

- 24.** (a) Oxidation:  $\{ \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \} \times 3$   
 Reduction:  $\{ \text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{NO(g)} + 2 \text{H}_2\text{O(l)} \} \times 2$   
 Net:  $3 \text{Zn(s)} + 2\text{NO}_3^-(\text{aq}) + 8 \text{H}^+(\text{aq}) \rightarrow 3 \text{Zn}^{2+}(\text{aq}) + 2 \text{NO(g)} + 4 \text{H}_2\text{O(l)}$
- (b) Oxidation:  $\{ \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \} \times 4$   
 Reduction:  $\text{NO}_3^-(\text{aq}) + 10 \text{H}^+(\text{aq}) + 8\text{e}^- \rightarrow \text{NH}_4^+(\text{aq}) + 3 \text{H}_2\text{O(l)}$   
 Net:  $4 \text{Zn(s)} + \text{NO}_3^-(\text{aq}) + 10 \text{H}^+(\text{aq}) \rightarrow 4 \text{Zn}^{2+}(\text{aq}) + \text{NH}_4^+(\text{aq}) + 3 \text{H}_2\text{O(l)}$
- (c) Oxidation:  $\{ \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^- \} \times 6$   
 Reduction:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O(l)}$   
 Net:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{Fe}^{2+}(\text{aq}) \rightarrow 6 \text{Fe}^{3+}(\text{aq}) + 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O(l)}$
- (d) Oxidation:  $\{ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \} \times 5$   
 Reduction:  $\{ \text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O(l)} \} \times 2$   
 Net:  $2\text{MnO}_4^-(\text{aq}) + 6 \text{H}^+(\text{aq}) + 5 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 8 \text{H}_2\text{O(l)} + 5 \text{O}_2(\text{g})$
- 25.** (a) Oxidation:  $\{ \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq}) \rightarrow \text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O(l)} + 3 \text{e}^- \} \times 2$   
 Reduction:  $\text{ClO}_3^-(\text{aq}) + 3 \text{H}_2\text{O(l)} + 6 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 6 \text{OH}^-(\text{aq})$   
 Net:  $2 \text{MnO}_2(\text{s}) + \text{ClO}_3^-(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow 2\text{MnO}_4^-(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O(l)}$
- (b) Oxidation:  $\{ \text{Fe(OH)}_3(\text{s}) + 5 \text{OH}^-(\text{aq}) \rightarrow \text{FeO}_4^{2-}(\text{aq}) + 4 \text{H}_2\text{O(l)} + 3 \text{e}^- \} \times 2$   
 Reduction:  $\{ \text{OCl}^-(\text{aq}) + \text{H}_2\text{O(l)} + 2 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq}) \} \times 3$   
 Net:  $2 \text{Fe(OH)}_3(\text{s}) + 3 \text{OCl}^-(\text{aq}) + 4 \text{OH}^-(\text{aq}) \rightarrow 2\text{FeO}_4^{2-}(\text{aq}) + 3 \text{Cl}^-(\text{aq}) + 5 \text{H}_2\text{O(l)}$
- (c) Oxidation:  $\{ \text{ClO}_2(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O(l)} + \text{e}^- \} \times 5$   
 Reduction:  $\text{ClO}_2(\text{aq}) + 2 \text{H}_2\text{O(l)} + 5 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 4 \text{OH}^-(\text{aq})$   
 Net:  $6 \text{ClO}_2(\text{aq}) + 6 \text{OH}^-(\text{aq}) \rightarrow 5\text{ClO}_3^-(\text{aq}) + \text{Cl}^-(\text{aq}) + 3 \text{H}_2\text{O(l)}$
- 26.** Oxidation:  $\{ \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{e}^- \} \times 5$   
 Reduction:  $\{ \text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O(l)} \} \times 2$   
 Net:  $2\text{MnO}_4^-(\text{aq}) + 16 \text{H}^+(\text{aq}) + 5 \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 8 \text{H}_2\text{O(l)} + 10 \text{CO}_2(\text{g})$
- $$[\text{MnO}_4^-] = \frac{0.2879 \text{ g Na}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mol Na}_2\text{C}_2\text{O}_4}{134.00 \text{ g Na}_2\text{C}_2\text{O}_4} \times \frac{1 \text{ mol C}_2\text{O}_4^{2-}}{1 \text{ mol Na}_2\text{C}_2\text{O}_4} \times \frac{2 \text{ mol MnO}_4^-}{5 \text{ mol Cl}_2\text{O}_4^{2-}}}{25.12 \text{ mL soln} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}}}$$
- $$= 0.03421 \text{ M}$$
 Thus, the molarity of  $\text{KMnO}_4$  is 0.03421 M.

## EXERCISES

### Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes

27. (a) Because its formula begins with hydrogen,  $\text{HC}_6\text{H}_5\text{O}$  is an acid. It is not listed in Table 5-1, so it is a weak acid. A weak acid is a *weak electrolyte*.  
 (b)  $\text{Li}_2\text{SO}_4$  is an ionic compound, that is, a salt. A salt is a *strong electrolyte*.  
 (c)  $\text{MgI}_2$  also is a salt, a *strong electrolyte*.  
 (d)  $(\text{CH}_3\text{CH}_2)_2\text{O}$  is a covalent compound whose formula does not begin with H. Thus, it is neither an acid nor a salt. It also is not built around nitrogen, and thus it does not behave as a weak base. This is a *nonelectrolyte*.  
 (e)  $\text{Sr}(\text{OH})_2$  is a *strong electrolyte*, one of the strong bases listed in Table 5-1.
29. (a) Barium bromide-strong electrolyte      (b) Propionic acid-weak electrolyte  
 (c) Ammonia-weak electrolyte

### Ion Concentrations

31. (a)  $[\text{Ca}^{2+}] = \frac{35.0 \text{ mg Ca}^{2+}}{1 \text{ L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Ca}^{2+}}{40.078 \text{ g Ca}^{2+}} = 8.73 \times 10^{-4} \text{ M Ca}^{2+}$   
 (b)  $[\text{K}^+] = \frac{25.6 \text{ mg K}^+}{100 \text{ mL}} \times \frac{1 \text{ mmol K}^+}{39.098 \text{ mg K}^+} = 6.55 \times 10^{-3} \text{ M K}^+ \text{ (assumes 3 sig. fig. in 100 mL)}$   
 (c)  $[\text{Zn}^{2+}] = \frac{0.168 \text{ mg Zn}^{2+}}{1 \text{ mL}} \times \frac{1 \text{ mmol Zn}^{2+}}{65.39 \text{ mg Zn}^{2+}} = 2.57 \times 10^{-3} \text{ M Zn}^{2+}$

33. Let us determine the concentration of each solution in  $\text{mg Na}^+ / \text{mL}$ . (assume 3 sig. fig. in 100 mL)

$$\text{(a)} \quad \text{mg Na}^+/\text{mL} = \frac{0.208 \text{ mmol Na}_2\text{SO}_4}{1 \text{ mL}} \times \frac{2 \text{ mmol Na}^+}{1 \text{ mmol Na}_2\text{SO}_4} \times \frac{23.0 \text{ mg Na}^+}{1 \text{ mmol Na}^+}$$

$$\text{mg Na}^+/\text{mL} = 9.57 \text{ mg Na}^+/\text{mL}$$

$$\text{(b)} \quad \text{mg Na}^+/\text{mL} = \frac{1.05 \text{ g NaCl}}{100 \text{ mL}} \times \frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}} \times \frac{1 \text{ mol Na}^+}{1 \text{ mol NaCl}} \times \frac{23.0 \text{ g Na}^+}{1 \text{ mol Na}^+} \times \frac{1000 \text{ mg}}{1 \text{ g}}$$

$$\text{mg Na}^+/\text{mL} = 4.13 \text{ mg Na}^+/\text{mL}$$

- (c) The solution with 14.7 mg  $\text{Na}^+ / \text{mL}$  has the highest concentration of  $\text{Na}^+$ .

**35. Moles of Chloride ion**

$$\begin{aligned}
 &= \left( 0.225 \text{ L} \times \frac{0.625 \text{ mol KCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol KCl}} \right) + \left( 0.615 \text{ L} \times \frac{0.385 \text{ mol MgCl}_2}{1 \text{ L soln}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol MgCl}_2} \right) \\
 &= 0.141 \text{ mol Cl}^- + 0.474 \text{ mol Cl}^- = 0.615 \text{ mol Cl}^- \quad [\text{Cl}^-] = \frac{0.615 \text{ mol Cl}^-}{0.225 \text{ L} + 0.615 \text{ L}} = 0.732 \text{ M}
 \end{aligned}$$

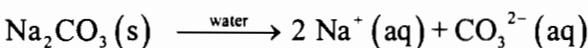
**Predicting Precipitation Reactions****37. Mixture Result (net ionic equation)**

- (a)  $\text{HI(aq)} + \text{Zn(NO}_3)_2\text{(aq)}$ : No reaction occurs.
- (b)  $\text{CuSO}_4\text{(aq)} + \text{Na}_2\text{CO}_3\text{(aq)}$ :  $\text{Cu}^{2+}\text{(aq)} + \text{CO}_3^{2-}\text{(aq)} \rightarrow \text{CuCO}_3\text{(s)}$
- (c)  $\text{Cu(NO}_3)_2\text{(aq)} + \text{Na}_3\text{PO}_4\text{(aq)}$ :  $3\text{Cu}^{2+}\text{(aq)} + 2\text{PO}_4^{3-}\text{(aq)} \rightarrow \text{Cu}_3(\text{PO}_4)_2\text{(s)}$

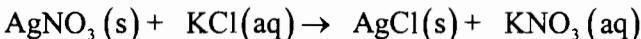
- 39. (a)** Add  $\text{K}_2\text{SO}_4\text{(aq)}$ ;  $\text{BaSO}_4\text{(s)}$  will form and  $\text{CaSO}_4$  will not precipitate.



- (b)** Add  $\text{H}_2\text{O(l)}$ ;  $\text{Na}_2\text{CO}_3\text{(s)}$  dissolves,  $\text{MgCO}_3\text{(s)}$  will not dissolve (appreciably).



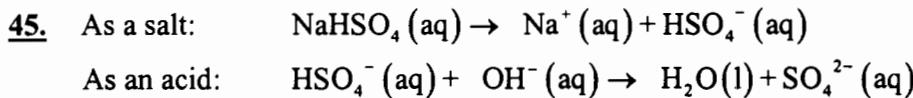
- (c)** Add  $\text{KCl(aq)}$ ;  $\text{AgCl(s)}$  will form, while  $\text{Cu(NO}_3)_2\text{(s)}$  will dissolve.

**41. Mixture Net ionic equation**

- (a)  $\text{Sr(NO}_3)_2\text{(aq)} + \text{K}_2\text{SO}_4\text{(aq)}$ :  $\text{Sr}^{2+}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \rightarrow \text{SrSO}_4\text{(s)}$
- (b)  $\text{Mg(NO}_3)_2\text{(aq)} + \text{NaOH(aq)}$ :  $\text{Mg}^{2+}\text{(aq)} + 2 \text{OH}^-\text{(aq)} \rightarrow \text{Mg(OH)}_2\text{(s)}$
- (c)  $\text{BaCl}_2\text{(aq)} + \text{K}_2\text{SO}_4\text{(aq)}$ :  $\text{Ba}^{2+}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \rightarrow \text{BaSO}_4\text{(s)}$   
(upon filtering,  $\text{KCl(aq)}$  is obtained)

**Acid-Base Reactions**

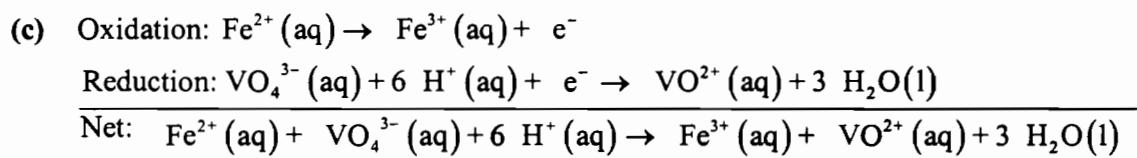
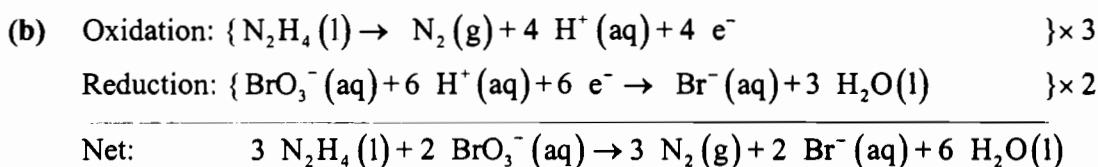
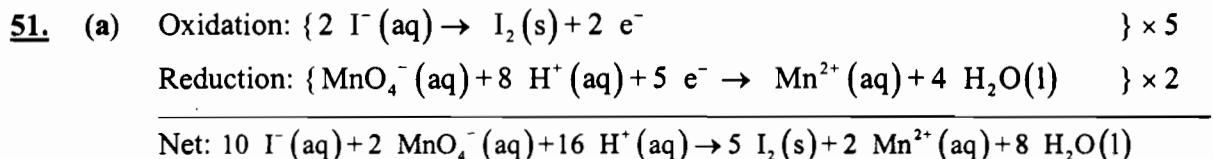
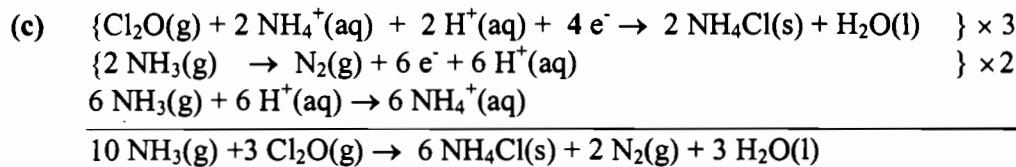
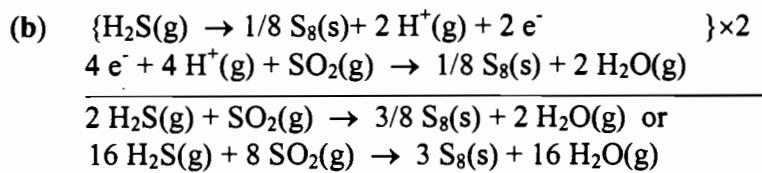
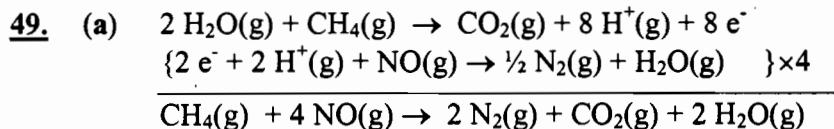
- 43. (a)**  $\text{NaHCO}_3\text{(s)} + \text{H}^+\text{(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$
- (b)**  $\text{CaCO}_3\text{(s)} + 2 \text{H}^+\text{(aq)} \rightarrow \text{Ca}^{2+}\text{(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$
- (c)**  $\text{Mg(OH)}_2\text{(s)} + 2 \text{H}^+\text{(aq)} \rightarrow \text{Mg}^{2+}\text{(aq)} + 2 \text{H}_2\text{O(l)}$
- (d)**  $\text{Mg(OH)}_2\text{(s)} + 2 \text{H}^+\text{(aq)} \rightarrow \text{Mg}^{2+}\text{(aq)} + 2 \text{H}_2\text{O(l)}$   
 $\text{Al(OH)}_3\text{(s)} + 3 \text{H}^+\text{(aq)} \rightarrow \text{Al}^{3+}\text{(aq)} + 3 \text{H}_2\text{O(l)}$
- (e)**  $\text{NaAl(OH)}_2\text{CO}_3\text{(s)} + 4 \text{H}^+\text{(aq)} \rightarrow \text{Al}^{3+}\text{(aq)} + \text{Na}^+\text{(aq)} + 3 \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$

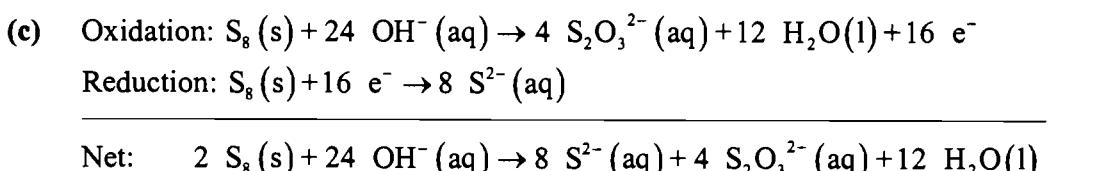
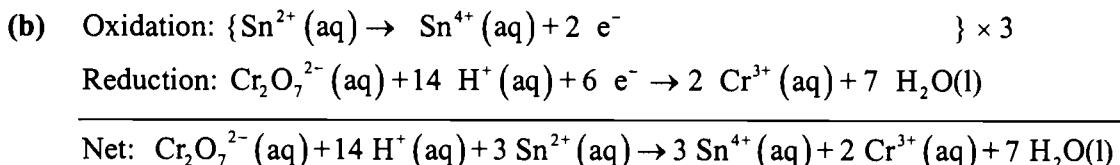
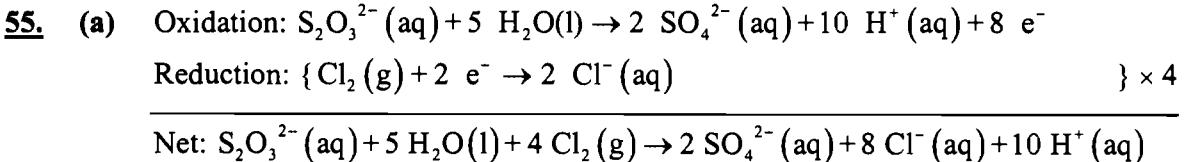
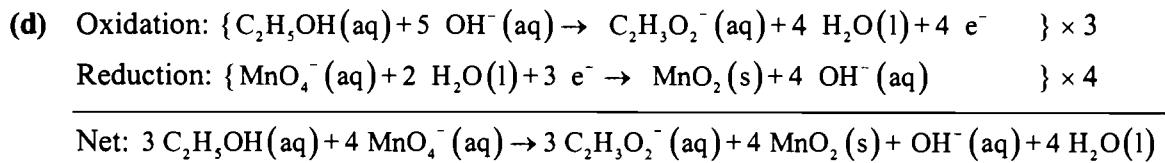
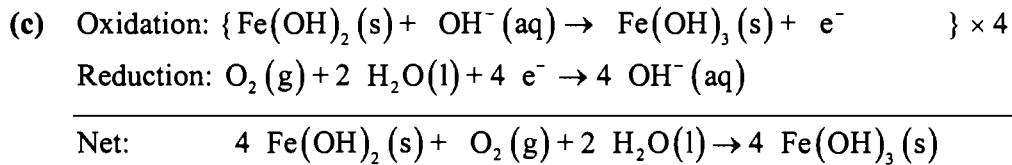
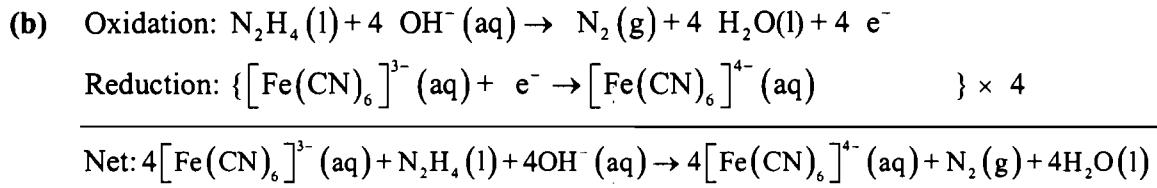
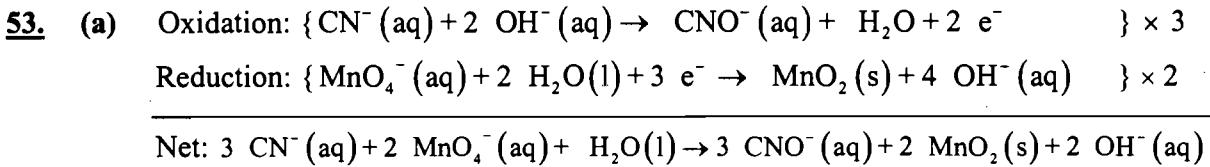
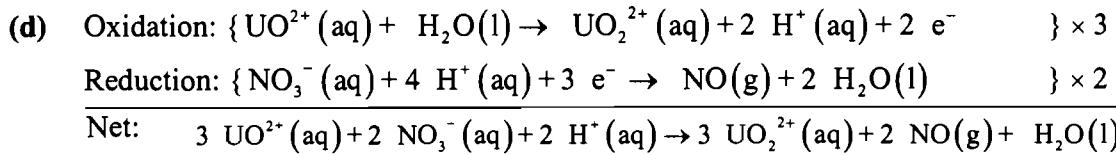


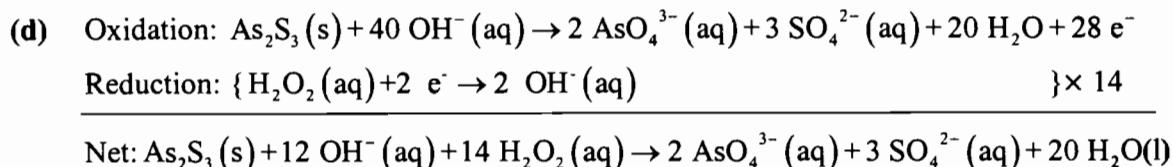
## Oxidation-Reduction (Redox) Equations

47. (a) In this reaction, iron is reduced from  $\text{Fe}^{3+}(\text{aq})$  to  $\text{Fe}^{2+}(\text{aq})$  and manganese is reduced from a +7 O.S. in  $\text{MnO}_4^-(\text{aq})$  to a +2 O.S. in  $\text{Mn}^{2+}(\text{aq})$ . Thus, there are two reductions and no oxidation, which is an impossibility.

(b) In this reaction, chlorine is oxidized from an O.S. of 0 in  $\text{Cl}_2(\text{aq})$  to an O.S. of +1 in  $\text{ClO}^-(\text{aq})$  and oxygen is oxidized from an O.S. of -1 in  $\text{H}_2\text{O}_2(\text{aq})$  to an O.S. of 0 in  $\text{O}_2(\text{g})$ . Consequently there are two oxidation reactions and no reduction reactions, also an impossibility.







## Oxidizing and Reducing Agents

57. The oxidizing agents experience a decrease in the oxidation state of one of their elements, while the reducing agents experience an increase in the oxidation state of one of their elements.
- (a)  $\text{SO}_3^{2-}(\text{aq})$  is the reducing agent; the O.S. of S = +4 in  $\text{SO}_3^{2-}$  and = +6 in  $\text{SO}_4^{2-}$ .  
 $\text{MnO}_4^-(\text{aq})$  is the oxidizing agent; the O.S. of Mn = +7 in  $\text{MnO}_4^-$  and +2 in  $\text{Mn}^{2+}$ .
- (b)  $\text{H}_2(\text{g})$  is the reducing agent; the O.S. of H = 0 in  $\text{H}_2(\text{g})$  and = +1 in  $\text{H}_2\text{O}(\text{g})$ .  
 $\text{NO}_2(\text{g})$  is the oxidizing agent; the O.S. of N = +4 in  $\text{NO}_2(\text{g})$  and -3 in  $\text{NH}_3(\text{g})$ .
- (c)  $[\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$  is the reducing agent; the O.S. of Fe = +2 in  $[\text{Fe}(\text{CN})_6]^{4-}$  and = +3 in  $[\text{Fe}(\text{CN})_6]^{3-}$ .  $\text{H}_2\text{O}_2(\text{aq})$  is the oxidizing agent; the O.S. of O = -1 in  $\text{H}_2\text{O}_2$  and = -2 in  $\text{H}_2\text{O}$ .

## Neutralization and Acid-Base Titrations

59.  $\text{NaOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$  is the titration reaction.
- $$[\text{NaOH}] = \frac{0.02834 \text{ L} \times \frac{0.1085 \text{ mol HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}}}{0.02500 \text{ L sample}} = 0.1230 \text{ M NaOH}$$
61. The net reaction is  $\text{OH}^-(\text{aq}) + \text{HC}_3\text{H}_5\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{C}_3\text{H}_5\text{O}_2^-(\text{aq})$
- $$\text{V}_{\text{base}} = 25.00 \text{ mL acid} \times \frac{0.3057 \text{ mmol HC}_3\text{H}_5\text{O}_2}{1 \text{ mL acid}} \times \frac{1 \text{ mmol KOH}}{1 \text{ mmol HC}_3\text{H}_5\text{O}_2} \times \frac{1 \text{ mL base}}{2.155 \text{ mmol KOH}} = 3.546 \text{ mL KOH solution}$$
63. The mass of acetylsalicylic acid is converted to the amount of NaOH, in millimoles, that will react with it.
- $$[\text{NaOH}] = \frac{0.32 \text{ g HC}_9\text{H}_7\text{O}_4}{23 \text{ mL NaOH(aq)}} \times \frac{1 \text{ mol HC}_9\text{H}_7\text{O}_4}{180.2 \text{ g HC}_9\text{H}_7\text{O}_4} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HC}_9\text{H}_7\text{O}_4} \times \frac{1000 \text{ mmol NaOH}}{1 \text{ mol NaOH}} = 0.077 \text{ M NaOH}$$

65. The equation for the reaction is  $\text{HNO}_3(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$ . This equation shows that equal numbers of moles are needed for a complete reaction. We compute the amount of each reactant.

$$\text{mmol HNO}_3 = 25.00 \text{ mL acid} \times \frac{0.132 \text{ mmol HNO}_3}{1 \text{ mL acid}} = 3.30 \text{ mmol HNO}_3$$

$$\text{mmol KOH} = 10.00 \text{ mL acid} \times \frac{0.318 \text{ mmol KOH}}{1 \text{ mL base}} = 3.18 \text{ mmol KOH}$$

There is more acid present than base. Thus, the resulting solution is acidic.

67.  $V_{\text{base}} = 5.00 \text{ mL vinegar} \times \frac{1.01 \text{ g vinegar}}{1 \text{ mL}} \times \frac{4.0 \text{ g HC}_2\text{H}_3\text{O}_2}{100.0 \text{ g vinegar}} \times \frac{1 \text{ mol HC}_2\text{H}_3\text{O}_2}{60.0 \text{ g HC}_2\text{H}_3\text{O}_2}$

$$\times \frac{1 \text{ mol NaOH}}{1 \text{ mol HC}_2\text{H}_3\text{O}_2} \times \frac{1 \text{ L base}}{0.1000 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 34 \text{ mL base}$$

69. Answer is (d): 120 % of necessary titrant added in titration of  $\text{NH}_3$

### Stoichiometry of Oxidation–Reduction Reactions

71.  $[ \text{MnO}_4^- ] = \frac{0.1078 \text{ g As}_2\text{O}_3 \times \frac{1 \text{ mol As}_2\text{O}_3}{197.84 \text{ g As}_2\text{O}_3} \times \frac{4 \text{ mol MnO}_4^-}{5 \text{ mol As}_2\text{O}_3} \times \frac{1 \text{ mol KMnO}_4}{1 \text{ mol MnO}_4^-}}{22.15 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.01968 \text{ M KMnO}_4$

73. First, determine the mass of Fe, then the percentage of iron in the ore.

$$\text{mass Fe} = 28.72 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.05051 \text{ mol Cr}_2\text{O}_7^{2-}}{1 \text{ L soln}} \times \frac{6 \text{ mol Fe}^{2+}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}^{2+}}$$

$$\text{mass Fe} = 0.4861 \text{ g Fe} \quad \% \text{Fe} = \frac{0.4861 \text{ g Fe}}{0.9132 \text{ g ore}} \times 100\% = 53.23\% \text{ Fe}$$

75. Oxidation:  $\{ \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2 \text{ CO}_2(\text{g}) + 2 \text{ e}^- \} \times 5$

- Reduction:  $\{ \text{MnO}_4^-(\text{aq}) + 8 \text{ H}^+(\text{aq}) + 5 \text{ e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{ H}_2\text{O}(\text{l}) \} \times 2$

---


$$\text{Net: } 5 \text{ C}_2\text{O}_4^{2-}(\text{aq}) + 2 \text{ MnO}_4^-(\text{aq}) + 16 \text{ H}^+(\text{aq}) \rightarrow 10 \text{ CO}_2(\text{g}) + 2 \text{ Mn}^{2+}(\text{aq}) + 8 \text{ H}_2\text{O}(\text{l})$$

$$\text{mass Na}_2\text{C}_2\text{O}_4 = 1.00 \text{ L satd soln} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{25.8 \text{ mL}}{50.0 \text{ mL satd soln}} \times \frac{0.02140 \text{ mol KMnO}_4}{1000 \text{ mL}}$$

$$\times \frac{1 \text{ mol MnO}_4^-}{1 \text{ mol KMnO}_4} \times \frac{5 \text{ mol C}_2\text{O}_4^{2-}}{2 \text{ mol MnO}_4^-} \times \frac{1 \text{ mol Na}_2\text{C}_2\text{O}_4}{1 \text{ mol C}_2\text{O}_4^{2-}} \times \frac{134.0 \text{ g Na}_2\text{C}_2\text{O}_4}{1 \text{ mol Na}_2\text{C}_2\text{O}_4}$$

$$\text{mass Na}_2\text{C}_2\text{O}_4 = 3.70 \text{ g Na}_2\text{C}_2\text{O}_4$$

## FEATURE PROBLEMS

- 96.** From the volume of titrant we can calculate both the amount in moles of  $\text{NaC}_5\text{H}_5$  and (through its molar mass of 88.08 g/mol) the mass of  $\text{NaC}_5\text{H}_5$  in a sample. The remaining mass in a sample is that of  $\text{C}_4\text{H}_8\text{O}$  (72.11 g/mol) whose amount in moles we calculate. The ratio of the molar amount of  $\text{C}_4\text{H}_8\text{O}$  in the sample to the molar amount of  $\text{NaC}_5\text{H}_5$  is the value of  $x$ .

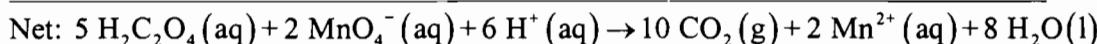
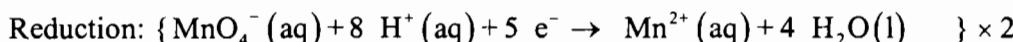
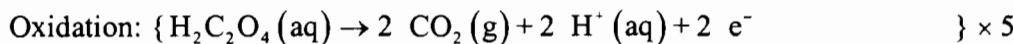
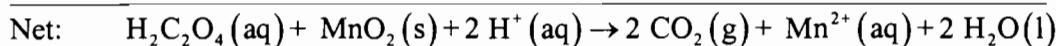
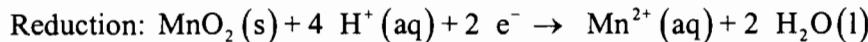
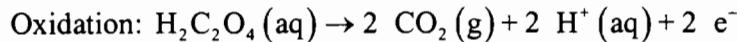
$$\text{moles of NaC}_5\text{H}_5 = 0.01492 \text{ L} \times \frac{0.1001 \text{ mol HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \times \frac{1 \text{ mol NaC}_5\text{H}_5}{1 \text{ mol NaOH}} \\ = 0.001493 \text{ mol NaC}_5\text{H}_5$$

$$\text{mass of C}_4\text{H}_8\text{O} = 0.242 \text{ g sample} - \left( 0.001493 \text{ mol NaC}_5\text{H}_5 \times \frac{88.08 \text{ g NaC}_5\text{H}_5}{1 \text{ mol NaC}_5\text{H}_5} \right) \\ = 0.110 \text{ g C}_4\text{H}_8\text{O}$$

$$x = \frac{0.110 \text{ g C}_4\text{H}_8\text{O} \times \frac{1 \text{ mol C}_4\text{H}_8\text{O}}{72.11 \text{ g C}_4\text{H}_8\text{O}}}{0.001493 \text{ mol NaC}_5\text{H}_5} = 1.02$$

For the second sample, parallel calculations give 0.001200 mol  $\text{NaC}_5\text{H}_5$ , 0.093 g  $\text{C}_4\text{H}_8\text{O}$ ,  $x = 1.1$ . There is rounding error in this second calculation because it is limited to two significant figures. The best answer is from the first run  $x \sim 1.02$  or 1. The formula is  $\text{NaC}_5\text{H}_5(\text{THF})_1$ .

- 97.** First, we balance the two equations.



Now we determine the mass of the excess oxalic acid.

$$\text{mass H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 0.03006 \text{ L} \times \frac{0.1000 \text{ mol KMnO}_4}{1 \text{ L}} \times \frac{1 \text{ mol MnO}_4^-}{1 \text{ mol KMnO}_4} \times \frac{5 \text{ mol H}_2\text{C}_2\text{O}_4}{2 \text{ mol MnO}_4^-} \\ \times \frac{1 \text{ mol H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}}{1 \text{ mol H}_2\text{C}_2\text{O}_4} \times \frac{126.07 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}}{1 \text{ mol H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}} \\ = 0.9474 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$$

The mass of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  that reacted with  $\text{MnO}_2$

$$= 1.651 \text{ g} - 0.9474 \text{ g} = 0.704 \text{ g} \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$$

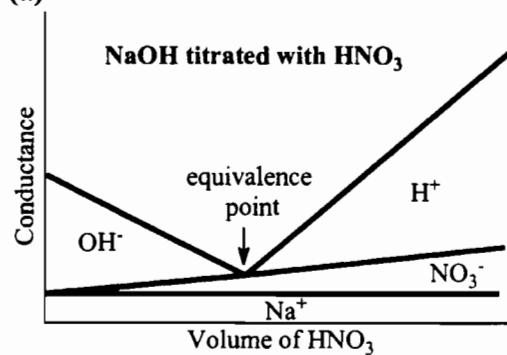
$$\text{mass MnO}_2 = 0.704 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{C}_2\text{O}_4}{126.07 \text{ g H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}} \times \frac{1 \text{ mol MnO}_2}{1 \text{ mol H}_2\text{C}_2\text{O}_4} \times \frac{86.9 \text{ g MnO}_2}{1 \text{ mol MnO}_2}$$

$$= 0.485 \text{ g MnO}_2$$

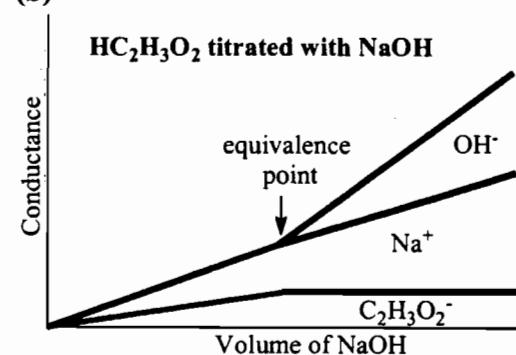
$$\% \text{ MnO}_2 = \frac{0.485 \text{ g MnO}_2}{0.533 \text{ g sample}} \times 100\% = 91.0\% \text{ MnO}_2$$

98.

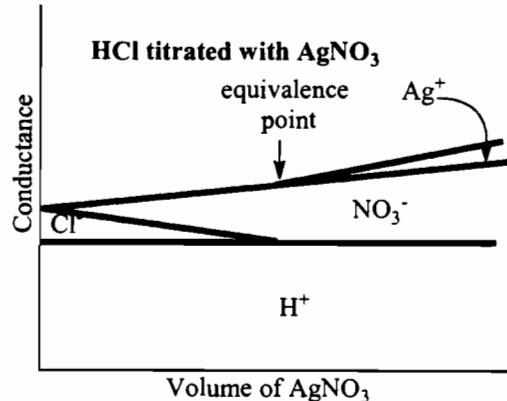
(a)



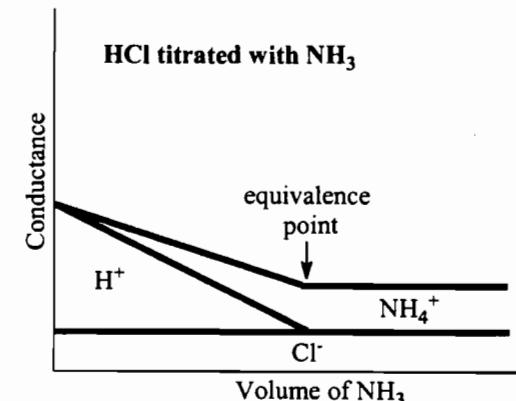
(b)



(c)



(d)



# CHAPTER 6

## GASES

### PRACTICE EXAMPLES

- 1A** The pressure measured by each liquid must be the same. They are related through  $P = g h d$ . Thus, we have the following  $g h_{\text{DEG}} d_{\text{DEG}} = g h_{\text{Hg}} d_{\text{Hg}}$ . The  $g$ 's cancel; we substitute known values:  $9.25 \text{ m DEG} \times 1.118 \text{ g/cm}^3 \text{ DEG} = h_{\text{Hg}} \times 13.6 \text{ g/cm}^3 \text{ Hg}$

$$h_{\text{Hg}} = 9.25 \text{ m} \times \frac{1.118 \text{ g/cm}^3}{13.6 \text{ g/cm}^3} = 0.760 \text{ m Hg}, P = 0.760 \text{ m Hg} = 760 \text{ mmHg}$$

- 1B** The solution is found through the expression relating density and height:  $h_{\text{TEG}} d_{\text{TEG}} = h_{\text{Hg}} d_{\text{Hg}}$ . We substitute known values and solve for triethylene glycol's density:  $7.39 \text{ m TEG} \times d_{\text{TEG}} = 757 \text{ mmHg} \times 13.6 \text{ g/cm}^3 \text{ Hg}$ . Using unit conversions, we get

$$d_{\text{TEG}} = \frac{0.757 \text{ m}}{7.39 \text{ m}} \times 13.6 \text{ g/cm}^3 = 1.39 \text{ g/cm}^3$$

- 2A** We know that  $P_{\text{gas}} = P_{\text{bar}} + \Delta P$  with  $P_{\text{bar}} = 748.2 \text{ mmHg}$ . We are told that  $\Delta P = 7.8 \text{ mmHg}$ . Thus,  $P_{\text{gas}} = 748.2 \text{ mmHg} + 7.8 \text{ mmHg} = 756.0 \text{ mmHg}$

- 2B** The difference in pressure between the two levels must be the same just expressed in different units. Hence, this problem is almost a repetition of Practice Example 6-1.  $h_{\text{Hg}} = 748.2 \text{ mmHg} - 739.6 \text{ mmHg} = 8.6 \text{ mmHg}$ . Again we have  $g h_g d_g = g h_{\text{Hg}} d_{\text{Hg}}$ . This becomes  $h_g \times 1.26 \text{ g/cm}^3 \text{ glycerol} = 8.6 \text{ mmHg} \times 13.6 \text{ g/cm}^3 \text{ Hg}$

$$h_g = 8.6 \text{ mmHg} \times \frac{13.6 \text{ g/cm}^3 \text{ Hg}}{1.26 \text{ g/cm}^3 \text{ glycerol}} = 93 \text{ mm glycerol}$$

- 3A**  $A = \pi r^2$  (here  $r = \frac{1}{2}(2.60 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}}) = 0.0130 \text{ m}$ )

$$A = \pi(0.0130 \text{ m})^2 = 5.31 \times 10^{-4} \text{ m}^2$$

$$F = m \times g = (1.000 \text{ kg})(9.81 \text{ m s}^{-2}) = 9.81 \text{ kg m s}^{-2} = 9.81 \text{ N}$$

$$P = \frac{F}{A} = \frac{9.81 \text{ N}}{5.31 \times 10^{-4} \text{ m}^2} = 18475 \text{ N m}^{-2} \text{ or } 1.85 \times 10^4 \text{ Pa}$$

$$P \text{ (torr)} = 1.85 \times 10^4 \text{ Pa} \times = 139 \text{ torr}$$

**3B** Final pressure = 100 mb.  $100 \text{ mb} \times \frac{101,325 \text{ Pa}}{1013.25 \text{ mb}} = 1.000 \times 10^4 \text{ Pa}$

The area of the cylinder is unchanged from that in Example 6-3,  $(1.32 \times 10^{-3} \text{ m}^2)$ .

$$P = \frac{F}{A} = 1.000 \times 10^4 \text{ Pa} = \frac{F}{1.32 \times 10^{-3} \text{ m}^2}$$

Solving for F, we find  $F = 13.2 \text{ (Pa)} \text{m}^2 = 13.2 \text{ (N m}^{-2}\text{)} \text{m}^2 = 13.2 \text{ N}$

$$F = m \times g = 13.2 \text{ kg m s}^{-2} = m \times 9.81 \text{ ms}^{-2}$$

$$\text{Total mass} = \text{mass of cylinder} + \text{mass added weight} = m = \frac{F}{g} = \frac{13.2 \text{ kg m s}^{-2}}{9.81 \text{ m s}^{-2}} = 1.35 \text{ kg}$$

An additional 350 grams must be added to the top of the 1.000 kg (1000 g) red cylinder to increase the pressure to 100 mb. It is not necessary to add a mass with the same cross sectional area. The pressure will only be exerted over the area that is the base of the cylinder on the surface beneath it.

**4A** Boyle's Law relates the pressure-volume product.  $P_1 V_1 = P_2 V_2$

$$5.25 \text{ atm} \times V_1 = 1.85 \text{ atm} \times 12.5 \text{ L} \quad V_1 = \frac{1.85 \text{ atm} \times 12.5 \text{ L}}{5.25 \text{ atm}} = 4.40 \text{ L}$$

**4B** Use Boyle's law, solved for the final pressure. After that, the pressure is converted to mmHg.

$$P_2 = P_1 \times \frac{V_1}{V_2} = 2.25 \text{ atm} \times \frac{1.50 \text{ L}}{8.10 \text{ L}} = 0.417 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 317 \text{ mmHg}$$

**5A** Charles's law states that the volume/temperature ratio is constant (temperature in kelvins).

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{0.250 \text{ L}}{(25 + 273.15) \text{ K}} = \frac{1.65 \text{ L}}{T_2}; \quad T_2 = \frac{298 \text{ K} \times 1.65 \text{ L}}{0.250 \text{ L}} = 1.97 \times 10^3 \text{ K} = 1.69 \times 10^3 \text{ }^\circ\text{C}$$

**5B** For oxygen: The increase in the volume will be directly proportional to the temperature increase (Kelvin scale). Assuming that the pressure remains constant,

$$\frac{V_i}{T_i} = \frac{nR}{P} = \frac{V_f}{T_f} \text{ or } \frac{V_f}{V_i} = \frac{T_f}{T_i} = \frac{(25.0 + 273.15)}{(-13.5 + 273.15)} = 1.15 \text{ (or a 15% increase in volume)}$$

For nitrogen: We expect the volume to increase 15% as well.

$$V_f = V_i \times 1.15 = 50.5 \text{ mL} \times 1.15 = 58.1 \text{ mL}$$

The temperature in Kelvin should also increase by 15%, i.e.

$$T_f = T_i \times 1.15 = (33.4 + 273.15) \times 1.15 = 353 \text{ K or } 79 \text{ }^\circ\text{C}$$

- 6A** The STP molar volume of 22.414 L enables us to determine the amount in moles of propane, from which we find the mass with the use of the molar mass.

$$\text{mass propane} = 30.0 \text{ L} \times \frac{1 \text{ mol}}{22.414 \text{ L}} \times \frac{44.10 \text{ g C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} = 59.0 \text{ g C}_3\text{H}_8$$

- 6B** A gas's STP molar volume is 22.414 L. In addition, we need the molar mass of  $\text{CO}_2(g)$ , 44.01 g/mol.

$$\text{CO}_2(g) \text{ volume} = 128 \text{ g} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{22.414 \text{ L at STP}}{1 \text{ mol CO}_2} = 65.2 \text{ L CO}_2(g) \text{ at STP}$$

- 7A** The ideal gas equation is solved for volume. Conversions are made within the equation.

$$V = \frac{nRT}{P} = \frac{\left(20.2 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3}\right) \times \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (-25 + 273) \text{ K}}{752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 24.4 \text{ L NH}_3$$

- 7B** The amount of  $\text{Cl}_2(g)$  is 0.193 mol  $\text{Cl}_2$  and the pressure is 0.980 atm, as they are in Example 6-7. This information is substituted into the ideal gas equation after it has been solved for temperature.

$$T = \frac{PV}{nR} = \frac{0.980 \text{ atm} \times 7.50 \text{ L}}{0.193 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}} = 464 \text{ K}$$

- 8A** The ideal gas equation is solved for amount and the quantities are substituted.

$$n = \frac{PV}{RT} = \frac{10.5 \text{ atm} \times 5.00 \text{ L}}{\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (30.0 + 273.15) \text{ K}} = 2.11 \text{ mol He}$$

**8B**

$$n = \frac{PV}{RT} = \frac{\left(6.67 \times 10^{-7} \text{ Pa} \times \frac{1 \text{ atm}}{101325 \text{ Pa}}\right) \left(3.45 \text{ m}^3 \times \frac{1000 \text{ L}}{1 \text{ m}^3}\right)}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(25 + 273.15) \text{ K}} = 9.28 \times 10^{-10} \text{ moles of N}_2$$

$$\text{molecules of N}_2 = 9.28 \times 10^{-10} \text{ mol N}_2 \times \frac{6.022 \times 10^{23} \text{ molecules of N}_2}{1 \text{ mole N}_2}$$

$$\text{molecules of N}_2 = 5.59 \times 10^{14} \text{ molecules N}_2$$

- 9A** The general gas equation is solved for volume, after the constant amount in moles is cancelled. Temperatures are converted to kelvin.

$$V_2 = \frac{V_1 P_1 T_2}{P_2 T_1} = \frac{1.00 \text{ mL} \times 2.14 \text{ atm} \times (37.8 + 273.2) \text{ K}}{1.02 \text{ atm} \times (36.2 + 273.2) \text{ K}} = 2.11 \text{ mL}$$

- 9B** The flask has a volume of 1.00 L and initially contains O<sub>2</sub>(g) at STP. The mass of O<sub>2</sub>(g) that must be released is obtained from the difference in the amount of O<sub>2</sub>(g) at the two temperatures, 273 K and 373 K. We also could compute the masses separately and subtract them.

$$\begin{aligned}\text{mass released} &= (n_{\text{STP}} - n_{100^\circ\text{C}}) \times M_{\text{O}_2} = \left( \frac{PV}{R273\text{K}} - \frac{PV}{R373\text{K}} \right) \times M_{\text{O}_2} = \frac{PV}{R} \left( \frac{1}{273\text{K}} - \frac{1}{373\text{K}} \right) \times M_{\text{O}_2} \\ &= \frac{1.00 \text{ atm} \times 1.00 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{273\text{K}} - \frac{1}{373\text{K}} \right) \times \frac{32.00 \text{ g}}{1 \text{ mol O}_2} = 0.383 \text{ g O}_2\end{aligned}$$

- 10A** The volume of the vessel is 0.09841 L. We substitute other values into the expression for molar mass.

$$M = \frac{mRT}{PV} = \frac{(40.4868 \text{ g} - 40.1305 \text{ g}) \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (22.4 \times 273.2) \text{ K}}{\left( 772 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) \times 0.09841 \text{ L}} = 86.5 \text{ g/mol}$$

- 10B** The gas's molar mass is its mass (1.27 g) divided by its amount in moles. The amount can be determined from the ideal gas equation.

$$n = \frac{PV}{RT} = \frac{\left( 737 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) \times 1.07 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol} \cdot \text{K}} \times (25 + 273) \text{ K}} = 0.0424 \text{ mol gas}$$

$$M = \frac{1.27 \text{ g}}{0.0424 \text{ mol}} = 30.0 \text{ g/mol} \text{ In good agreement with the molar mass of NO, } 30.006 \text{ g/mol.}$$

- 11A** The molar mass of He is 4.003 g/mol. This is substituted into the expression for density.

$$d = \frac{MP}{RT} = \frac{4.003 \text{ g mol}^{-1} \times 0.987 \text{ atm}}{0.08206 \text{ L} \cdot \text{atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.162 \text{ g/L}$$

When compared to the density of air under the same conditions (1.16 g/L, based on the “average molar mass of air”=28.8g/mol) the density of He is only about one seventh as much. He is less dense (“lighter”) than air.

- 11B** The suggested solution is a simple one; merely solve for the temperature.

$$T = \frac{MP}{Rd} = \frac{\frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \left( 745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right)}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times \frac{1.00 \text{ g}}{1 \text{ L}}} = 382 \text{ K}$$

However, suppose that you have forgotten the convenient formula for the density of an ideal gas? You can still solve a problem such as this one. The density of 1.00 g/L indicates a mass of 1.00 g of gas in a 1.00-L volume. Of course, the mass of a gas, given its identity (oxygen in this case) enables us to determine the amount in moles of the gas ( $n$  in the ideal gas equation). Then, we can solve the ideal gas equation for the desired property, such as temperature, as follows:

$$T = \frac{PV}{nR} = \frac{\left(745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times 1.00 \text{ L}}{\left(1.00 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2}\right) \times \frac{0.08206 \text{ L atm}}{\text{mol K}}} = 382 \text{ K}$$

**12A** The balanced equation is  $2 \text{ NaN}_3(\text{s}) \xrightarrow{\Delta} 2 \text{ Na}(\text{l}) + 3 \text{ N}_2(\text{g})$

$$\text{moles N}_2 = \frac{PV}{RT} = \frac{\left(776 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times 20.0 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times (30.0 + 273.2) \text{ K}} = 0.821 \text{ mol N}_2$$

Now, solve the stoichiometry problem.

$$\text{mass NaN}_3 = 0.821 \text{ mol N}_2 \times \frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \times \frac{65.01 \text{ g NaN}_3}{1 \text{ mol NaN}_3} = 35.6 \text{ g NaN}_3$$

**12B** Here we are not dealing with gaseous reactants; the law of combining volumes cannot be used. From the ideal gas equation we determine the amount of  $\text{N}_2(\text{g})$  per liter under the specified conditions. Then we determine the amount of  $\text{Na}(\text{l})$  produced simultaneously, and finally the mass of that  $\text{Na}(\text{l})$ .

$$\text{mass of Na(l)} = \frac{\left(751 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times 1.000 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times (25 + 273) \text{ K}} \times \frac{2 \text{ mol Na}}{3 \text{ mol N}_2} \times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}} = 0.619 \text{ g Na(l)}$$

**13A** The law of combining volumes permits us to use stoichiometric coefficients for volume ratios.

$$\text{O}_2 \text{ volume} = 1.00 \text{ L NO(g)} \times \frac{5 \text{ L O}_2}{4 \text{ L NO}} = 1.25 \text{ L O}_2(\text{g})$$

- 13B** The first task is to balance the chemical equation. There must be three moles of hydrogen for every mole of nitrogen in both products (because of the formula of  $\text{NH}_3$ ) and reactants:  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ . The volumes of gaseous reactants and products are related by their stoichiometric coefficients, as long as all gases are measured at the same temperature and pressure.

$$\text{volume NH}_3(\text{g}) = 225 \text{ L H}_2(\text{g}) \times \frac{2 \text{ L NH}_3(\text{g})}{3 \text{ L H}_2(\text{g})} = 150. \text{ L NH}_3$$

- 14A** We can work easily with the ideal gas equation, with a new temperature of  $T = (55 + 273) \text{ K} = 328 \text{ K}$ . The amount of Ne added is readily computed.

$$n_{\text{Ne}} = 12.5 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} = 0.619 \text{ mol Ne}$$

$$P = \frac{n_{\text{total}}RT}{V} = \frac{(1.75 + 0.619)\text{mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 328 \text{ K}}{5.0 \text{ L}} = 13 \text{ atm}$$

- 14B** The total volume initially is  $2.0 \text{ L} + 8.0 \text{ L} = 10.0 \text{ L}$ . These two mixed ideal gases then obey the general gas equation as if they were one gas.

$$P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = \frac{1.00 \text{ atm} \times 10.0 \text{ L} \times 298 \text{ K}}{2.0 \text{ L} \times 273 \text{ K}} = 5.5 \text{ atm}$$

- 15A** The partial pressures are proportional to the mole fractions.

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{tot}}} \times P_{\text{tot}} = \frac{0.00278 \text{ mol H}_2\text{O}}{0.197 \text{ mol CO}_2 + 0.00278 \text{ mol H}_2\text{O}} \times 2.50 \text{ atm} = 0.0348 \text{ atm H}_2\text{O(g)}$$

$$P_{\text{CO}_2} = P_{\text{tot}} - P_{\text{H}_2\text{O}} = 2.50 \text{ atm} - 0.0348 \text{ atm} = 2.47 \text{ atm CO}_2(\text{g})$$

- 15B** Expression (6.17) indicates that, in a mixture of gases, the mole percent equals the volume percent, which in turn equals the pressure percent. Thus, we can apply these volume percents—converted to fractions by dividing by 100—directly to the total pressure.

$$\text{N}_2 \text{ pressure} = 0.7808 \times 748 \text{ mmHg} = 584 \text{ mmHg},$$

$$\text{O}_2 \text{ pressure} = 0.2095 \times 748 \text{ mmHg} = 157 \text{ mmHg},$$

$$\text{CO}_2 \text{ pressure} = 0.00036 \times 748 \text{ mmHg} = 0.27 \text{ mmHg},$$

$$\text{Ar pressure} = 0.0093 \times 748 \text{ mmHg} = 7.0 \text{ mmHg}$$

**16A** First compute the moles of  $\text{H}_2(\text{g})$ , then use stoichiometry to convert to moles of  $\text{HCl}$ .

$$\text{amount HCl} = \frac{\left( (755 - 25.2) \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) \times 0.0355 \text{ L}}{\frac{0.0821 \text{ L atm}}{\text{mol K}} \times (26 + 273) \text{ K}} \times \frac{6 \text{ mol HCl}}{3 \text{ mol H}_2} = 0.00278 \text{ mol HCl}$$

**16B** The volume occupied by the  $\text{O}_2(\text{g})$  at its partial pressure is the same as the volume occupied by the mixed gases: water vapor and  $\text{O}_2(\text{g})$ . The partial pressure of  $\text{O}_2(\text{g})$  is found by difference.

$$\text{O}_2 \text{ pressure} = 749.2 \text{ total pressure} - 23.8 \text{ mmHg} (\text{H}_2\text{O pressure}) = 725.4 \text{ mmHg}$$

The mass of  $\text{Ag}_2\text{O}$  is related to the amount of  $\text{O}_2(\text{g})$  produced.

$$\text{moles O}_2 = 8.07 \text{ g sample} \times \frac{88.3 \text{ g Ag}_2\text{O}}{100.0 \text{ g sample}} \times \frac{1 \text{ mol Ag}_2\text{O}}{231.74 \text{ g Ag}_2\text{O}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol Ag}_2\text{O}} = 0.0154 \text{ mol O}_2$$

The volume of  $\text{O}_2(\text{g})$  is found with the ideal gas law.

$$V = \frac{nRT}{P} = \frac{0.0154 \text{ mol O}_2 \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 25) \text{ K}}{725.4 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 0.395 \text{ L O}_2$$

**17A** The gas with the smaller molar mass,  $\text{NH}_3$  at 17.0 g/mol, has the greater root-mean-square speed

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{0.0170 \text{ kg mol}^{-1}}} = 661 \text{ m/s}$$

$$\text{17B bullet speed} \frac{2180 \text{ mi}}{1 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{5280 \text{ ft}}{1 \text{ mi}} \times \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 974.5 \text{ m/s}$$

Solve the rms-speed equation (6.20) for temperature by first squaring both sides.

$$(u_{\text{rms}})^2 = \frac{3RT}{M} \quad T = \frac{(u_{\text{rms}})^2 M}{3R} = \frac{\left( \frac{974.5 \text{ m}}{1 \text{ s}} \right)^2 \times \frac{2.016 \times 10^{-3} \text{ kg}}{1 \text{ mol H}_2}}{3 \times \frac{8.3145 \text{ kg m}^2}{\text{s}^2 \text{ mol K}}} = 76.75 \text{ K}$$

We expected the temperature to be lower than 298 K. Note that the speed of the bullet is about half the speed of a  $\text{H}_2$  molecule at 298 K. To halve the speed of a molecule, its temperature must be divided by four.

- 18A** The only difference is the molar mass of the gas.  $2.2 \times 10^{-4}$  mol N<sub>2</sub> effuses through the orifice in 105 s.

$$\frac{\text{? mol O}_2}{2.2 \times 10^{-4} \text{ mol N}_2} = \sqrt{\frac{M_{N_2}}{M_{O_2}}} = \sqrt{\frac{28.014 \text{ g/mol}}{31.999 \text{ g/mol}}} = 0.9357$$

$$\text{moles O}_2 = 0.9357 \times 2.2 \times 10^{-4} = 2.1 \times 10^{-4} \text{ mol O}_2$$

- 18B** The two rates of effusion are related as the square root of the ratio of the molar masses of the two gases. The lighter gas, H<sub>2</sub>, effuses faster, and thus requires a shorter time for the same amount of gas to effuse.

$$\text{H}_2 \text{ time} = \text{N}_2 \text{ time} \times \sqrt{\frac{M_{H_2}}{M_{N_2}}} = 105 \text{ s} \times \sqrt{\frac{2.016 \text{ g H}_2/\text{mol H}_2}{28.014 \text{ g N}_2/\text{mol N}_2}} = 28.2 \text{ s}$$

- 19A** The times of effusion are related as the square root of the molar mass. It requires 87.3 s for Kr to effuse.

$$\frac{\text{unknown time}}{\text{Kr time}} = \sqrt{\frac{M_{\text{unk}}}{M_{\text{Kr}}}} \quad \text{substitute in values} \quad \frac{131.3 \text{ s}}{87.3 \text{ s}} = \sqrt{\frac{M_{\text{unk}}}{83.80 \text{ g/mol}}} = 1.50$$

$$M_{\text{unk}} = (1.504)^2 \times 83.80 \text{ g/mol} = 1.90 \times 10^2 \text{ g/mol}$$

- 19B** This problem is solved in virtually the same manner as Practice Example 18B. The lighter gas is ethane, with a molar mass of 30.07 g/mol.

$$\text{C}_2\text{H}_6 \text{ time} = \text{Kr time} \times \sqrt{\frac{M(\text{C}_2\text{H}_6)}{M(\text{Kr})}} = 87.3 \text{ s} \times \sqrt{\frac{30.07 \text{ g C}_2\text{H}_6/\text{mol C}_2\text{H}_6}{83.80 \text{ g Kr/mol Kr}}} = 52.3 \text{ s}$$

- 20A** Because one mole of gas is being considered, the value of  $n^2a$  is numerically the same as the value of  $a$ , and the value of  $nb$  is numerically the same as the value of  $b$ .

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 273 \text{ K}}{(2.00 - 0.0427) \text{ L}} - \frac{3.59 \text{ L}^2 \text{ atm}}{(2.00 \text{ L})^2} = 11.4 \text{ atm} - 0.898 \text{ atm} \\ = 10.5 \text{ atm CO}_2(\text{g}) \quad \text{compared with 9.9 atm for Cl}_2(\text{g})$$

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 273 \text{ K}}{2.00 \text{ L}} = 11.2 \text{ atm}$$

Cl<sub>2</sub>(g) shows a greater deviation from ideal gas behavior than does CO<sub>2</sub>(g).

- 20B** Because one mole of gas is being considered, the value of  $n^2a$  is numerically the same as the value of  $a$ , and the value of  $nb$  is numerically the same as the value of  $b$ .

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 273 \text{ K}}{(2.00 - 0.0399) \text{ L}} - \frac{1.49 \text{ L}^2 \text{ atm}}{(2.00 \text{ L})^2} = 11.4 \text{ atm} - 0.373 \text{ atm} \\ = 11.1 \text{ atm CO(g)}$$

compared to 9.9 atm for  $\text{Cl}_2(\text{g})$ , 11.2 atm for an ideal gas, and 10.5 atm for  $\text{CO}_2(\text{g})$ . Thus,  $\text{Cl}_2(\text{g})$  displays the greatest deviation from ideality.

## REVIEW QUESTIONS

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- “atm” is the abbreviation for “atmosphere,” a unit of pressure equal to 760 mmHg, 101,325 Pa, or 14.7 lb / in.<sup>2</sup>.
  - “STP” is the abbreviation for “standard temperature and pressure:” 0°C and 1 atm pressure.
  - $R$  is the symbol for the ideal gas constant. It has a value of 0.08206 L atm mol<sup>-1</sup> K<sup>-1</sup>.
  - Partial pressure is the pressure that one of the gases in a mixture of gases would exert if it were present in the container by itself under the same conditions.
  - “ $u_{\text{rms}}$ ” is the abbreviation for the root mean square speed of a number of moving objects, molecules in our considerations. It is the square root of the average of the squares of the speeds. It also is the median speed: half the molecules are traveling faster than this speed, and half are traveling slower.
- The absolute zero of temperature, -273.15°C, is the lowest temperature possible. All molecular motion is thought to cease at this temperature.
  - A gas is collected over water by bubbling the gas into an upside-down container that is filled with water. The gas rises to the top of the container, displacing the water, and is trapped in the container.
  - Effusion of a gas refers to the very slow leakage of the gas out of a small hole in a container and into a vacuum.
  - The law of combining volumes states that gases, when present at the same temperature and pressure, react in volumes that are related as small whole numbers. These small whole numbers turn out to be the stoichiometric coefficients.

3. (a) A barometer is a device used to measure absolute pressures; it measures the difference in pressure between some gas and a vacuum. A manometer measures the difference in pressure between two gases.
- (b) Celsius and Kelvin temperatures both have the same size degree, large enough that 100 degrees span the temperature range from the boiling point to the freezing point of water. The zero point of Celsius temperature is the freezing point of water; that of Kelvin is  $-273.15^{\circ}\text{C}$ , absolute zero.
- (c) The ideal gas equation relates the properties of pressure, volume, temperature, and amount for one gas. The general gas equation relates the initial and final values of these four properties, or the properties for two gases.
- (d) An ideal gas is one that obeys the ideal gas law. On a molecular level, the molecules of such a gas are dimensionless points that exert no forces of attraction or repulsion. The molecules of a real gas occupy some space (but not much compared to the volume of a gas container) and exert weak attractions on each other. At room temperature and pressure the differences in the properties of real and ideal gases are almost insignificant.

4. (a)  $P = 736 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.968 \text{ atm}$

(b)  $P = 58.2 \text{ cm Hg} \times \frac{1 \text{ atm}}{76 \text{ cmHg}} = 0.766 \text{ atm}$

(c)  $P = 892 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.17 \text{ atm}$

(d)  $P = 225 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ atm}}{101,325 \text{ Pa}} = 2.22 \text{ atm}$

5. (a)  $h = 0.984 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 748 \text{ mmHg}$       (b)  $h = 928 \text{ torr} = 928 \text{ mmHg}$

(c)  $h = 142 \text{ ft H}_2\text{O} \times \frac{12 \text{ in}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in}} \times \frac{10 \text{ mmH}_2\text{O}}{1 \text{ cm H}_2\text{O}} \times \frac{1 \text{ mmHg}}{13.6 \text{ mmH}_2\text{O}} \times \frac{1 \text{ mHg}}{1000 \text{ mmHg}} = 3.18 \text{ mHg}$

6. The atmospheric pressure is less than the pressure of the gas.  
 The difference in pressures is  $\Delta P = 16.5 \text{ mmHg} - 7.9 \text{ mmHg} = 8.6 \text{ mmHg}$   
 $P_{\text{gas}} = P_{\text{atm}} + \Delta P = 744 \text{ mmHg} + 8.6 \text{ mmHg} = 753 \text{ mmHg}$

7. (a)  $V = 26.7 \text{ L} \times \frac{762 \text{ mmHg}}{385 \text{ mmHg}} = 52.8 \text{ L}$

(b)  $V = 26.7 \text{ L} \times \frac{762 \text{ mmHg}}{3.68 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}}} = 7.27 \text{ L}$

8. Apply Charles's law:  $V = kT$ .  $T_i = 26 + 273 = 299 \text{ K}$

$$(a) \quad T = 273 + 98 = 371 \text{ K} \quad V = 886 \text{ mL} \times \frac{371 \text{ K}}{299 \text{ K}} = 1.10 \times 10^3 \text{ mL}$$

$$(b) \quad T = 273 - 20 = 253 \text{ K} \quad V = 886 \text{ mL} \times \frac{253 \text{ K}}{299 \text{ K}} = 7.50 \times 10^2 \text{ mL}$$

9. Apply Charles's law.  $T_f = (22 + 273) \text{ K} \times \frac{165 \text{ mL}}{57.3 \text{ mL}} = 849 \text{ K} = 576^\circ\text{C}$

10. STP:  $P = 1 \text{ atm}$  and  $T = 273.15 \text{ K}$  (note: one mole of gas at STP occupies 22.414 L).

$$V = \frac{nRT}{P} = \frac{\left(49.6 \text{ g C}_2\text{H}_2 \times \frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g}}\right) \left(0.08206 \frac{\text{L atm}}{\text{K mol}}\right) 273.15 \text{ K}}{1 \text{ atm}} = 42.7 \text{ L C}_2\text{H}_2$$

$$\text{Alternatively } V = n \times V_m = \left(49.6 \text{ g C}_2\text{H}_2 \times \frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g}}\right) \times \frac{22.414 \text{ L at STP}}{1 \text{ mol}} = 42.7 \text{ L C}_2\text{H}_2$$

11. STP:  $P = 1 \text{ atm}$  and  $T = 273.15 \text{ K}$  (note: one mole of gas at STP occupies 22.414 L).

$$V = \frac{nRT}{P} = \frac{\left(250.0 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.906 \text{ g}}\right) \left(0.08206 \frac{\text{L atm}}{\text{K mol}}\right) 273.15 \text{ K}}{1 \text{ atm}} = 42.7 \text{ L Cl}_2$$

$$\text{Alternatively } V = n \times V_m = \left(250.0 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.906 \text{ g}}\right) \times \frac{22.414 \text{ L at STP}}{1 \text{ mol}} = 79.03 \text{ L Cl}_2$$

12. The gas with the greatest density at STP is the one with the highest molar mass:  $\text{Cl}_2 = 70.9 \text{ g/mol}$ ,  $\text{SO}_3 = 80.1 \text{ g/mol}$ ,  $\text{N}_2\text{O} = 44.0 \text{ g/mol}$ ; and  $\text{PF}_3 = 88.0 \text{ g/mol}$ . Thus,  $\text{PF}_3$  would have the highest STP density of the four gases listed.

13. Assume that the  $\text{CO}_2(\text{g})$  behaves ideally and use the ideal gas law:  $PV = nRT$

$$V = \frac{nRT}{P} = \frac{\left(89.2 \text{ g} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g}}\right) 0.08206 \frac{\text{L atm}}{\text{mol K}} (37 + 273.2) \text{ K}}{737 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 5.32 \times 10^4 \text{ mL}$$

$$P = \frac{nRT}{V} = \frac{\left(285 \text{ g} \times \frac{1 \text{ mol SO}_2}{64.07 \text{ g}}\right) 0.08206 \frac{\text{L atm}}{\text{mol K}} (27 + 273.2) \text{ K}}{40.0 \text{ L}} = 2.74 \text{ atm}$$

15. Use the ideal gas law to determine the amount in moles of the given quantity of gas.

$$n = \frac{PV}{RT} = \frac{\left(743 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \left(115 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right)}{0.08206 \frac{\text{L atm}}{\text{mol K}} (273.2 + 66.3) \text{ K}} = 0.00404 \text{ mol gas}$$

$$M = \frac{0.418 \text{ g}}{0.00404 \text{ mol}} = 103 \text{ g/mol}$$

16. Density,  $d(\text{g/L}) = \text{molar mass, } M \text{ (g/mol)} \div \text{molar volume, } V/n \text{ (L/mol)}$

$$V/n = \frac{RT}{P} = \frac{0.08206 \frac{\text{L atm}}{\text{mol K}} \times (32.7 + 273.2) \text{ K}}{758 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 25.2 \frac{\text{L}}{\text{mol}}$$

$$d = \frac{44.01 \frac{\text{g}}{\text{mol}}}{25.2 \frac{\text{L}}{\text{mol}}} = 1.75 \frac{\text{g}}{\text{L}}$$

17. Each mole of gas occupies 22.4 L at STP.

$$\text{H}_2 \text{ STP volume} = 1.000 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol H}_2(\text{g})}{2 \text{ mol Al(s)}} \times \frac{22.4 \text{ L H}_2(\text{g}) \text{ at STP}}{1 \text{ mol H}_2}$$

$$= 1.25 \text{ L H}_2(\text{g})$$

18. Determine first the amount of CO<sub>2</sub>(g) that can be removed. Then use the ideal gas law.

$$\text{mol CO}_2 = 1.00 \text{ kg LiOH} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol LiOH}}{23.95 \text{ g LiOH}} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol LiOH}} = 20.9 \text{ mol CO}_2$$

$$V = \frac{nRT}{P} = \frac{20.9 \text{ mol} \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (25.9 + 273.2) \text{ K}}{751 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 519 \text{ L CO}_2(\text{g})$$

19. Determine the total amount of gas; then use the ideal gas law, assuming that the gases behave ideally.

$$\text{moles gas} = \left( 15.2 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} \right) + \left( 34.8 \text{ g Ar} \times \frac{1 \text{ mol Ar}}{39.95 \text{ g Ar}} \right)$$

$$= 0.753 \text{ mol Ne} + 0.871 \text{ mol Ar} = 1.624 \text{ mol gas}$$

$$V = \frac{nRT}{P} = \frac{1.624 \text{ mol} \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (26.7 + 273.2) \text{ K}}{7.15 \text{ atm}} = 5.59 \text{ L gas}$$

20. 2.24 L H<sub>2</sub>(g) at STP is 0.100 mol H<sub>2</sub>(g). After 0.10 mol He is added, the container holds 0.20 mol gas.

$$V = \frac{nRT}{P} = \frac{0.20 \text{ mol} \times 0.0821 \frac{\text{L atm}}{\text{mol K}} (273 + 100) \text{ K}}{1.00 \text{ atm}} = 6.1 \text{ L gas}$$

21. (a) The total pressure is the sum of all of the partial pressures of  $O_2(g)$  and the vapor pressure of water.

$$P_{\text{total}} = P_{O_2} + P_{H_2O} = 756 \text{ mmHg} = P_{O_2} + 19 \text{ mmHg}$$

$$P_{O_2} = (756 - 19) \text{ mmHg} = 737 \text{ mmHg}$$

- (b) The volume percent is equal to the pressure percent.

$$\%O_2(\text{g}) \text{ by volume} = \frac{V_{O_2}}{V_{\text{total}}} \times 100\% = \frac{P_{O_2}}{P_{\text{total}}} \times 100\% = \frac{737 \text{ mmHg of } O_2}{756 \text{ mm Hg total}} \times 100\% = 97.5\%$$

- (c) Determine the mass of  $O_2(\text{g})$  collected by multiplying the amount of  $O_2$  collected, in moles, by the molar mass of  $O_2(\text{g})$ .

$$\text{mass } O_2 = \frac{PV}{RT} M = \frac{\left(737 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \left(89.3 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right)}{0.08206 \frac{\text{L atm}}{\text{mol K}} (21.3 + 273.2) \text{ K}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2}$$

$$\text{mass } O_2 = 0.115 \text{ g } O_2$$

22. (1) is the true statement; average molecular kinetic energy depends only on absolute temperature, which is the same for these two gases. (2) is incorrect, since average molecular speed depends also on molar mass, which is different for these two gases. (3) also is incorrect, since volumes at the same temperature and pressure depend on the amount in moles, which is different for these two gases. And (4) is incorrect; the effusion rates at the same temperature and pressure depends inversely on the square root of the molar masses, which differ for these two gases.

23. Effusion time is proportional to the square root of molar mass.

$$\frac{\text{effusion time for NO}}{\text{effusion time for } Cl_2} = \sqrt{\frac{30.01 \text{ g/mol NO}}{70.91 \text{ g/mol } Cl_2}} = 0.6505 = \frac{\text{NO effusion time}}{28.6 \text{ s}}$$

$$\text{NO effusion time} = 0.6505 \times 28.6 \text{ s} = 18.6 \text{ s.}$$

24. The best choice for ideal behavior is (3), 200°C and 0.50 atm. Gases are closest to ideal at high temperatures where the molecules move rapidly, and low pressures where molecules are relatively far apart.

## EXERCISES

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### Pressure and Its Measurement

25. We use:  $h_{\text{benz}} d_{\text{benz}} = h_{\text{Hg}} d_{\text{Hg}}$

$$h_{\text{benz}} = 0.970 \text{ atm} \times \frac{0.760 \text{ m Hg}}{1 \text{ atm}} \times \frac{13.6 \text{ g/cm}^3 \text{ Hg}}{0.879 \text{ g/cm}^3 \text{ benzene}} = 11.4 \text{ m benzene}$$

27. The mercury level difference equals the difference in pressure between the container and the atmosphere. This mercury level difference is

$\Delta P = 276 \text{ mmHg} - 49 \text{ mmHg} = 227 \text{ mmHg}$ . Since the mercury level in the arm open to the atmosphere is higher than in the arm connected to the container, the pressure in the container is higher than atmospheric pressure.

$$P = \Delta P + P_{\text{atm}} = 227 \text{ mmHg} + 749 \text{ mmHg} = 976 \text{ mmHg}$$

29.  $F = m \times g$  and  $1 \text{ atm} = 101325 \text{ Pa} = 101325 \text{ kg m}^{-1} \text{ s}^{-2} = P = \frac{F}{A} = \frac{m \times 9.81 \text{ m s}^{-2}}{1 \text{ m}^2}$

$$\text{mass (per m}^2\text{)} = \frac{101325 \text{ kg m}^{-1} \text{ s}^{-2} \times 1 \text{ m}^2}{9.81 \text{ m s}^{-2}} = 10329 \text{ kg}$$

$$(\text{Note: } 1 \text{ m}^2 = (100 \text{ cm})^2 = 10,000 \text{ cm}^2)$$

$$P (\text{kg cm}^{-2}) = \frac{m}{A} = \frac{10329 \text{ kg}}{10,000 \text{ cm}^2} = 1.03 \text{ kg cm}^{-2}$$

### The Simple Gas Laws

31.  $P_i = P_f \times \frac{V_f}{V_i} = \left( 721 \text{ mmHg} \times \frac{35.8 \text{ L} + 1875 \text{ L}}{35.8 \text{ L}} \right) \times \frac{1 \text{ atm}}{760 \text{ mm H}_2\text{O}} = 50.6 \text{ atm}$

33. Assuming pressure and moles of gas is kept constant, volume is directly proportional to the temperature in kelvins (Charles' Law).

$$1 \text{ }^{\circ}\text{C} \rightarrow 2 \text{ }^{\circ}\text{C} \text{ Volume increase} = \frac{V_f}{V_i} = \frac{T_f}{T_i} = \frac{(2 + 273.15)}{(1 + 273.15)} = 1.00365 \text{ (increase of 0.37 \%)}$$

$$10 \text{ }^{\circ}\text{C} \rightarrow 20 \text{ }^{\circ}\text{C} \text{ Volume increase} = \frac{(20 + 273.15)}{(10 + 273.15)} = 1.035 \text{ (increase of 3.5 \%)}$$

Volume doubles when the temperature in Kelvin doubles (i.e.  $273 \text{ K} \rightarrow 546 \text{ K}$ )

35. (a) mass =  $27.6 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mol}}{22.414 \text{ L STP}} = 0.00123 \text{ mol PH}_3 \times \frac{34.0 \text{ g PH}_3}{1 \text{ mol PH}_3} \times \frac{1000 \text{ mg}}{1 \text{ g}}$   
 $= 41.8 \text{ mg PH}_3$

(b) number of molecules of  $\text{PH}_3 = 0.00123 \text{ mol PH}_3 \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol PH}_3}$   
 number of molecules of  $\text{PH}_3 = 7.41 \times 10^{20} \text{ molecules}$

37. At the higher elevation of the mountains, the atmospheric pressure is lower than at the beach. However, the bag is leak proof; no gas escapes. Thus, the gas inside the bag expands in the lower pressure until the bag is filled to nearly bursting. (It would have been difficult to predict this result. The temperature in the mountains is usually lower than at the beach. The lower temperature would *decrease* the pressure of the gas.)

## General Gas Equation

39. Because the number of moles of gas does not change,  $\frac{P_i \times V_i}{T_i} = nR = \frac{P_f \times V_f}{T_f}$  is obtained from the ideal gas equation. This expression can be rearranged as follows.

$$V_f = \frac{V_i \times P_i \times T_f}{P_f \times T_i} = \frac{4.25 \text{ L} \times 748 \text{ mmHg} \times (273.2 + 26.8) \text{ K}}{742 \text{ mmHg} \times (273.2 + 25.6) \text{ K}} = 4.30 \text{ L}$$

41. Volume and Pressure are constant hence:  $n_i T_i = \frac{P V}{R} = n_f T_f$

$$\frac{n_f}{n_i} = \frac{T_i}{T_f} = \frac{(21 + 273.15)}{(210 + 273.15)} = 0.609 \quad (60.9 \% \text{ of the gas remains})$$

Hence, 39.1% of the gas must be released: Mass of gas released =  $12.5 \text{ g} \times \frac{39.1}{100} = 4.89 \text{ g}$

## Ideal Gas Equation

43.  $P = \frac{nRT}{V} = \frac{\left(35.8 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2}\right) \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times (46 + 273.2) \text{ K}}{12.8 \text{ L}} = 2.29 \text{ atm}$

45.  $T = \frac{PV}{nR} = \frac{3.50 \text{ atm} \times 72.8 \text{ L}}{1.85 \text{ mol} \times 0.08206 \frac{\text{L atm}}{\text{mol K}}} = 1.68 \times 10^3 \text{ K}$

$$t(\text{°C}) = 1.68 \times 10^3 - 273 = 1.41 \times 10^3 \text{ °C}$$

## Determining Molar Mass

- 47.** We first determine the empirical formula of propylene.

$$\text{moles C} = 85.63 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.130 \text{ mol C} \quad \div 7.130 \rightarrow 1.000 \text{ mol C}$$

$$\text{moles H} = 14.37 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 14.26 \text{ mol H} \quad \div 7.130 \rightarrow 2.000 \text{ mol H}$$

The empirical formula is  $\text{CH}_2$  and the empirical molar mass is 14.0 g/mol. The molar mass of propylene is 42.08 g/mol, three times the empirical molar mass. The molecular formula is  $\text{C}_3\text{H}_6$ , three times the empirical formula.

$$\text{49. (a)} \quad M = \frac{mRT}{PV} = \frac{0.231 \text{ g} \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (23 + 273) \text{ K}}{\left(749 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times \left(102 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right)} = 55.8 \text{ g/mol}$$

- (b)** The formula contains 4 atoms of carbon. (5 atoms of carbon gives a molar mass of at least 60-too high-and 3 C atoms gives a molar mass of 36-too low to be made up by adding H's.) To produce a molar mass of 56 with 4 carbons requires the inclusion of 8 atoms of H in the formula of the compound:  $\text{C}_4\text{H}_8$ .

## Gas Densities

$$\text{51. } d = \frac{MP}{RT} \quad \rightarrow \quad P = \frac{dRT}{M} = \frac{1.80 \text{ g/L} \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (32 + 273) \text{ K}}{28.0 \text{ g/mol}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}}$$

$$P = 1.22 \times 10^3 \text{ mmHg}$$

$$\text{53. (a)} \quad d = \frac{MP}{RT} = \frac{28.96 \text{ g/mol} \times 1.00 \text{ atm}}{0.0821 \frac{\text{L atm}}{\text{mol K}} \times (273 + 25) \text{ K}} = 1.18 \text{ g/L air}$$

$$\text{(b)} \quad d = \frac{MP}{RT} = \frac{44.0 \text{ g/mol CO}_2 \times 1.00 \text{ atm}}{0.08206 \frac{\text{L atm}}{\text{mol K}} \times (273 + 25) \text{ K}} = 1.80 \text{ g/L CO}_2$$

Since this density is greater than that of air, the balloon will not rise in air when filled with  $\text{CO}_2$  at  $25^\circ\text{C}$ .

55.  $d = \frac{MP}{RT}$  becomes  $M = \frac{dRT}{P} = \frac{2.64 \text{ g/L} \times 0.0821 \frac{\text{L atm}}{\text{mol K}} \times (310 + 273)\text{K}}{775 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 124 \text{ g/mol}$

Since the atomic mass of phosphorus is 31.0, the formula of phosphorus molecules in the vapor is  $\text{P}_4$ . (4 atoms/molecule  $\times$  31.0 = 124)

## Gases in Chemical Reactions

57. Balanced equation:  $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$

Use the law of combining volumes.  $\text{O}_2$  volume = 75.6 L  $\text{C}_3\text{H}_8 \times \frac{5 \text{ L O}_2}{1 \text{ L C}_3\text{H}_8} = 378 \text{ L O}_2$

59. Determine the moles of  $\text{SO}_2(\text{g})$  produced and then use the ideal gas equation.

$$2.7 \times 10^6 \text{ lb coal} \times \frac{3.28 \text{ lb S}}{100.00 \text{ lb coal}} \times \frac{454 \text{ g S}}{1 \text{ lb S}} \times \frac{1 \text{ mol S}}{32.1 \text{ g S}} \times \frac{1 \text{ mol SO}_2}{1 \text{ mol S}} = 1.3 \times 10^6 \text{ mol SO}_2$$

$$V = \frac{nRT}{P} = \frac{1.3 \times 10^6 \text{ mol SO}_2 \times 0.0821 \frac{\text{L atm}}{\text{mol K}} \times 296 \text{ K}}{738 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.3 \times 10^7 \text{ L SO}_2$$

61. Determine the moles and volume of  $\text{O}_2$  liberated.  $2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

$$\begin{aligned} \text{mol O}_2 &= 10.0 \text{ mL soln} \times \frac{1.01 \text{ g}}{1 \text{ mL}} \times \frac{0.0300 \text{ g H}_2\text{O}_2}{1 \text{ g soln}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.0 \text{ g H}_2\text{O}_2} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}_2} \\ &= 0.00446 \text{ mol O}_2 \end{aligned}$$

$$V = \frac{0.00446 \text{ mol O}_2 \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (22 + 273) \text{ K}}{752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 109 \text{ mL O}_2$$

## Mixtures of Gases

63. The two pressures are related as are the number of moles of  $\text{N}_2(\text{g})$  to the total number of moles.

$$\text{moles N}_2 = \frac{PV}{RT} = \frac{28.2 \text{ atm} \times 53.7 \text{ L}}{0.08206 \frac{\text{L atm}}{\text{mol K}} \times (26 + 273) \text{ K}} = 61.7 \text{ mol N}_2$$

$$\text{total moles of gas} = 61.7 \text{ mol N}_2 \times \frac{75.0 \text{ atm}}{28.2 \text{ atm}} = 164 \text{ mol gas}$$

$$\text{mass Ne} = (164 \text{ mol total} - 61.7 \text{ mol N}_2) \times \frac{20.18 \text{ g Ne}}{1 \text{ mol Ne}} = 2.06 \times 10^3 \text{ g Ne}$$

**65.** Initial Pressure of the cylinder

$$P = \frac{nRT}{V} = \frac{(1.60 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{31.998 \text{ g O}_2})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{2.24 \text{ L}} = 0.500 \text{ atm}$$

We need to quadruple the pressure from 0.500 atm to 2.00 atm.

The mass of O<sub>2</sub> needs to quadruple. 1.60 g → 6.40 g or add 4.80 g O<sub>2</sub>

(this answer eliminates answer (a) and (b) as being correct)

Could also increase the pressure by adding the same number of another gas (e.g. He)  
 Mass of He = n<sub>He</sub> × M<sub>He</sub>

$$(\text{note: moles of O}_2 \text{ needed} = 4.80 \text{ g} \times \frac{1 \text{ mol O}_2}{31.998 \text{ g O}_2} = 0.150 \text{ moles} = 0.150 \text{ moles of He})$$

$$\text{Mass of He} = 0.150 \text{ moles} \times \frac{4.0026 \text{ g He}}{1 \text{ mol He}} = 0.600 \text{ g He} \text{ ((d) is correct, add 0.600 g of He)}$$

$$67. \text{ (a)} \quad P_{\text{ben}} = \frac{nRT}{V} = \frac{\left(0.728 \text{ g} \times \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6}\right) \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times (35 + 273)}{2.00 \text{ L}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 89.5 \text{ mmHg}.$$

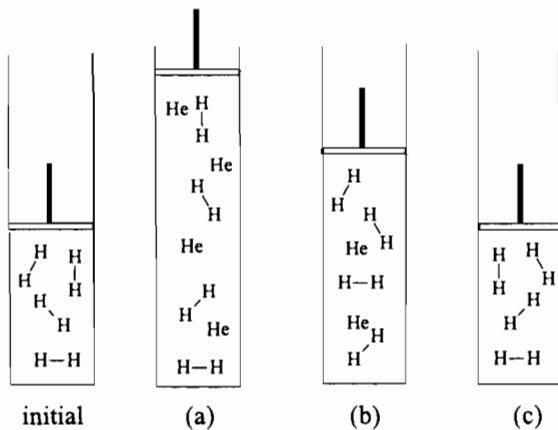
$$P_{\text{total}} = 89.5 \text{ mmHg C}_6\text{H}_6(\text{g}) + 752 \text{ mmHg Ar(g)} = 842 \text{ mmHg}$$

$$\text{(b)} \quad P_{\text{benzene}} = 89.5 \text{ mmHg} \quad P_{\text{Ar}} = 752 \text{ mmHg}$$

$$69. \quad 1.00 \text{ g H}_2 \approx 0.50 \text{ mol H}_2 \quad 1.00 \text{ g He} \approx 0.25 \text{ mol He}$$

Adding 1.00 g of He to a vessel, which only contains 1.00 g of H<sub>2</sub> results in the number of moles of gas being increased by 50%. Situation (b) best represents the resulting mixture as the volume has increased by 50%

70.



## Collecting Gases over Liquids

71. The pressure of the liberated  $\text{H}_2(\text{g})$  is  $744 \text{ mmHg} - 23.8 \text{ mmHg} = 720. \text{ mmHg}$

$$V = \frac{nRT}{P} = \frac{\left(1.65 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Al}}\right) 0.08206 \frac{\text{L atm}}{\text{mol K}} (273 + 25) \text{ K}}{720. \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 2.37 \text{ L H}_2(\text{g})$$

This is the total volume of both gases, each with a different partial pressure.

73. We first determine the pressure of the gas collected. This would be its "dry gas" pressure and, when added to 22.4 mmHg, gives the barometric pressure.

$$P = \frac{nRT}{V} = \frac{\left(1.46 \text{ g} \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2}\right) 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 297 \text{ K}}{1.16 \text{ L}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 729 \text{ mmHg}$$

$$\text{barometric pressure} = 729 \text{ mm Hg} + 22.4 \text{ mmHg} = 751 \text{ mmHg}$$

## Kinetic Molecular Theory

$$\underline{75.} \quad u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3145 \frac{\text{J}}{\text{mol K}} \times 303 \text{ K}}{\frac{70.91 \times 10^{-3} \text{ kg Cl}_2}{1 \text{ mol Cl}_2}}} = 326 \text{ m/s}$$

$$77. M = \frac{3RT}{(u_{\text{rms}})^2} = \frac{3 \times 8.3145 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K}}{\left( 2180 \frac{\text{mi}}{\text{hr}} \times \frac{1 \text{ hr}}{3600 \text{ sec}} \times \frac{5280 \text{ ft}}{1 \text{ mi}} \times \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{1 \text{ m}}{39.37 \text{ in.}} \right)^2} = 0.00783 \text{ kg/mol}$$

$= 7.83 \text{ g/mol. The molecular mass of the gas is } 7.83 \text{ u.}$

79. We equate the two expressions for root mean square speed, cancel the common factors, and solve for the temperature of Ne. Note that the units of molar masses do not have to be in kg/mol in this calculation; they simply must be expressed in the same units.

$$\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R \times 300 \text{ K}}{4.003}} = \sqrt{\frac{3R \times T_{\text{Ne}}}{20.18}} \quad \text{square both sides: } \frac{300 \text{ K}}{4.003} = \frac{T_{\text{Ne}}}{20.18}$$

$$\text{Solve for } T_{\text{Ne}}: T_{\text{Ne}} = 300 \text{ K} \times \frac{20.18}{4.003} = 1.51 \times 10^3 \text{ K}$$

## Diffusion and Effusion of Gases

$$81. \frac{\text{rate (NO}_2\text{)}}{\text{rate (N}_2\text{O)}} = \sqrt{\frac{M(\text{N}_2\text{O})}{M(\text{NO}_2)}} = \sqrt{\frac{44.02}{46.01}} = 0.9781 = \frac{x \text{ mol NO}_2/t}{0.00484 \text{ mol N}_2\text{O}/t}$$

$$\text{mol NO}_2 = 0.00484 \text{ mol} \times 0.9781 = 0.00473 \text{ mol NO}_2$$

$$83. \text{(a)} \quad \frac{\text{rate (N}_2\text{)}}{\text{rate (O}_2\text{)}} = \sqrt{\frac{M(\text{O}_2)}{M(\text{N}_2)}} = \sqrt{\frac{32.00}{28.01}} = 1.07$$

$$\text{(b)} \quad \frac{\text{rate (H}_2\text{O)}}{\text{rate (D}_2\text{O)}} = \sqrt{\frac{M(\text{D}_2\text{O})}{M(\text{H}_2\text{O})}} = \sqrt{\frac{20.0}{18.02}} = 1.05$$

$$\text{(c)} \quad \frac{\text{rate (}^{14}\text{CO}_2\text{)}}{\text{rate (}^{12}\text{CO}_2\text{)}} = \sqrt{\frac{M(\text{}^{12}\text{CO}_2)}{M(\text{}^{14}\text{CO}_2)}} = \sqrt{\frac{44.0}{46.0}} = 0.978$$

$$\text{(d)} \quad \frac{\text{rate (}^{235}\text{UF}_6\text{)}}{\text{rate (}^{238}\text{UF}_6\text{)}} = \sqrt{\frac{M(\text{}^{238}\text{UF}_6)}{M(\text{}^{235}\text{UF}_6)}} = \sqrt{\frac{352}{349}} = 1.004$$

## Nonideal Gases

$$85. \text{ For Cl}_2(\text{g}), n^2a = 6.49 \text{ L}^2 \text{ atm and } nb = 0.0562 \text{ L. } P_{\text{vdw}} = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

At 0°C,  $P_{\text{vdw}} = 9.90 \text{ atm}$  and  $P_{\text{ideal}} = 11.2 \text{ atm}$ , off by 1.3 atm or + 13%

$$(a) \text{ At } 100^\circ\text{C } P_{\text{ideal}} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 373 \text{ K}}{2.00 \text{ L}} = 15.3 \text{ atm}$$

$$P_{\text{vdw}} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times T}{(2.00 - 0.0562) \text{ L}} - \frac{6.49 \text{ L}^2 \text{ atm}}{(2.00 \text{ L})^2} = 0.0422 T \text{ atm} - 1.62 \text{ atm}$$

$$= 0.0422 \times 373 \text{ K} - 1.62 = 14.1 \text{ atm} \quad P_{\text{ideal}} \text{ is off by } 1.2 \text{ atm or } +8.5\%$$

$$(b) \text{ At } 200^\circ\text{C } P_{\text{ideal}} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 473 \text{ K}}{2.00 \text{ L}} = 19.4 \text{ atm}$$

$$P_{\text{vdw}} = 0.0422 \times 473 \text{ K} - 1.62 = 18.3 \text{ atm} \quad P_{\text{ideal}} \text{ is off by } 1.0 \text{ atm or } +5.7\%$$

$$(c) \text{ At } 400^\circ\text{C } P_{\text{ideal}} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 673 \text{ K}}{2.00 \text{ L}} = 27.6 \text{ atm}$$

$$P_{\text{vdw}} = 0.0422 \times 673 \text{ K} - 1.62 = 26.8 \text{ atm} \quad P_{\text{ideal}} \text{ is off by } 0.8 \text{ atm or } +3.0\%$$

## FEATURE PROBLEMS

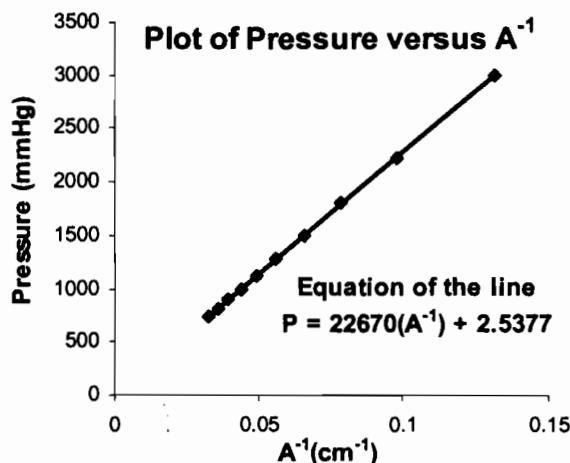
110. Boyle's Law relates  $P$  and  $V$ , i.e.  $P \times V = \text{constant}$ . If  $V$  is proportional to the value of A, and  $P_{\text{gas}} = P_{\text{bar}} + P_{\text{Hg}}$  (i.e. the pressure of the gas equals the sum of the barometric pressure and the pressure exerted by the mercury column), then a comparison of individual  $A \times P$  products should show a consistent result or a constant.

A (cm)	P <sub>bar</sub> (atm)	P <sub>Hg</sub> (mmHg)	P <sub>gas</sub> (mmHg)	A × P <sub>gas</sub> (cm × mmHg)
27.9	739.8	71	810.8	22621
30.5	739.8	0	739.8	22564
25.4	739.8	157	896.8	22779
22.9	739.8	257	996.8	22827
20.3	739.8	383	1123	22793
17.8	739.8	538	1278	22745
15.2	739.8	754	1494	22706
12.7	739.8	1056	1796	22807
10.2	739.8	1476	2216	22601
7.6	739.8	2246	2986	22692

Since consistent  $A \times P_{\text{gas}}$  results are observed, that these data conform reasonably well (within experimental uncertainty) to Boyle's Law.

111.

$P_{\text{gas}}$ (mmHg)	$1/A \propto 1/V$ (cm <sup>-1</sup> )
810.8	0.0358
739.8	0.0328
896.8	0.0394
996.8	0.0437
1123	0.0493
1278	0.0562
1494	0.0658
1796	0.0787
2216	0.0980
2986	0.1316



Plot: slope = constant from Feature Problem 110

Factors that would affect the slope of this straight line are related to deviations real gases exhibit from ideality. At higher pressures, real gases tend to interact more, exerting forces of attraction and repulsion that Boyle's Law does not take into account.

112. Nitryl Fluoride  $65.01 \text{ u} \left( \frac{49.4}{100} \right) = 32.1 \text{ u of X}$

Nitrosyl Fluoride  $49.01 \text{ u} \left( \frac{32.7}{100} \right) = 16.0 \text{ u of X}$

Thionyl Fluoride  $86.07 \text{ u} \left( \frac{18.6}{100} \right) = 16.0 \text{ u of X}$

Sulfuryl Fluoride  $102.07 \text{ u} \left( \frac{31.4}{100} \right) = 32.0 \text{ u of X}$

The atomic mass of X is 16 u which corresponds to the element oxygen. The number of atoms of X (oxygen) in each compound is given below:

Nitryl Fluoride = 2 atoms of O

Nitrosyl Fluoride = 1 atom of O

Thionyl Fluoride = 1 atom of O

Sulfuryl Fluoride = 2 atoms of O

113. (a) First convert pressures from mmHg to atm:

density (g/L)	pressure (atm)	density/pressure (g/L·atm)
1.428962	1.0000	1.428962 $\cong$ 1.4290
1.071485	0.75000	1.428647 $\cong$ 1.4286
0.714154	0.50000	1.428308 $\cong$ 1.4283
0.356985	0.25000	1.42794 $\cong$ 1.4279
average =		1.4285 g/L·atm

$$(b) M_{O_2} = \frac{d}{P} RT$$

$$M_{O_2} = 1.4285 \text{ g/L} \cdot \text{atm} \times 0.082057 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times 273.15 \text{ K}$$

$$M_{O_2} = 32.0182 \text{ g/mol}$$

Thus, the atomic mass of O<sub>2</sub> = M<sub>O<sub>2</sub></sub> / 2 = 16.0009.

This compares favorably with the value of 15.9994 given in the front of the text.

# CHAPTER 7

## THERMOCHEMISTRY

### PRACTICE EXAMPLES

- 1A** The heat absorbed is the product of the mass of water, its specific heat ( $4.18 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ), and the temperature change that occurs.

$$\text{heat energy} = 237 \text{ g} \times \frac{4.18 \text{ J}}{\text{g }^{\circ}\text{C}} \times (37.0 \text{ }^{\circ}\text{C} - 4.0 \text{ }^{\circ}\text{C}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 32.7 \text{ kJ of heat energy}$$

- 1B** The heat absorbed is the product of the amount of mercury, its molar heat capacity, and the temperature change that occurs.

$$\begin{aligned} \text{heat energy} &= \left( 2.50 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Hg}}{200.59 \text{ g Hg}} \right) \times \frac{28.0 \text{ J}}{\text{mol }^{\circ}\text{C}} \times [-6.0 - (-20.0)] \text{ }^{\circ}\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 4.89 \text{ kJ of heat energy} \end{aligned}$$

- 2A** First calculate the quantity of heat lost by the lead. This heat energy must be absorbed by the surroundings (water). We assume 100% efficiency in the energy transfer.

$$q_{\text{lead}} = 1.00 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{0.13 \text{ J}}{\text{g }^{\circ}\text{C}} \times (35.2 \text{ }^{\circ}\text{C} - 100.0 \text{ }^{\circ}\text{C}) = -8.4 \times 10^3 \text{ J} = -q_{\text{water}}$$

$$8.4 \times 10^3 \text{ J} = m_{\text{water}} \times \frac{4.18 \text{ J}}{\text{g }^{\circ}\text{C}} \times (35.2 \text{ }^{\circ}\text{C} - 28.5 \text{ }^{\circ}\text{C}) = 28m_{\text{water}} \quad m_{\text{water}} = \frac{8.4 \times 10^3}{28} = 3.0 \times 10^2 \text{ g}$$

- 2B** We use the same equation, equating the heat lost by the copper to the heat absorbed by the water, except now we solve for final temperature.

$$q_{\text{Cu}} = 100.0 \text{ g} \times \frac{0.385 \text{ J}}{\text{g }^{\circ}\text{C}} \times (x \text{ }^{\circ}\text{C} - 100.0 \text{ }^{\circ}\text{C}) = -50.0 \text{ g} \times \frac{4.18 \text{ J}}{\text{g }^{\circ}\text{C}} \times (x \text{ }^{\circ}\text{C} - 26.5 \text{ }^{\circ}\text{C}) = -q_{\text{water}}$$

$$38.5x - 3850 = -209x + 5539 \text{ J} \quad 38.5x + 209x = 5539 + 3850 \rightarrow 247.5x = 9389$$

$$x = \frac{9389}{247.5} = 37.9 \text{ }^{\circ}\text{C}$$

- 3A** The molar mass of  $\text{C}_8\text{H}_8\text{O}_3$  is 152.15 g/mol. The calorimeter has a heat capacity of  $4.90 \text{ kJ }^{\circ}\text{C}^{-1}$

$$q_{\text{calor}} = \frac{4.90 \text{ kJ }^{\circ}\text{C}^{-1} \times (30.09 \text{ }^{\circ}\text{C} - 24.89 \text{ }^{\circ}\text{C})}{1.013 \text{ g}} \times \frac{152.15 \text{ g}}{1 \text{ mol}} = 3.83 \times 10^3 \text{ kJ/mol}$$

$$\Delta H_{\text{comb}} = -q_{\text{calor}} = -3.83 \times 10^3 \text{ kJ/mol}$$

- 3B** The heat that is liberated by the benzoic acid's combustion serves to raise the temperature of the assembly. We designate the calorimeter's heat capacity by  $C$ .

$$q_{rxn} = 1.176 \text{ g} \times \frac{-26.42 \text{ kJ}}{1 \text{ g}} = -31.07 \text{ kJ} = -q_{calorim}$$

$$q_{calorim} = C\Delta t = 31.07 \text{ kJ} = C \times 4.96^\circ\text{C} \quad C = \frac{31.07 \text{ kJ}}{4.96^\circ\text{C}} = 6.26 \text{ kJ} / {}^\circ\text{C}$$

- 4A** The heat that is liberated by the reaction raises the temperature of the reaction mixture. We assume that this reaction mixture has the same density and specific heat as pure water.

$$q_{calorim} = \left( 200.0 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \right) \times \frac{4.18 \text{ J}}{\text{g} {}^\circ\text{C}} \times (30.2 - 22.4) {}^\circ\text{C} = 6.52 \times 10^3 \text{ J} = -q_{rxn}$$

$$\text{moles AgCl} = 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.00 \text{ M AgNO}_3}{1 \text{ L}} \times \frac{1 \text{ mol AgCl}}{1 \text{ mol AgNO}_3} = 0.100 \text{ mol AgCl}$$

$$q_{rxn} = \frac{-6.52 \times 10^3 \text{ J}}{0.100 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -65.2 \text{ kJ/mol}$$

Because  $q_{rxn}$  is a negative quantity, the precipitation reaction is exothermic.

- 4B** The assumptions include no heat loss to the surroundings or to the calorimeter, a solution density of 1.00 g/mL, a specific heat of  $4.18 \text{ J g}^{-1} {}^\circ\text{C}^{-1}$ , and that the initial and final solution volumes are the same. The equation for the reaction that occurs is  $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$ . Since the two reactants combine in a one to one mole ratio, the limiting reactant is the one present in smaller amount.

$$\text{amount HCl} = 100.0 \text{ mL} \times \frac{1.020 \text{ mmol HCl}}{1 \text{ mL soln}} = 102.0 \text{ mmol HCl}$$

$$\text{amount NaOH} = 50.0 \text{ mL} \times \frac{1.988 \text{ mmol NaOH}}{1 \text{ mL soln}} = 99.4 \text{ mmol NaOH}$$

NaOH is the limiting reactant.

$$q_{neutr} = 99.4 \text{ mmol NaOH} \times \frac{1 \text{ mmol H}_2\text{O}}{1 \text{ mmol NaOH}} \times \frac{1 \text{ mol H}_2\text{O}}{1000 \text{ mmol H}_2\text{O}} \times \frac{-56 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = -5.5_7 \text{ kJ}$$

$$q_{calorim} = -q_{neutr} = 5.5_7 \text{ kJ} = (100.0 + 50.0) \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{4.18 \text{ J}}{\text{g} {}^\circ\text{C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times (t - 24.52^\circ\text{C})$$

$$= 0.627t - 15.3_7 \quad t = \frac{5.5_7 + 15.3_7}{0.627} = 33.4^\circ\text{C}$$

$$5A \quad w = -P\Delta V = -0.750 \text{ atm} (+1.50 \text{ L}) = -1.13 \text{ L atm} \times \frac{101.33 \text{ J}}{1 \text{ L atm}} = -114 \text{ J}$$

114 J of work is done by system

**5B** Determine the initial number of moles:

$$n = 50.0 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.014 \text{ g N}_2} = 1.785 \text{ moles of N}_2$$

$$V = \frac{nRT}{P} = \frac{(1.785 \text{ mol N}_2)(0.08206 \text{ Latm K}^{-1}\text{mol}^{-1})(293.15 \text{ K})}{2.50 \text{ atm}} = 17.2 \text{ L}$$

$$\Delta V = 17.2 - 75.0 \text{ L} = -57.8 \text{ L}$$

$$w = -P\Delta V = -2.50 \text{ atm}(-57.8 \text{ L}) \times \frac{101.33 \text{ J}}{1 \text{ L atm}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = +14.6 \text{ kJ work done on system.}$$

**6A** The work is  $w = +355 \text{ J}$ . The heat flow is  $q = -185 \text{ J}$ . These two are related to the energy change of the system by the first law equation:  $\Delta U = q + w$ , which becomes

$$\Delta U = +355 \text{ J} - 185 \text{ J} = +1.70 \times 10^2 \text{ J}$$

**6B** The internal energy change is  $\Delta U = -125 \text{ J}$ . The heat flow is  $q = +54 \text{ J}$ . These two are related to the work done on the system by the first law equation:  $\Delta U = q + w$ , which becomes  $-125 \text{ J} = +54 \text{ J} + w$ . The solution to this equation is  $w = -125 \text{ J} - 54 \text{ J} = -179 \text{ J}$ , which means that 179 J of work is done by the system.

**7A** Heat that is given off has a negative sign. In addition, we use the molar mass of sucrose, 342.30 g/mol.

$$\text{sucrose mass} = -1.00 \times 10^3 \text{ kJ} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{-5.65 \times 10^3 \text{ kJ}} \times \frac{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} = 60.6 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}$$

**7B** Although the equation does not say so explicitly, 56 kJ of heat is given off per mole of water formed. The equation then is the source of a conversion factor.

$$\text{heat flow} = 25.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1045 \text{ mol HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}} \times \frac{56 \text{ kJ evolved}}{1 \text{ mol H}_2\text{O}}$$

$$\text{heat flow} = 0.15 \text{ kJ heat evolved}$$

**8A**  $V_{ice} = (2.00 \text{ cm})^3 = 8.00 \text{ cm}^3$

$$m_{ice} = m_{water} = 8.00 \text{ cm}^3 \times 0.917 \text{ g cm}^{-3} = 7.34 \text{ g ice} = 7.34 \text{ g H}_2\text{O}$$

$$\text{moles of ice} = 7.34 \text{ g ice} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 0.407 \text{ moles of ice}$$

$$q_{overall} = q_{ice}(-10 \text{ to } 0 \text{ }^\circ\text{C}) + q_{fus} + q_{water}(0 \text{ to } 23.2 \text{ }^\circ\text{C})$$

$$q_{overall} = m_{ice}(\text{sp. ht.})_{ice}\Delta T + n_{ice}\Delta H_{fus} + m_{water}(\text{sp. ht.})_{water}\Delta T$$

$$q_{overall} = 7.34 \text{ g}(10.0 \text{ }^\circ\text{C})(2.01 \frac{\text{J}}{\text{g }^\circ\text{C}}) + 0.407 \text{ mol ice}(6.01 \frac{\text{kJ}}{\text{mol}}) + 7.34 \text{ g}(23.2 \text{ }^\circ\text{C})(4.184 \frac{\text{J}}{\text{g }^\circ\text{C}})$$

$$q_{overall} = 0.148 \text{ kJ} + 2.45 \text{ kJ} + 0.712 \text{ kJ}$$

$$q_{overall} = 3.31 \text{ kJ (absorbs)}$$

**8B**  $5.00 \times 10^3 \text{ kJ} = q_{\text{ice}}(-15 \text{ to } 0 \text{ }^\circ\text{C}) + q_{\text{fus}} + q_{\text{water}}(0 \text{ to } 25 \text{ }^\circ\text{C}) + q_{\text{vap}}$

$$5.00 \times 10^3 \text{ kJ} = m_{\text{ice}}(\text{sp. ht.})_{\text{ice}} \Delta T + n_{\text{ice}} \Delta H_{\text{fus}} + m_{\text{water}}(\text{sp. ht.})_{\text{water}} \Delta T + n_{\text{water}} \Delta H_{\text{vap}}$$

$$5.00 \times 10^6 \text{ J} = m(15.0 \text{ }^\circ\text{C})(2.01 \frac{\text{J}}{\text{g }^\circ\text{C}}) + \left( \frac{m}{18.015 \text{ g H}_2\text{O/mol H}_2\text{O}} \times 6.01 \times 10^3 \frac{\text{J}}{\text{mol}} \right)$$

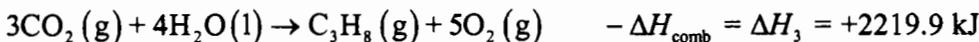
$$+ m(25.0 \text{ }^\circ\text{C})(4.184 \frac{\text{J}}{\text{g }^\circ\text{C}}) + \left( \frac{m}{18.015 \text{ g H}_2\text{O/mol}} (44.0 \times 10^3 \frac{\text{J}}{\text{mol}}) \right)$$

$$5.00 \times 10^6 \text{ J} = m(30.15 \text{ J/g}) + m(333.6 \text{ J/g}) + m(104.5 \text{ J/g}) + m(2.44 \times 10^3 \text{ J/g})$$

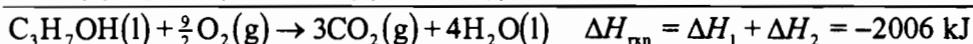
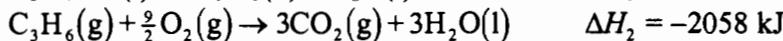
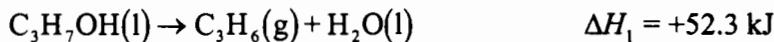
$$5.00 \times 10^6 \text{ J} = m(2.91 \times 10^3 \text{ J/g})$$

$$m = \frac{5.00 \times 10^6 \text{ J}}{2.91 \times 10^3 \text{ J/g}} = 1718 \text{ g or } 1.72 \text{ kg H}_2\text{O}$$

**9A** We combine the three combustion reactions to produce the hydrogenation reaction.

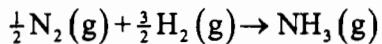


**9B** The combustion reaction has propanol and  $\text{O}_{2(\text{g})}$  as reactants; the products are  $\text{CO}_{2(\text{g})}$  and  $\text{H}_2\text{O}(\text{l})$ . Reverse the reaction given and combine it with the combustion reaction of  $\text{C}_3\text{H}_6(\text{g})$ .



**10A** The enthalpy of formation is the enthalpy change for the reaction in which one mole of the product,  $\text{C}_6\text{H}_{13}\text{O}_2\text{N}(\text{s})$ , is produced from appropriate amounts of the most stable forms of the elements.  $6 \text{ C(graphite)} + \frac{13}{2}\text{H}_2(\text{g}) + \text{O}_2(\text{g}) + \frac{1}{2}\text{N}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{13}\text{O}_2\text{N}(\text{s})$

**10B** The enthalpy of formation is the enthalpy change for the reaction in which one mole of the product,  $\text{NH}_3(\text{g})$ , is produced from appropriate amounts of the most stable forms of the elements, in this case from 0.5 mol  $\text{N}_2(\text{g})$  and 1.5 mol  $\text{H}_2(\text{g})$ , that is, for the reaction:

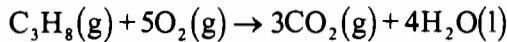


The specified reaction is twice the reverse of the formation reaction, and its enthalpy change is twice negative of the enthalpy of formation of  $\text{NH}_3(\text{g})$ :

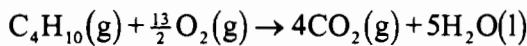
$$-2 \times (-46.11 \text{ kJ}) = +92.22 \text{ kJ}$$

**11A**  $\Delta H_{rxn}^{\circ} = 2 \times \Delta H_f^{\circ} [\text{CO}_2(\text{g})] + 3 \times \Delta H_f^{\circ} [\text{H}_2\text{O}(\text{l})] - \Delta H_f^{\circ} [\text{CH}_3\text{CH}_2\text{OH}(\text{l})] - 3 \times \Delta H_f^{\circ} [\text{O}_2(\text{g})]$   
 $= [2 \times (-393.5 \text{ kJ})] + [3 \times (-285.8 \text{ kJ})] - [-277.7 \text{ kJ}] - [3 \times 0.00 \text{ kJ}] = -1367 \text{ kJ}$

**11B** We write the combustion reaction for each compound, and use that reaction to determine the compound's heat of combustion.



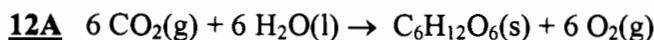
$$\begin{aligned}\Delta H_{\text{combustion}}^{\circ} &= 3 \times \Delta H_f^{\circ} [\text{CO}_2(\text{g})] + 4 \times \Delta H_f^{\circ} [\text{H}_2\text{O}(\text{l})] - \Delta H_f^{\circ} [\text{C}_3\text{H}_8(\text{g})] - 5 \times \Delta H_f^{\circ} [\text{O}_2(\text{g})] \\ &= [3 \times (-393.5 \text{ kJ})] + [4 \times (-285.8 \text{ kJ})] - [-103.8] - [5 \times 0.00 \text{ kJ}] \\ &= -1181 \text{ kJ} - 1143 \text{ kJ} + 103.8 - 0.00 = -2220. \text{ kJ/mol C}_3\text{H}_8\end{aligned}$$



$$\begin{aligned}\Delta H_{\text{combustion}}^{\circ} &= 4 \times \Delta H_f^{\circ} [\text{CO}_2(\text{g})] + 5 \times \Delta H_f^{\circ} [\text{H}_2\text{O}(\text{l})] - \Delta H_f^{\circ} [\text{C}_4\text{H}_{10}(\text{g})] - 6.5 \times \Delta H_f^{\circ} [\text{O}_2(\text{g})] \\ &= [4 \times (-393.5 \text{ kJ})] + [5 \times (-285.8 \text{ kJ})] - [-125.6] - [6.5 \times 0.00 \text{ kJ}] \\ &= -1574 \text{ kJ} - 1429 \text{ kJ} + 125.6 - 0.00 = -2877 \text{ kJ/mol C}_4\text{H}_{10}\end{aligned}$$

In 1.00 mole of the mixture there are 0.62 mol  $\text{C}_3\text{H}_8(\text{g})$  and 0.38 mol  $\text{C}_4\text{H}_{10}(\text{g})$ .

$$\begin{aligned}\text{heat of combustion} &= \left( 0.62 \text{ mol C}_3\text{H}_8 \times \frac{-2220. \text{ kJ}}{1 \text{ mol C}_3\text{H}_8} \right) + \left( 0.38 \text{ mol C}_4\text{H}_{10} \times \frac{-2877 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} \right) \\ &= -1.4 \times 10^3 \text{ kJ} - 1.1 \times 10^3 \text{ kJ} = -2.5 \times 10^3 \text{ kJ/mole of mixture}\end{aligned}$$



$$\Delta H_{rxn}^{\circ} = 2803 \text{ kJ} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants}$$

$$2803 \text{ kJ} = [1 \text{ mol}(\Delta H_f^{\circ} [\text{C}_6\text{H}_{12}\text{O}_6(\text{s})]) + 6 \text{ mol}(0 \frac{\text{kJ}}{\text{mol}})] - [6 \text{ mol}(-393.5 \frac{\text{kJ}}{\text{mol}}) + 6 \text{ mol}(-285.8 \frac{\text{kJ}}{\text{mol}})]$$

$$2803 \text{ kJ} = \Delta H_f^{\circ} [\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] - [-4075.8 \text{ kJ}]. \text{ Thus, } \Delta H_f^{\circ} [\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] = -1273 \text{ kJ}$$

**12B**  $\Delta H_{\text{comb}}^{\circ} [\text{CH}_3\text{OCH}_3(\text{l})] = -31.70 \frac{\text{kJ}}{\text{g}} \quad \text{Molar Mass}_{\text{CH}_3\text{OCH}_3} = 46.069 \text{ g mol}^{-1}$

$$\Delta H_{\text{comb}}^{\circ} [\text{CH}_3\text{OCH}_3(\text{l})] = -31.70 \frac{\text{kJ}}{\text{g}} \times 46.069 \frac{\text{g}}{\text{mol}} = -1460 \frac{\text{kJ}}{\text{mol}} \text{ kJ} = \Delta H_{rxn}^{\circ}$$

$$\Delta H_{rxn}^{\circ} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants} \quad \text{Reaction: } \text{CH}_3\text{OCH}_3(\text{l}) + 3 \text{ O}_2(\text{g}) \rightarrow 2 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O}(\text{l})$$

$$-1460 \text{ kJ} = [2 \text{ mol}(-393.5 \frac{\text{kJ}}{\text{mol}}) + 3 \text{ mol}(-285.8 \frac{\text{kJ}}{\text{mol}})] - [1 \text{ mol}(\Delta H_f^{\circ} [\text{CH}_3\text{OCH}_3(\text{l})]) + 3 \text{ mol}(0 \frac{\text{kJ}}{\text{mol}})]$$

$$-1460 \text{ kJ} = -1644.4 \text{ kJ} - \Delta H_f^{\circ} [\text{CH}_3\text{OCH}_3(\text{l})] \quad \text{Hence, } \Delta H_f^{\circ} [\text{CH}_3\text{OCH}_3(\text{l})] = -184 \text{ kJ}$$

**13A** The net ionic equation is:  $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$  and we have the following:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \Delta H_f^{\circ}[\text{AgI}(\text{s})] - \Delta H_f^{\circ}[\text{Ag}^+(\text{aq})] - \Delta H_f^{\circ}[\text{I}^-(\text{aq})] \\ &= -61.84 \text{ kJ/mol} - (+105.6 \text{ kJ/mol}) - (-55.19 \text{ kJ/mol}) = -112.3 \text{ kJ/mol}\end{aligned}$$

**13B**  $2 \text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CO}_3(\text{s})$

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= -39.9 \text{ kJ} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants} = \\ -39.9 \text{ kJ} &= \Delta H_f^{\circ}[\text{Ag}_2\text{CO}_3(\text{s})] - [2 \text{ mol}(105.6 \frac{\text{kJ}}{\text{mol}}) + 1 \text{ mol}(-677.1 \frac{\text{kJ}}{\text{mol}})] \\ -39.9 \text{ kJ} &= \Delta H_f^{\circ}[\text{Ag}_2\text{CO}_3(\text{s})] + 465.9 \text{ kJ} \quad \text{Hence, } \Delta H_f^{\circ}[\text{Ag}_2\text{CO}_3(\text{s})] = -505.8 \text{ kJ/mol}\end{aligned}$$

## REVIEW QUESTIONS

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- $\Delta H$ , the enthalpy change, is the quantity of heat absorbed or released when a process occurs at constant pressure.
  - $P\Delta V$ , the change in volume multiplied by a constant pressure, is the expression for the pressure-volume work in a process that occurs at constant pressure.
  - $\Delta H_f^{\circ}$ , the standard enthalpy of formation, is the heat absorbed or released at constant pressure when 1 mole of product is formed from the most stable form of the elements, with reactants and products in their standard states.
  - Standard state is defined as a pressure of exactly 1 bar for a pure substance, or an aqueous solute at a 1 M concentration, each at a temperature of interest.
  - A fossil fuel is a material that can be burned for heat and that was produced by material that lived eons ago.
- The law of conservation of energy states that energy is neither created nor destroyed during a process.
  - Bomb calorimetry is the technique of running a chemical reaction in a constant-volume container and measuring the heat absorbed or released by the process.
  - A function of state is a measurable property that depends only on the initial and final conditions of a process and not on its path.
  - An enthalpy diagram represents the enthalpy values of reactants and products by their vertical positions, and the progress of the reaction horizontally.
  - Hess's law states that if several reactions can be combined to form a net reaction, the enthalpy changes for those reactions combine in the same way to produce the enthalpy change of the net reaction.

3. (a) The system is that part of the universe that we are considering, in which we are interested. The surroundings are the rest of the universe, particularly the rest that influences the system.
- (b) Heat is energy in transport that is associated with either a difference in temperature (i.e. sensible heat) or a phase change (such as solid to liquid) of a material (i.e. latent heat). Work is organized energy that has the ability to exert a force through a distance.
- (c) The specific heat of a substance is the quantity of heat needed to raise the temperature of one *gram* of that substance by  $1.00^{\circ}\text{C}$ . The (molar) heat capacity of a substance is the quantity of heat needed to raise the temperature (of one *mole*) of that substance by  $1.00^{\circ}\text{C}$ .
- (d) An endothermic reaction is one that absorbs heat from the surroundings. An exothermic reaction is one that evolves heat to the surroundings.
- (e) A constant-volume process takes place in a sealed container with rigid walls where the volume does not change (i.e. a reaction in a bomb calorimeter). A constant-pressure process takes place under a constant external pressure (i.e. an open container or a chamber with a flexible wall or movable piston)

4. (a)  $q = 9.25 \text{ L} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times \frac{1.00 \text{ g}}{1 \text{ cm}^3} \times \frac{1.00 \text{ cal}}{1 \text{ g}^{\circ}\text{C}} \times (29.4^{\circ}\text{C} - 22.0^{\circ}\text{C}) \times \frac{1 \text{ kcal}}{1000 \text{ cal}} = +68.5 \text{ kcal}$

(b)  $q = 5.85 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{0.903 \text{ J}}{\text{g}^{\circ}\text{C}} \times (-33.5^{\circ}\text{C}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -177 \text{ kJ}$

5.  $\text{heat} = \text{mass} \times \text{sp ht} \times \Delta T$  becomes  $\Delta T = \frac{\text{heat}}{\text{mass} \times \text{sp. ht.}}$

(a)  $\Delta T = \frac{+875 \text{ J}}{12.6 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}} = +16.6^{\circ}\text{C}$

$$T_f = T_i + \Delta T = 22.9^{\circ}\text{C} + 16.6^{\circ}\text{C} = 39.5^{\circ}\text{C}$$

(b)  $\Delta T = \frac{-1.05 \text{ kcal} \times \frac{1000 \text{ cal}}{1 \text{ kcal}}}{\left(1.59 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}}\right) 0.032 \frac{\text{cal}}{\text{g}^{\circ}\text{C}}} = -21^{\circ}\text{C}$

$$T_f = T_i + \Delta T = 78.2^{\circ}\text{C} - 21^{\circ}\text{C} = 57^{\circ}\text{C}$$

6. (a)  $\text{sp. ht.} = \frac{\text{heat}}{\text{mass} \times \Delta T} = \frac{186 \text{ J}}{15.0 \text{ g} \times (29.6 - 22.3)} = 1.7 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

$$(b) \Delta T = \frac{\text{heat}}{\text{mass} \times \text{sp. ht.}} = \frac{-2.75 \text{ kcal} \times \frac{1000 \text{ cal}}{1 \text{ kcal}}}{\left(2.25 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}}\right) 1.00 \frac{\text{cal}}{\text{g}^\circ\text{C}}} = -1.22^\circ\text{C}$$

$$T_f = T_i + \Delta T = 23.1^\circ\text{C} - 1.22^\circ\text{C} = 21.9^\circ\text{C}$$

7. The heat capacities of the two substances are added and then multiplied by the temperature change.

$$\Delta H = \left(118 \text{ g Cu} \times \frac{0.385 \text{ J}}{\text{g}^\circ\text{C}} + 197 \text{ g H}_2\text{O} \times \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}}\right) (79.2^\circ\text{C} - 22.7^\circ\text{C}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = +49.1 \text{ kJ}$$

8. Heat is transferred from the iron to the water.

$$q_{\text{water}} = 981 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times (34.4 - 22.1)^\circ\text{C} = 5.04 \times 10^4 \text{ J} = -q_{\text{iron}}$$

$$q_{\text{iron}} = -5.04 \times 10^4 \text{ J} = 1.22 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \text{sp. ht.} \times (34.4 - 126.5)^\circ\text{C} = -1.12 \times 10^5 \times (\text{sp. ht.})$$

$$\text{sp. ht.} = \frac{-5.04 \times 10^4}{-1.12 \times 10^5} = \frac{0.450 \text{ J}}{\text{g}^\circ\text{C}}$$

9. If the two volumes were the same, a straight average of the temperatures would be the final temperature. But that is not true, so option (3) [50°C] is incorrect. In fact, there is more of the cooler water (100.0 mL) than of the warmer water (75.0 mL). The cooler side of the straight average should be somewhat favored, but not grossly so; option (4) [28°C] is incorrect. In order to arrive at 40°C, the cold water should increase by 20°C and the warm water should decrease by 40°C; their masses, and thus their volume should be in the inverse relationship as their temperature changes: 2:1. That is not the case, so option (1) [40°C] is incorrect. The correct final temperature is likely to be 46°C, option (2).

10. (a)  $\Delta U = q + w = 67 \text{ J heat} - 67 \text{ J work} = 0 \text{ J}$   
 (b)  $\Delta U = q + w = 356 \text{ J heat} - 592 \text{ J work} = -236 \text{ J}$   
 (c)  $\Delta U = q + w = -38 \text{ J heat} + 171 \text{ J work} = +133 \text{ J}$   
 (d)  $\Delta U = q + w = 0 \text{ J heat} - 416 \text{ J work} = -416 \text{ J}$

11. (a)  $q = \frac{-29.4 \text{ kJ}}{0.584 \text{ g C}_3\text{H}_8} \times \frac{44.10 \text{ g C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} = -2.22 \times 10^3 \text{ kJ/mol C}_3\text{H}_8$

$$(b) q = \frac{-1.26 \text{ kcal}}{0.136 \text{ g C}_{10}\text{H}_{16}\text{O}} \times \frac{4.184 \text{ kJ}}{1 \text{ kcal}} \times \frac{152.24 \text{ g C}_{10}\text{H}_{16}\text{O}}{1 \text{ mol C}_{10}\text{H}_{16}\text{O}} = -5.90 \times 10^3 \text{ kJ/mol C}_{10}\text{H}_{16}\text{O}$$

$$(c) q = \frac{-58.3 \text{ kJ}}{2.35 \text{ mL (CH}_3)_2\text{CO}} \times \frac{1 \text{ mL}}{0.791 \text{ g}} \times \frac{58.08 \text{ g (CH}_3)_2\text{CO}}{1 \text{ mol (CH}_3)_2\text{CO}} = -1.82 \times 10^3 \text{ kJ/mol (CH}_3)_2\text{CO}$$

$$12. \text{ heat capacity} = \frac{\text{heat absorbed}}{\Delta T} = \frac{5228 \text{ cal}}{4.39^\circ\text{C}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 4.98 \text{ kJ/}^\circ\text{C}$$

$$13. \text{ Heat absorbed by calorimeter} = q_{\text{comb}} \times \text{moles} = \text{heat capacity} \times \Delta T \text{ or } \Delta T = \frac{q_{\text{comb}} \times \text{moles}}{\text{heat capacity}}$$

$$(a) \Delta T = \frac{\left(1014.2 \frac{\text{kcal}}{\text{mol}} \times 4.184 \frac{\text{kJ}}{\text{kcal}}\right) \left(0.3268 \text{ g} \times \frac{1 \text{ mol C}_8\text{H}_{10}\text{O}_2\text{N}_4}{194.19 \text{ g C}_8\text{H}_{10}\text{O}_2\text{N}_4}\right)}{5.136 \text{ kJ/}^\circ\text{C}} = 1.390^\circ\text{C}$$

$$T_f = T_i + \Delta T = 22.43^\circ\text{C} + 1.390^\circ\text{C} = 23.82^\circ\text{C}$$

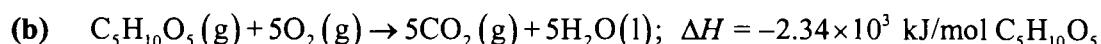
$$(b) \Delta T = \frac{2444 \frac{\text{kJ}}{\text{mol}} \left(1.35 \text{ mL} \times \frac{0.805 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol C}_4\text{H}_8\text{O}}{72.11 \text{ g C}_4\text{H}_8\text{O}}\right)}{5.136 \text{ kJ/}^\circ\text{C}} = 7.17^\circ\text{C}$$

$$T_f = 22.43^\circ\text{C} + 7.17^\circ\text{C} = 29.60^\circ\text{C}$$

$$14. (a) \frac{\text{heat}}{\text{mass}} = \frac{\text{heat cap.} \times \Delta t}{\text{mass}} = \frac{4.728 \text{ kJ/}^\circ\text{C} \times (27.19 - 23.29)^\circ\text{C}}{1.183 \text{ g}} = 15.6 \text{ kJ/g xylose}$$

$$\Delta H = \text{heat given off/g} \times M(\text{g/mol}) = \frac{-15.6 \text{ kJ}}{1 \text{ g C}_5\text{H}_{10}\text{O}_5} \times \frac{150.13 \text{ g C}_5\text{H}_{10}\text{O}_5}{1 \text{ mol}}$$

$$\Delta H = -2.34 \times 10^3 \text{ kJ/mol C}_5\text{H}_{10}\text{O}_5$$



15. This is first a limiting reactant problem. There is  $0.1000 \text{ L} \times 0.300 \text{ M} = 0.0300 \text{ mol HCl}$  and  $1.82 / 65.39 = 0.0278 \text{ mol Zn}$ . Stoichiometry demands 2 mol HCl for every 1 mol Zn. HCl is the limiting reactant. The reaction is exothermic. We neglect the slight excess of Zn(s), and assume that the volume of solution remains 100.0 mL and its specific heat,  $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ . The enthalpy change, in kJ/mol Zn, is

$$\Delta H = -\frac{100.0 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{4.18 \text{ J}}{\text{g }^\circ\text{C}} \times (30.5 - 20.3)^\circ\text{C}}{0.0300 \text{ mol HCl} \times \frac{1 \text{ mol Zn}}{2 \text{ mol HCl}}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -284 \text{ kJ/mol Zn}$$

16. (a) Because the temperature of the mixture decreases, the reaction (the system) must have absorbed heat from the reaction mixture (the surroundings). Consequently, the reaction must be endothermic.
- (b) We assume that the specific heat of the solution is  $4.18 \text{ J g}^{-1} \text{ C}^{-1}$ . The enthalpy change in kJ/mol KCl is obtained by the heat absorbed per gram KCl.

$$\Delta H = - \frac{(0.75 + 35.0) \text{ g} \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} (23.6 - 24.8)^\circ\text{C}}{0.75 \text{ g KCl}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = +18 \text{ kJ / mol}$$

17. As indicated by the negative sign for the enthalpy change, this is an exothermic reaction; the temperature of the system should increase.

$$q_{\text{rxn}} = 0.136 \text{ mol KC}_2\text{H}_3\text{O}_2 \times \frac{-15.3 \text{ kJ}}{1 \text{ mol KC}_2\text{H}_3\text{O}_2} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -2.08 \times 10^3 \text{ J} = -q_{\text{calorim}}$$

Now, we assume that the density of water is 1.00 g/mL, the specific heat of the solution in the calorimeter is  $4.18 \text{ J g}^{-1} \text{ C}^{-1}$ , and no heat is lost by the calorimeter.

$$q_{\text{calorim}} = 2.08 \times 10^3 \text{ J} = \left( \left( 525 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \right) + \left( 0.136 \text{ mol KC}_2\text{H}_3\text{O}_2 \times \frac{98.14 \text{ g}}{1 \text{ mol KC}_2\text{H}_3\text{O}_2} \right) \right) \times \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times \Delta T = 2.25 \times 10^3 \Delta T$$

$$\Delta T = \frac{2.08 \times 10^3}{2.25 \times 10^3} = +0.924^\circ\text{C} \quad T_{\text{final}} = T_{\text{initial}} + \Delta T = 25.1^\circ\text{C} + 0.924^\circ\text{C} = 26.0^\circ\text{C}$$

18. (a)  $\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) \quad \Delta H^\circ = +82.05 \text{ kJ / mol}$
- (b)  $\text{S}(\text{rhombic}) + \text{O}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{SO}_2\text{Cl}_2(\text{l}) \quad \Delta H^\circ = -394.1 \text{ kJ / mol}$
- (c)  $\text{CH}_3\text{CH}_2\text{COOH}(\text{l}) + \frac{7}{2}\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -1527 \text{ kJ / mol}$

19. (a) heat evolved =  $1.325 \text{ g C}_4\text{H}_{10} \times \frac{1 \text{ mol C}_4\text{H}_{10}}{58.123 \text{ g C}_4\text{H}_{10}} \times \frac{2877 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} = 65.59 \text{ kJ}$ ,

or heat =  $-65.59 \text{ kJ}$

(b) heat evolved =  $28.4 \text{ L}_{\text{STP}} \text{ C}_4\text{H}_{10} \times \frac{1 \text{ mol C}_4\text{H}_{10}}{22.414 \text{ L}_{\text{STP}} \text{ C}_4\text{H}_{10}} \times \frac{2877 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} = 3.65 \times 10^3 \text{ kJ}$ ,

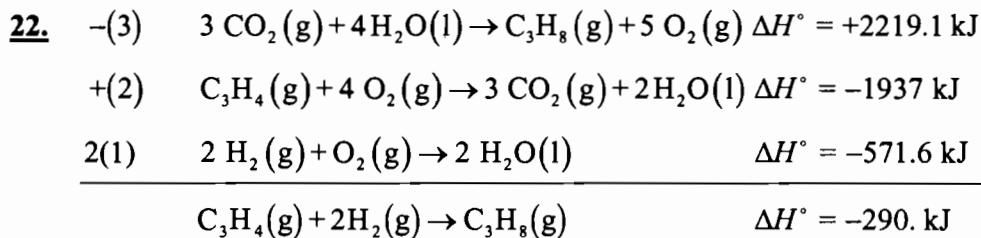
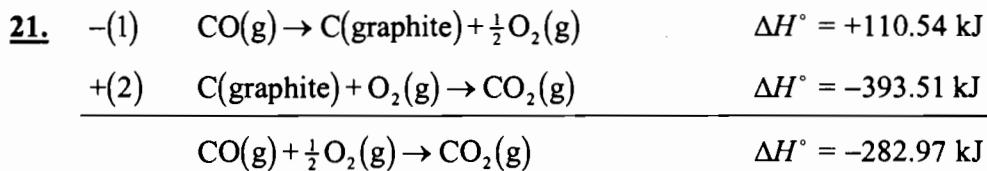
or heat =  $-3.65 \times 10^3 \text{ kJ}$

- (c) Use the ideal gas equation to determine the amount of propane in moles and multiply this amount by 2877 kJ heat produced per mole.

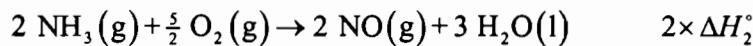
$$\text{heat evolved} = \frac{\left(738 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times 12.6 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times (273.2 + 23.6) \text{ K}} \times \frac{2877 \text{ kJ}}{1 \text{ mol C}_4\text{H}_{10}} = 1.45 \times 10^3 \text{ kJ,}$$

$$\text{or heat} = -1.45 \times 10^3 \text{ kJ}$$

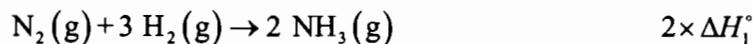
20. The formation reaction for  $\text{NH}_3(\text{g})$  is  $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$ . The given reaction is two-thirds the reverse of the formation reaction. The sign of the enthalpy is changed and it is multiplied by two-thirds. Thus, the enthalpy of the given reaction is  $-(-46.11 \text{ kJ}) \times \frac{2}{3} = +30.74 \text{ kJ}$ .



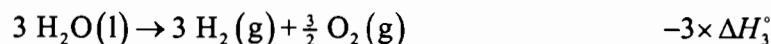
23. The second reaction is the only one in which  $\text{NO}(\text{g})$  appears; it must be run twice to produce  $2\text{NO}(\text{g})$ .



The first reaction is the only one that can eliminate  $2\text{NH}_3(\text{g})$ ; it must be run twice to eliminate  $2\text{NH}_3(\text{g})$ .



We triple and reverse the third reaction to eliminate  $3\text{H}_2(\text{g})$ .



24. (a)  $\Delta H^\circ = \Delta H_f^\circ[C_2H_6(g)] + \Delta H_f^\circ[CH_4(g)] - \Delta H_f^\circ[C_3H_8(g)] - \Delta H_f^\circ[H_2(g)]$

$$\Delta H^\circ = -84.68 - 74.81 - (-103.8) - 0.00 = -55.7 \text{ kJ}$$

(b)  $\Delta H^\circ = 2\Delta H_f^\circ[SO_2(g)] + 2\Delta H_f^\circ[H_2O(l)] - 2\Delta H_f^\circ[H_2S(g)] - 3\Delta H_f^\circ[O_2(g)]$

$$\Delta H^\circ = 2(-296.8) + 2(-285.8) - 2(-20.63) - 3(0.00) = -1124 \text{ kJ}$$

25.  $\Delta H^\circ = \Delta H_f^\circ[H_2O(l)] + \Delta H_f^\circ[NH_3(g)] - \Delta H_f^\circ[NH_4^+(aq)] - \Delta H_f^\circ[OH^-(aq)]$

$$\Delta H^\circ = -285.8 + (-46.11) - (-132.5) - (-230.0) = +30.6 \text{ kJ}$$

26.  $ZnO(s) + SO_2(g) \rightarrow ZnS(s) + \frac{3}{2}O_2(g); \quad \Delta H^\circ = -(-878.2 \text{ kJ})/2 = +439.1 \text{ kJ}$

$$439.1 \text{ kJ} = \Delta H_f^\circ[ZnS(s)] + \frac{3}{2}\Delta H_f^\circ[O_2(g)] - \Delta H_f^\circ[ZnO(s)] - \Delta H_f^\circ[SO_2(g)]$$

$$439.1 \text{ kJ} = \Delta H_f^\circ[ZnS(s)] + \frac{3}{2}(0.00) - (-348.3) - (-296.8)$$

$$\Delta H_f^\circ[ZnS(s)] = 439.1 - 348.3 - 296.8 = -206.0 \text{ kJ/mol}$$

## EXERCISES

### Heat Capacity (Specific Heat)

27. heat gained by the water = heat lost by the metal; heat = mass  $\times$  sp. ht.  $\times$   $\Delta T$

(a)  $50.0 \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} (38.9 - 22.0)^\circ\text{C} = 3.53 \times 10^3 \text{ J} = -150.0 \text{ g} \times \text{sp. ht.} \times (38.9 - 100.0)^\circ\text{C}$

$$\text{sp. ht.} = \frac{3.53 \times 10^3 \text{ J}}{150.0 \text{ g} \times 61.1^\circ\text{C}} = 0.385 \text{ J g}^{-1} \text{ C}^{\circ-1} \text{ for Zn}$$

(b)  $50.0 \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} (28.8 - 22.0)^\circ\text{C} = 1.4 \times 10^3 \text{ J} = -150.0 \text{ g} \times \text{sp. ht.} \times (28.8 - 100.0)^\circ\text{C}$

$$\text{sp. ht.} = \frac{1.4 \times 10^3 \text{ J}}{150.0 \text{ g} \times 71.2^\circ\text{C}} = 0.13 \text{ J g}^{-1} \text{ C}^{\circ-1} \text{ for Pt}$$

(c)  $50.0 \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} (52.7 - 22.0)^\circ\text{C} = 6.42 \times 10^3 \text{ J} = -150.0 \text{ g} \times \text{sp. ht.} \times (52.7 - 100.0)^\circ\text{C}$

$$\text{sp. ht.} = \frac{6.42 \times 10^3 \text{ J}}{150.0 \text{ g} \times 47.3^\circ\text{C}} = 0.905 \text{ J g}^{-1} \text{ C}^{\circ-1} \text{ for Al}$$

$$\underline{29.} \quad q_{\text{water}} = 375 \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^{\circ}\text{C}} (87 - 26)^{\circ}\text{C} = 9.56 \times 10^4 \text{ J} = -q_{\text{iron}}$$

$$q_{\text{iron}} = -9.56 \times 10^4 \text{ J} = 465 \text{ g} \times 0.449 \frac{\text{J}}{\text{g}^{\circ}\text{C}} (87 - T_f) = 1.82 \times 10^4 \text{ J} - 2.09 \times 10^2 \text{ J} T_f$$

$$T_f = \frac{-9.56 \times 10^4 - 1.8 \times 10^4}{-2.09 \times 10^2} = 5.44 \times 10^2 \text{ }^{\circ}\text{C} \text{ or } 5.4 \times 10^2 \text{ }^{\circ}\text{C}$$

The number of significant figures in the final answer is limited by the two significant figures in the temperatures given.

$$\underline{31.} \quad \text{heat lost by Mg} = \text{heat gained by water}$$

$$-\left(1.00 \text{ kg Mg} \times \frac{1000 \text{ g}}{1 \text{ kg}}\right) 1.024 \frac{\text{J}}{\text{g}^{\circ}\text{C}} (T_f - 40.0 \text{ }^{\circ}\text{C}) = \left(1.00 \text{ L} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times \frac{1.00 \text{ g}}{1 \text{ cm}^3}\right) 4.18 \frac{\text{J}}{\text{g}^{\circ}\text{C}} (T_f - 20.0 \text{ }^{\circ}\text{C})$$

$$-1.024 \times 10^3 T_f + 4.10 \times 10^4 = 4.18 \times 10^3 T_f - 8.36 \times 10^4$$

$$4.10 \times 10^4 + 8.36 \times 10^4 = (4.18 \times 10^3 + 1.024 \times 10^3) T_f \rightarrow 12.46 \times 10^4 = 5.20 \times 10^3 T_f$$

$$T_f = \frac{12.46 \times 10^4}{5.20 \times 10^3} = 24.0 \text{ }^{\circ}\text{C}$$

$$\underline{33.} \quad \text{heat lost by copper} = \text{heat gained by glycerol}$$

$$-74.8 \text{ g} \times \frac{0.385 \text{ J}}{\text{g}^{\circ}\text{C}} \times (31.1 \text{ }^{\circ}\text{C} - 143.2 \text{ }^{\circ}\text{C}) = 165 \text{ mL} \times \frac{1.26 \text{ g}}{1 \text{ mL}} \times \text{sp. ht.} \times (31.1 \text{ }^{\circ}\text{C} - 24.8 \text{ }^{\circ}\text{C})$$

$$3.23 \times 10^3 = 1.3 \times 10^3 \times (\text{sp. ht.}) \quad \text{sp. ht.} = \frac{3.23 \times 10^3}{1.3 \times 10^3} = 2.5 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$$

$$\text{molar heat capacity} = 2.5 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} \times \frac{92.1 \text{ g}}{1 \text{ mol C}_3\text{H}_8\text{O}_3} = 2.3 \times 10^2 \text{ J mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$$

## Heats of reaction

$$\underline{35.} \quad \text{heat} = 283 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Ca(OH)}_2}{74.09 \text{ g Ca(OH)}_2} \times \frac{65.2 \text{ kJ}}{1 \text{ mol Ca(OH)}_2} = 2.49 \times 10^5 \text{ kJ of heat evolved.}$$

$$\underline{37.} \quad \text{(a)} \quad \text{mass} = 2.80 \times 10^7 \text{ kJ} \times \frac{1 \text{ mol CH}_4}{890.3 \text{ kJ}} \times \frac{16.04 \text{ g CH}_4}{1 \text{ mol CH}_4} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 504 \text{ kg CH}_4.$$

- (b) First determine the moles of  $\text{CH}_4$  present, with the ideal gas law.

$$\text{mol CH}_4 = \frac{\left(768 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) 1.65 \times 10^4 \text{ L}}{0.08206 \frac{\text{L atm}}{\text{mol K}} \times (18.6 + 273.2) \text{ K}} = 696 \text{ mol CH}_4$$

$$\text{heat energy} = 696 \text{ mol CH}_4 \times \frac{-890.3 \text{ kJ}}{1 \text{ mol CH}_4} = -6.20 \times 10^5 \text{ kJ of heat energy}$$

$$(c) V_{\text{H}_2\text{O}} = \frac{6.21 \times 10^5 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} (60.0 - 8.8)^\circ\text{C}} \times \frac{1 \text{ mL H}_2\text{O}}{1 \text{ g}} = 2.90 \times 10^6 \text{ mL} = 2.90 \times 10^3 \text{ L H}_2\text{O}$$

39. Since the molar mass of  $\text{H}_2$  (2.0 g/mol) is  $\frac{1}{16}$  of the molar mass of  $\text{O}_2$  (32.0 g/mol) and only twice as many moles of  $\text{H}_2$  are needed as  $\text{O}_2$ , we see that  $\text{O}_2(\text{g})$  is the limiting reagent in this reaction.

$$\frac{180}{2} \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \times \frac{241.8 \text{ kJ heat}}{0.500 \text{ mol O}_2} = 1.4 \times 10^3 \text{ kJ heat}$$

41. (a) We first compute the heat produced by this reaction, then determine the value of  $\Delta H$  in kJ/mol KOH.

$$q_{\text{calorimeter}} = (0.205 + 55.9) \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} (24.4 - 23.5) = 2 \times 10^2 \text{ J heat} = -q_{\text{rxn}}$$

$$\Delta H = -\frac{2 \times 10^2 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}}}{0.205 \text{ g} \times \frac{1 \text{ mol KOH}}{56.1 \text{ g KOH}}} = -5 \times 10^1 \text{ kJ / mol}$$

- (b) The  $\Delta T$  here is known to just one significant figure ( $0.9^\circ\text{C}$ ). Doubling the amount of KOH should give a temperature change known to two significant figures ( $1.6^\circ\text{C}$ ) and using twenty times the mass of KOH should give a temperature change known to three significant figures ( $16.0^\circ\text{C}$ ). This would require 4.10 g KOH rather than the 0.205 g KOH actually used, and would increase the precision from one part in five to one part in 500, or  $\sim 0.2\%$ . Note that as the mass of KOH is increased and the mass of  $\text{H}_2\text{O}$  stays constant, the assumption of a constant specific heat becomes less valid.

- 43.** Let  $x$  be the mass, (in grams), of  $\text{NH}_4\text{Cl}$  added to the water.  $\text{heat} = \text{mass} \times \text{sp. ht.} \times \Delta T$

$$x \times \frac{1 \text{ mol } \text{NH}_4\text{Cl}}{53.49 \text{ g } \text{NH}_4\text{Cl}} \times \frac{14.7 \text{ kJ}}{1 \text{ mol } \text{NH}_4\text{Cl}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = - \left( \left( 1400 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \right) + x \right) 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} (10. - 25)^\circ\text{C}$$

$$275x = 8.8 \times 10^4 + 63x; \quad x = \frac{8.8 \times 10^4}{275 - 63} = 4.2 \times 10^2 \text{ g } \text{NH}_4\text{Cl}$$

Our final value is approximate because of the assumed density (1.00 g/mL). The solution's density probably is a bit larger than 1.00 g/mL. Many aqueous solutions are somewhat more dense than water.

- 45.** We assume that the solution volumes are additive; that is, that 200.0 mL of solution is formed. Then we compute the heat needed to warm the solution and the cup, and then  $\Delta H$  for the reaction.

$$\text{heat} = \left( 200.0 \text{ mL} \times \frac{1.02 \text{ g}}{1 \text{ mL}} \right) 4.02 \frac{\text{J}}{\text{g}^\circ\text{C}} (27.8 - 21.1)^\circ\text{C} + 10 \frac{\text{J}}{\text{C}} (27.8 - 21.1) = 5.6 \times 10^3 \text{ J}$$

$$\Delta H_{\text{neutr.}} = \frac{-5.6 \times 10^3 \text{ J}}{0.100 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -56 \text{ kJ/mol} \quad (-55.6 \text{ kJ/mol to three significant figures})$$

## Enthalpy Changes and States of Matter

- 47.**  $q_{\text{H}_2\text{O(l)}} = q_{\text{H}_2\text{O(s)}} \quad m(\text{sp. ht.})_{\text{H}_2\text{O(l)}} \Delta T_{\text{H}_2\text{O(l)}} = \text{mol}_{\text{H}_2\text{O(s)}} \Delta H_{\text{fus H}_2\text{O(s)}}$

$$(3.50 \text{ mol H}_2\text{O} \times \frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}})(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})(50.0^\circ\text{C}) = \left( \frac{m}{18.015 \text{ g H}_2\text{O}} \times 6.01 \times 10^3 \frac{\text{J}}{\text{mol}} \right)$$

$$13.2 \times 10^3 \text{ J} = m(333.6 \text{ J g}^{-1}) \quad \text{Hence, } m = 39.6 \text{ g}$$

- 49.** Assume  $\text{H}_2\text{O(l)}$  density = 1.00 g  $\text{mL}^{-1}$  (at 28.5  $^\circ\text{C}$ )  $-q_{\text{lost by ball}} = q_{\text{gained by water}} + q_{\text{vap water}}$

$$-[(125 \text{ g})(0.50 \frac{\text{J}}{\text{g}^\circ\text{C}})(100 - 52.5)^\circ\text{C}] = [(75.0 \text{ g})(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})(100.0 - 28.5)^\circ\text{C}] + n_{\text{H}_2\text{O}} \Delta H_{\text{vap}}$$

$$26562.5 \text{ J} = 22436.7 \text{ J} + n_{\text{H}_2\text{O}} \Delta H_{\text{vap}} \quad (\text{Note: } n_{\text{H}_2\text{O}} = \frac{\text{mass}_{\text{H}_2\text{O}}}{\text{molar mass}_{\text{H}_2\text{O}}})$$

$$4125.8 \text{ J} = (m_{\text{H}_2\text{O}}) \left( \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \right) (40.6 \times 10^3 \frac{\text{J}}{\text{mol}})$$

$$m_{\text{H}_2\text{O}} = 1.83 \text{ g H}_2\text{O} \cong 2 \text{ g H}_2\text{O} \quad (1 \text{ sig. fig.})$$

## Bomb Calorimetry

51. To determine the heat capacity of the calorimeter, recognize that the heat evolved by the reaction is the negative of the heat of combustion.

$$\text{heat capacity} = \frac{\text{heat evolved}}{\Delta T} = \frac{1.620 \text{ g C}_{10}\text{H}_8 \times \frac{1 \text{ mol C}_{10}\text{H}_8}{128.2 \text{ g C}_{10}\text{H}_8} \times \frac{5156.1 \text{ kJ}}{1 \text{ mol C}_{10}\text{H}_8}}}{8.44^\circ\text{C}} = 7.72 \text{ kJ/}^\circ\text{C}$$

53. The temperature should increase as the result of an exothermic combustion reaction.

$$\Delta T = 1.227 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} \times \frac{5.65 \times 10^3 \text{ kJ}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \times \frac{1^\circ\text{C}}{3.87 \text{ kJ}} = 5.23^\circ\text{C}$$

## Pressure Volume Work

55. (a)  $P\Delta V = 3.5 \text{ L} \times (748 \text{ mmHg}) \left( \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) = 3.44 \text{ L atm}$  or  $3.4 \text{ L atm}$

(b)  $1 \text{ L kPa} = 1 \text{ J}$ , hence,

$$3.44 \text{ L atm} \times \left( \frac{101.325 \text{ kPa}}{1 \text{ atm}} \right) \times \left( \frac{1 \text{ J}}{1 \text{ L kPa}} \right) = 3.49 \times 10^2 \text{ J}$$
 or  $3.5 \times 10^2 \text{ J}$

(c)  $3.49 \times 10^2 \text{ J} \times \left( \frac{1 \text{ cal}}{4.184 \text{ J}} \right) = 83.4 \text{ cal}$  or  $83 \text{ cal}$

57. There is no way to use the expansion process to raise or lower a weight in the surroundings, so there can be no work.

59. (a) No pressure-volume work done (no gases are formed or consumed).  
 (b)  $2 \text{ NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$   $\Delta n_{\text{gas}} = -1$  mole. Work is done on the system by the surroundings (compression).  
 (c)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ . Formation of a gas,  $\Delta n_{\text{gas}} = +1$  mole, results in an expansion. The system does work on the surroundings.

61. (a)  $\Delta U = q + w = +58 \text{ J} + (-58 \text{ J}) = 0$   
 (b)  $\Delta U = q + w = +125 \text{ J} + (-687 \text{ J}) = -562 \text{ J}$   
 (c)  $280 \text{ cal} \times (4.184 \frac{\text{J}}{\text{cal}}) = 1171.52 \text{ J} = 1.17 \text{ kJ}$   $\Delta U = q + w = -1.17 \text{ kJ} + 1.25 \text{ kJ} = 0.08 \text{ kJ}$   
63. (a) Yes, the gas does work ( $w = \text{negative value}$ ).  
 (b) Yes, the gas exchanges energy with the surroundings, it absorbs energy.  
 (c) The temperature of the gas stays the same if the process is isothermal.  
 (d)  $\Delta U$  for the gas must equal zero by definition (temperature is not changing).

- 65.** Impossible, ideal gas expanding isothermally means that  $\Delta U = 0 = q + w$ , or  $w = -q$ , not  $w = -2q$ .
- 67.** According the First Law of Thermodynamics, the answer is (c). Both (a)  $q_v$  and (b)  $q_p$  are heats of chemical reaction carried out under conditions of constant volume and constant pressure respectively. Both  $\Delta U$  and  $\Delta H$  incorporate terms related to work as well as heat.
- 69.**  $\text{C}_3\text{H}_8\text{O(l)} + 9/2 \text{O}_2\text{(g)} \rightarrow 3 \text{CO}_2\text{(g)} + 4 \text{H}_2\text{O(l)} \quad \Delta n_{\text{gas}} = -1.5 \text{ mol}$
- (a)  $\Delta U = -33.41 \frac{\text{kJ}}{\text{g}} \times \frac{60.096 \text{ g C}_3\text{H}_8\text{O}}{1 \text{ mol C}_3\text{H}_8\text{O}} = -2008 \frac{\text{kJ}}{\text{mol}}$
- (b)  $\Delta H = \Delta U - w, = \Delta U - (-P\Delta V) = \Delta U - (-\Delta n_{\text{gas}}RT) = \Delta U + \Delta n_{\text{gas}}RT$   
 $\Delta H = -2008 \frac{\text{kJ}}{\text{mol}} + (-1.5 \text{ mol})(\frac{8.3145 \times 10^{-3} \text{ kJ}}{\text{K mol}})(298.15 \text{ K}) = -2012 \frac{\text{kJ}}{\text{mol}}$

### Hess's Law

- 71.**  $2\text{HCl(g)} + \text{C}_2\text{H}_4\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2\text{(l)} + \text{H}_2\text{O(l)} \quad \Delta H^\circ = -318.7 \text{ kJ}$
- 
- $\text{Cl}_2\text{(g)} + \text{H}_2\text{O(l)} \rightarrow 2\text{HCl(g)} + \frac{1}{2}\text{O}_2\text{(g)} \quad \Delta H^\circ = 0.5(+202.4) = +101.2 \text{ kJ}$
- 
- $\text{C}_2\text{H}_4\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2\text{(l)} \quad \Delta H^\circ = -217.5 \text{ kJ}$
- 
- 73.**  $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta H^\circ = -283.0 \text{ kJ}$
- $3\text{C(graphite)} + 6\text{H}_2\text{(g)} \rightarrow 3\text{CH}_4\text{(g)} \quad \Delta H^\circ = 3(-74.81) = -224.43 \text{ kJ}$
- $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)} \quad \Delta H^\circ = 2(-285.8) = -571.6 \text{ kJ}$
- $3\text{CO(g)} \rightarrow \frac{3}{2}\text{O}_2\text{(g)} + 3\text{C(graphite)} \quad \Delta H^\circ = 3(+110.5) = +331.5 \text{ kJ}$
- 
- $4\text{CO(g)} + 8\text{H}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 3\text{CH}_4\text{(g)} + 2\text{H}_2\text{O(l)} \quad \Delta H^\circ = -747.5 \text{ kJ}$
- 
- 75.**  $\text{CH}_4\text{(g)} + \text{CO}_2\text{(g)} \rightarrow 2\text{CO(g)} + 2\text{H}_2\text{(g)} \quad \Delta H^\circ = +247 \text{ kJ}$
- $2\text{CH}_4\text{(g)} + 2\text{H}_2\text{O(g)} \rightarrow 2\text{CO(g)} + 6\text{H}_2\text{(g)} \quad \Delta H^\circ = 2(+206 \text{ kJ}) = +412 \text{ kJ}$
- $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(g)} \quad \Delta H^\circ = -802 \text{ kJ}$
- 
- $4\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow 4\text{CO(g)} + 8\text{H}_2\text{(g)} \quad \Delta H^\circ = -143 \text{ kJ}$
- $\div 4 \text{ produces } \text{CH}_4\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)} + 2\text{H}_2\text{(g)} \quad \Delta H^\circ = -35.8 \text{ kJ}$

## Standard Enthalpies (Heats) of Formation

77. The compounds that have negative standard enthalpies of formation are more stable than the elements from which they are made. Those that have positive standard enthalpies of formation are less stable than the elements. It is unlikely that many compounds would have zero standard enthalpy of formation. Such compounds would be exactly as stable as the elements from which they are made.

79.  $\Delta H^\circ = 4\Delta H_f^\circ[\text{HCl}(g)] + \Delta H_f^\circ[\text{O}_2(g)] - 2\Delta H_f^\circ[\text{Cl}_2(g)] - 2\Delta H_f^\circ[\text{H}_2\text{O}(l)]$   
 $= 4(-92.31) + (0.00) - 2(0.00) - 2(-285.8) = +202.4 \text{ kJ}$

81. Balanced equation:  $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$   
 $\Delta H^\circ = 2\Delta H_f^\circ[\text{CO}_2(g)] + 3\Delta H_f^\circ[\text{H}_2\text{O}(l)] - \Delta H_f^\circ[\text{C}_2\text{H}_5\text{OH}(l)] - 3\Delta H_f^\circ[\text{O}_2(g)]$   
 $= 2(-393.5) + 3(-285.8) - (-277.7) - 3(0.00) = -1366.7 \text{ kJ}$

83.  $\Delta H^\circ = -397.3 \text{ kJ} = \Delta H_f^\circ[\text{CCl}_4(g)] + 4\Delta H_f^\circ[\text{HCl}(g)] - \Delta H_f^\circ[\text{CH}_4(g)] - 4\Delta H_f^\circ[\text{Cl}_2(g)]$   
 $= \Delta H_f^\circ[\text{CCl}_4(g)] + 4(-92.31) - (-74.81) - 4(0.00) = \Delta H_f^\circ[\text{CCl}_4(g)] - 294.4$   
 $\Delta H_f^\circ[\text{CCl}_4(g)] = -397.3 + 294.4 = -102.9 \text{ kJ}$

85.  $\Delta H^\circ = \Delta H_f^\circ[\text{Al}(\text{OH})_3(s)] - \Delta H_f^\circ[\text{Al}^{3+}(\text{aq})] - 3\Delta H_f^\circ[\text{OH}^-(\text{aq})]$   
 $= (-1276) - (-531) - 3(-230.0) = -55 \text{ kJ}$

87. Balanced equation:  $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$   
 $\Delta H^\circ = \Delta H_f^\circ[\text{CaO}(s)] + \Delta H_f^\circ[\text{CO}_2(g)] - \Delta H_f^\circ[\text{CaCO}_3(s)]$   
 $= -635.1 - 393.5 - (-1207) = +178 \text{ kJ}$

$$\text{heat} = 1.35 \times 10^3 \text{ kg CaCO}_3 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \times \frac{178 \text{ kJ}}{1 \text{ mol CaCO}_3} = 2.40 \times 10^6 \text{ kJ}$$

## FEATURE PROBLEMS

110.  $1^\circ\text{F} = 5/9^\circ\text{C} = 0.555^\circ\text{C}$        $1 \text{ lb} = 453.6 \text{ g}$

$$E_p = mgh$$

$$E_p = (772 \text{ lb})(9.80665 \text{ m s}^{-2})(1 \text{ ft}) = 7.57 \times 10^3 \frac{\text{lb m ft}}{\text{s}^2}$$

$$E_p = 7.57 \times 10^3 \frac{\text{lb m ft}}{\text{s}^2} \times \frac{0.3048 \text{ m}}{\text{ft}} \times \frac{0.4536 \text{ kg}}{\text{lb}}$$

$$E_p = 1047 \frac{\text{kg m}^2}{\text{s}^2} = 1047 \text{ J} = 1.05 \text{ kJ}$$

The statement is validated.

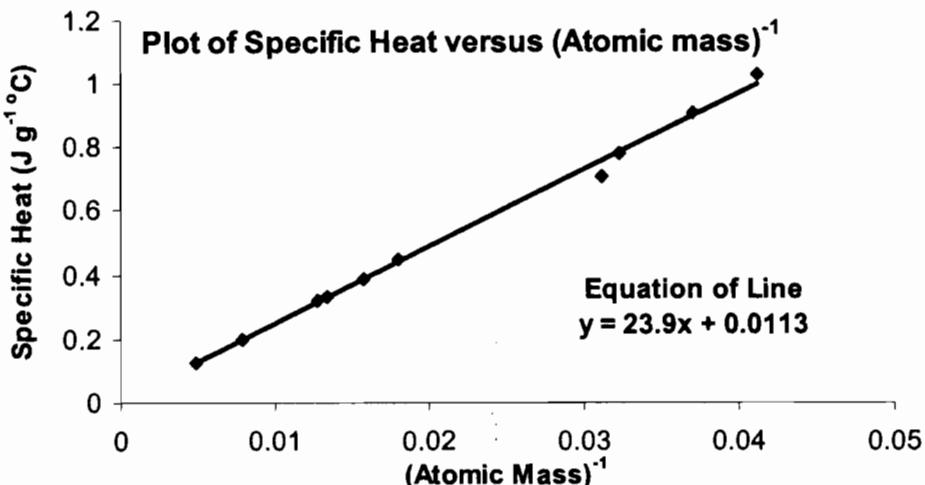
$$q = m \times (\text{sp. ht.})\Delta T$$

$$q = 453.6 \text{ g}(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})(0.556^\circ\text{C})$$

$$q = 1054 \text{ J}$$

$$q = 1.05 \text{ kJ}$$

- 111. (a)** We plot specific heat vs. the inverse of atomic mass.



- (b)** The equation of the line is: Specific Heat =  $23.9 \div (\text{atomic mass}) + 0.0113$

$$0.23 \text{ J g}^{-1} \text{ } ^\circ\text{C} = 23.9 \div (\text{atomic mass}) + 0.0113$$

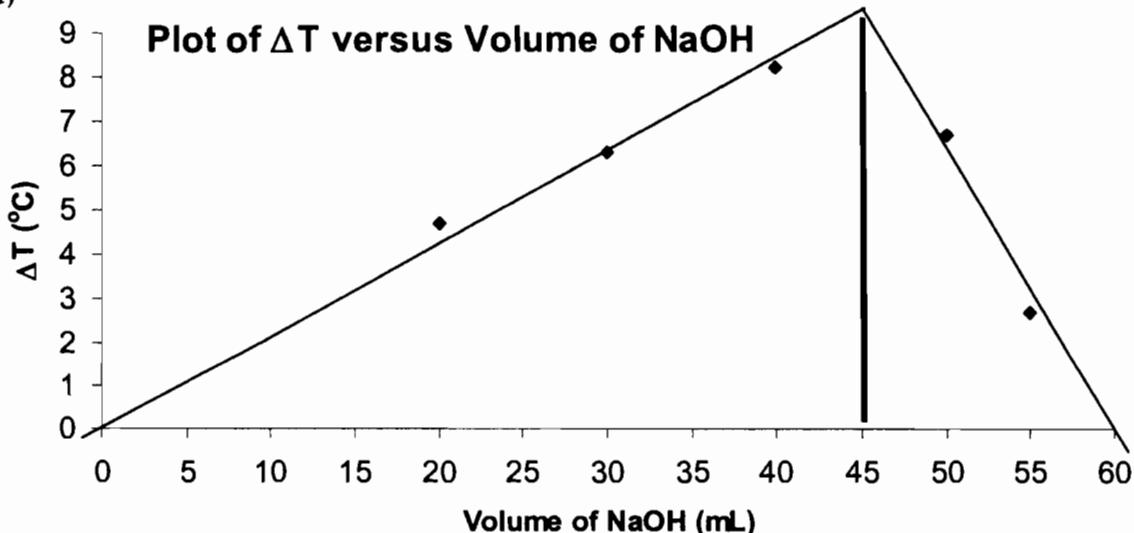
$$\text{atomic mass} = \frac{23.9}{0.23 - 0.0113} = 109 \text{ u or } 110 \text{ u (2 sig fig)};$$

Cadmium's tabulated atomic mass is 112.4 u.

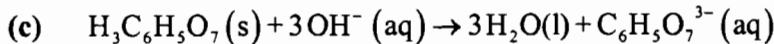
**(c)**  $\text{sp. ht.} = \frac{450 \text{ J}}{75.0 \text{ g} \times 15.^\circ\text{C}} = 0.40 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1} = 0.0113 + 23.9/\text{atomic mass}$

$$\text{atomic mass} = \frac{23.9}{0.40 - 0.0113} = 61.5 \text{ u or } 62 \text{ u Metal most likely Cu (63.5 u)}$$

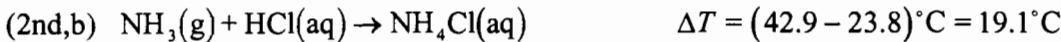
- 112.** The plot's maximum is the equivalence point. (assume  $\Delta T = 0$  at 0 mL of added NaOH, (i.e. only 60 mL of citric acid) and that  $\Delta T = 0$  at 60 mL of NaOH (i.e. no citric acid added)



- (a) The equivalence point occurs with 45.0 mL of 1.00 M NaOH(aq) [45.0 mmol NaOH] and 15.0 mL of 1.00 M citric acid [15.0 mmol citric acid]. Again, we assume that  $\Delta T = 0$  if no NaOH added ( $V_{\text{NaOH}} = 0$  mL) and  $\Delta T = 0$  if no citric acid is added ( $V_{\text{NaOH}} = 60$ ).
- (b) Heat is a product of the reaction, just as chemical species (products) are. Products are maximized at the exact stoichiometric proportions. Since each reaction mixture has the same volume, and thus about the same mass to heat, the temperature also is a maximum at this point.



113. The reactions, and their temperature changes, are as follows.



The sum of reactions (2nd,a) + (2nd,b) produces the same change as the 1<sup>st</sup> reaction. We now compute the heat absorbed by the surroundings for each. Hess's law is demonstrated if  $\Delta H_1 = \Delta H_{2a} + \Delta H_{2b}$ , where in each case  $\Delta H = -q$ .

$$q_1 = [(100.0 \text{ mL} + 8.00 \text{ mL}) \times 1.00 \text{ g/mL}] 4.18 \text{ J g}^{-1} \text{ C}^{-1} \times 12.0^\circ\text{C} = 5.42 \times 10^3 \text{ J} = -\Delta H_1$$

$$q_{2a} = [(100.0 \text{ mL} \times 1.00 \text{ g/mL}) 4.18 \text{ J g}^{-1} \text{ C}^{-1} \times (-6.1^\circ\text{C})] = -2.55 \times 10^3 \text{ J} = -\Delta H_{2a}$$

$$q_{2b} = [(100.0 \text{ mL} \times 1.00 \text{ g/mL}) 4.18 \text{ J g}^{-1} \text{ C}^{-1} \times (19.1^\circ\text{C})] = 7.98 \times 10^3 \text{ J} = -\Delta H_{2b}$$

$$\Delta H_{2a} + \Delta H_{2b} = +2.55 \times 10^3 \text{ J} - 7.98 \times 10^3 \text{ J} = -5.43 \times 10^3 \text{ J} \approx -5.42 \times 10^3 \text{ J} = \Delta H_1$$

Thus, the argument is complete.

114. According to the kinetic-molecular theory of gases, the internal energy of an ideal gas,  $U$ , is proportional to the average translational kinetic energy for the gas particles,  $\bar{e}_k$ , which in turn is proportional to  $3/2 RT$ . Thus the internal energy for a fixed amount of an ideal gas depends only on its temperature, i.e.  $U = 3/2 nRT$ , where  $U$  is the internal energy (J),  $n$  is the number of moles of gas particles,  $R$  is the gas constant ( $\text{J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is the temperature (K).

If the temperature of the gas sample is changed, the resulting change in internal energy is given by  $\Delta U = 3/2 nR\Delta T$ .

- (a) At constant volume,  $q_v = nC_v\Delta T$ . Assuming that no work is done  $\Delta U = q_v$  so,  $\Delta U = q_v = 3/2 nR\Delta T = nC_v\Delta T$ . (divide both sides by  $n\Delta T$ )  $C_v = 3/2 R = 12.5 \text{ J/K mol}$ .

- (b) The heat flow at constant pressure  $q_p$  is the  $\Delta H$  for the process (i.e.,  $q_p = \Delta H$ ) and we know that  $\Delta H = \Delta U - w$  and  $w = -P\Delta V = -nR\Delta T$   
 Hence,  $q_p = \Delta U - w = \Delta U - (-nR\Delta T) = \Delta U + nR\Delta T$  and  $q_p = nC_p\Delta T$  and  $\Delta U = 3/2 nR\Delta T$   
 Consequently  $q_p = nC_p\Delta T = nR\Delta T + 3/2 nR\Delta T$  (divide both sides by  $n\Delta T$ )  
 Now,  $C_p = R + 3/2 R = 5/2 R = 20.8 \text{ J/K}\cdot\text{mol}$

115. (a) Determine the volume between 2.40 atm and 1.30 atm using  $PV = nRT$  that is, plug in the pressure into:

$$V = \frac{0.100 \text{ mol} \times 0.08206 \frac{\text{L atm}}{\text{K mol}} \times 298 \text{ K}}{P} = \frac{2.445 \text{ L atm}}{P}$$

For  $P = 2.40 \text{ atm}$ :  $V = 1.02 \text{ L}$

For  $P = 2.30 \text{ atm}$ :  $V = 1.06 \text{ L}$   $P\Delta V = 2.30 \text{ atm} \times -0.04 \text{ L} = -0.092 \text{ L atm}$

For  $P = 2.20 \text{ atm}$ :  $V = 1.11 \text{ L}$   $P\Delta V = 2.20 \text{ atm} \times -0.05 \text{ L} = -0.11 \text{ L atm}$

For  $P = 2.10 \text{ atm}$ :  $V = 1.16 \text{ L}$   $P\Delta V = 2.10 \text{ atm} \times -0.05 \text{ L} = -0.11 \text{ L atm}$

For  $P = 2.00 \text{ atm}$ :  $V = 1.22 \text{ L}$   $P\Delta V = 2.00 \text{ atm} \times -0.06 \text{ L} = -0.12 \text{ L atm}$

For  $P = 1.90 \text{ atm}$ :  $V = 1.29 \text{ L}$   $P\Delta V = 1.90 \text{ atm} \times -0.06 \text{ L} = -0.12 \text{ L atm}$

For  $P = 1.80 \text{ atm}$ :  $V = 1.36 \text{ L}$   $P\Delta V = 1.80 \text{ atm} \times -0.07 \text{ L} = -0.13 \text{ L atm}$

For  $P = 1.70 \text{ atm}$ :  $V = 1.44 \text{ L}$   $P\Delta V = 1.70 \text{ atm} \times -0.08 \text{ L} = -0.14 \text{ L atm}$

For  $P = 1.60 \text{ atm}$ :  $V = 1.53 \text{ L}$   $P\Delta V = 1.60 \text{ atm} \times -0.09 \text{ L} = -0.14 \text{ L atm}$

For  $P = 1.50 \text{ atm}$ :  $V = 1.63 \text{ L}$   $P\Delta V = 1.50 \text{ atm} \times -0.10 \text{ L} = -0.15 \text{ L atm}$

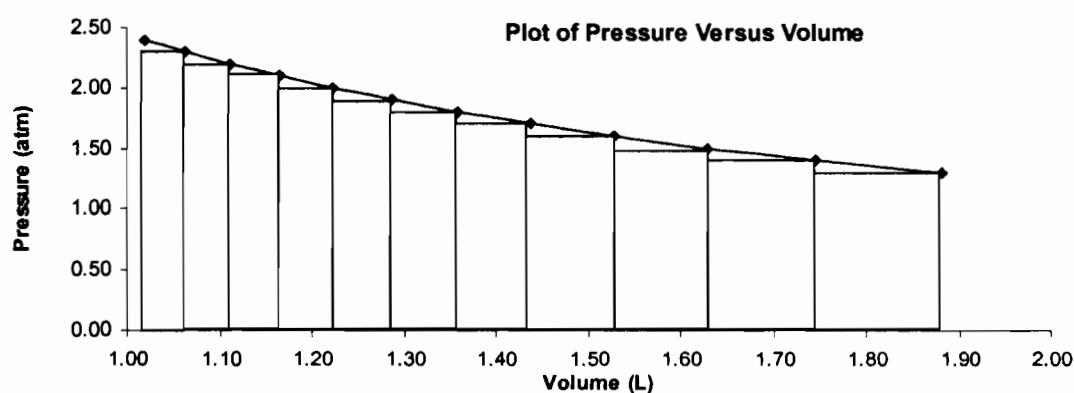
For  $P = 1.40 \text{ atm}$ :  $V = 1.75 \text{ L}$   $P\Delta V = 1.40 \text{ atm} \times -0.12 \text{ L} = -0.17 \text{ L atm}$

For  $P = 1.30 \text{ atm}$ :  $V = 1.88 \text{ L}$   $P\Delta V = 1.30 \text{ atm} \times -0.13 \text{ L} = -0.17 \text{ L atm}$

$$\text{Total Work} = -\sum P\Delta V = -1.45 \text{ L atm}$$

Expressed in joules, the work is  $-1.45 \text{ L atm} \times 101.325 \text{ J/L atm} = -147 \text{ J}$

(b)



- (c) The total work done in the two-step expansion is minus the total of the area of the two rectangles under the graph is  $-1.29 \text{ L atm}$  or  $-131 \text{ J}$ . In the 11-step expansion in (b), the total area of the rectangles is  $1.45 \text{ L atm}$  or  $-147 \text{ J}$ . If the expansion were divided into a larger number of stages, the total area of the rectangles would be still greater. The maximum amount of work is for an expansion with an infinite number of stages and is equal to the area under the pressure-volume curve between  $V = 1.02 \text{ L}$  and  $1.88 \text{ L}$ . This area is also obtained as the integral obtained from the expression:

$dw = -PdV = -nRT(dV/V)$ . The value obtained is:

$$w = -nRT \times \ln V_f/V_i = 0.100 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln (1.88 \text{ L}/1.02 \text{ L})$$

$$w = -152 \text{ J}$$

- (d) The maximum work of compression is for a one-stage compression using an external pressure of  $2.40 \text{ atm}$  and producing a compression in volume of  $1.02 \text{ L} - 1.88 \text{ L} = -0.86 \text{ L}$ :

$$w = -P\Delta V = (2.40 \text{ atm} \times 0.86 \text{ L}) \times 101.33 \text{ J/L atm} = 209 \text{ J}$$

The minimum work would be that done in an infinite number of steps and would be the same as the work determined in (c) but with a positive sign, that is,  $+152 \text{ J}$ .

- (e) Because the internal energy of an ideal gas is a function only of temperature, and the temperature remains constant,  $\Delta U = 0$ . Because  $\Delta U = q + w = 0$ ,  $q = -w$ , that is,  $-209 \text{ J}$  corresponding to the maximum work of compression and  $-152 \text{ J}$  corresponding to the minimum work of compression.

- (f) When the expansion described in part in (c),

$$q = -w = nRT \ln V_f/V_i \quad \text{and} \quad q/T = nR \ln V_f/V_i$$

Because the terms on the right side are all constants or functions of state, so too is the term on the left,  $q/T$ . In Chapter 20, we learn that  $q/T$  is equal to  $\Delta S$ , the change in a state function called *entropy*.

# CHAPTER 8

## THE ATMOSPHERIC GASES AND HYDROGEN

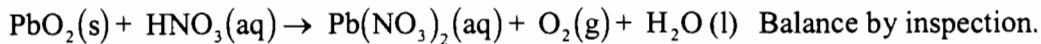
### PRACTICE EXAMPLES

**1A** By volume, the atmosphere is 0.934% Ar.  $V_{\text{air}} = 5.00 \text{ L Ar} \times \frac{100.00 \text{ L air}}{0.934 \text{ L Ar}} = 535 \text{ L air}$

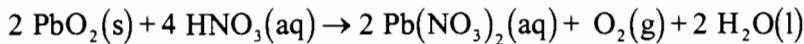
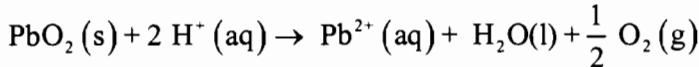
**1B** Calculate the volume of  $\text{CO}_2(\text{g})$ , and of air. The atmosphere is 0.037%  $\text{CO}_2(\text{g})$  by volume.

$$V_{\text{air}} = \frac{nRT}{P} = \frac{\frac{5.00 \text{ g CO}_2}{44.01 \text{ g CO}_2} \times \left( 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K} \right)}{1 \text{ atm}} \times \frac{100.00 \text{ L air}}{0.037 \text{ L CO}_2} = 7.5 \times 10^3 \text{ L air}$$

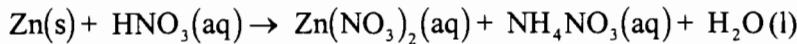
**2A** First substitute chemical formulas for names:



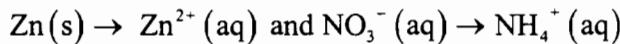
The oxidation and reduction reactants are in the same substance,  $\text{PbO}_2(\text{s})$ .



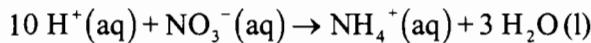
**2B** First substitute chemical formulas for names.



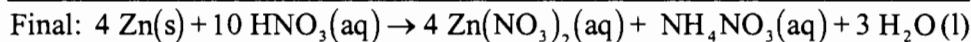
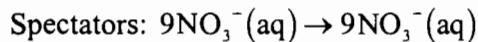
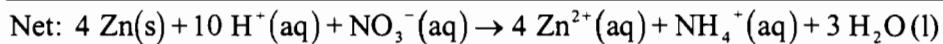
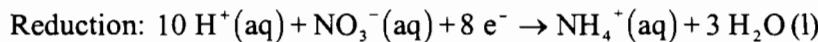
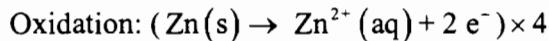
Then write the two skeleton half-equations:



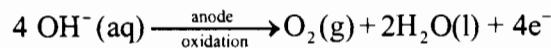
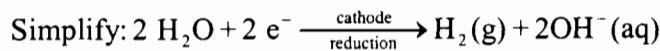
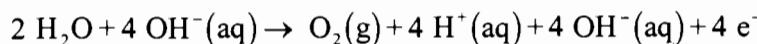
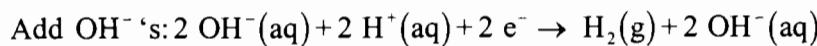
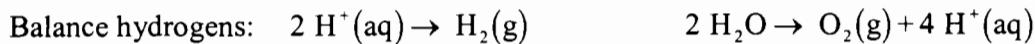
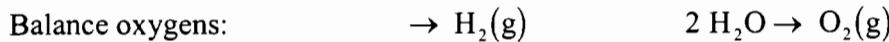
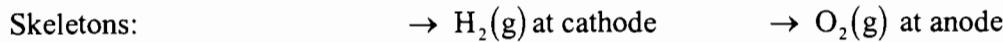
Balance the nitrogen half-equation for oxygen:



Balance the two half-equations for charge with electrons and then combine them to produce the net ionic equation. Finally, add in the nitrate spectator ions.



- 3A** As we learned in Chapter 5, half-equations for reactions in basic solution are initially balanced as if they occur in acidic solution. Both of the products in this case are composed of the elements of water. It is easiest to begin with skeleton half-equations that contain only products.



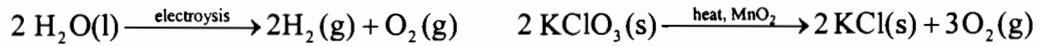
- 3B** First substitute chemical formulas for names:  $\text{Li}_2\text{O}_2(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{Li}_2\text{CO}_3(\text{s}) + \text{O}_2(\text{g})$   
 Simply use “2” as the stoichiometric coefficient of all species except  $\text{O}_2(\text{g})$ .  
 $2 \text{Li}_2\text{O}_2(\text{s}) + 2 \text{CO}_2(\text{g}) \rightarrow 2 \text{Li}_2\text{CO}_3(\text{s}) + \text{O}_2(\text{g})$ . Oxygen has an oxidation state of  $-1$  in  $\text{Li}_2\text{O}_2(\text{s})$ , and  $-2$  in  $\text{Li}_2\text{CO}_3(\text{s})$  and  $0$  in  $\text{O}_2(\text{g})$ . Thus,  $\text{Li}_2\text{O}_2(\text{s})$  is both an oxidizing agent and a reducing agent.

## REVIEW QUESTIONS

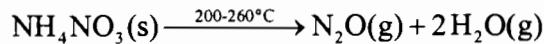
- Relative humidity is the ratio of the partial pressure of water vapor to the vapor pressure of water at a given temperature.
  - A noble gas is one of the elements in periodic table family 8A: He, Ne, Ar, Kr, Xe, and Rn. These elements are called “noble” because they form few compounds with the other elements. Like “nobility”, they do not associate with the other elements.
  - A chlorofluorocarbon is a compound, derived from a hydrocarbon that contains the elements carbon, chlorine, and fluorine. These compounds are good-to-excellent refrigerants, but their release into the atmosphere is implicated in the destruction of the ozone layer in the upper atmosphere.
  - A nonstoichiometric compound is one in which the ratio of moles of the constituent elements is not a ratio of small whole numbers.

- 2.** (a) Fractional Distillation is a method used to separate a mixture of volatile components of different boiling points. The mixture is distilled starting at the lowest boiling point where the distillate is collected as one fraction. When the temperature of the vapor rises, the next highest boiling component of the mixture distills. This component is then collected as a separate fraction.
- (b) Electrolysis is the process by which a non-spontaneous redox reaction is made spontaneous through the passage of electric current from an external power source.
- (c) Hydrogenation reaction is a reaction where molecular hydrogen ( $H_2(g)$ ) is added to double or triple bonds. Reaction is generally done in the presence of a catalyst and may involve high pressures and temperatures.
- (d) Dew and frost formation result from fluctuations in the relative humidity with temperature. When water vapor condenses on the earth's surface - this is known as dew; however, if the temperature drops below  $0\text{ }^{\circ}\text{C}$ , frost formation results (frozen dew).
- 3.** (a) The troposphere is the first 12 km of the Earth's atmosphere, the region in which we live and within which weather occurs. The stratosphere is the next layer, 12 to 50 km above the Earth's surface.
- (b) An allotrope is a form of an element that differs from another form in physical and chemical properties. An isotope is an alternative version of an atom that differs in the neutron number.
- (c) A "fuel-lean" mixture in an engine is one in which there is more air than is needed to completely burn the fuel. In a "fuel-rich" mixture, there is an abundance of fuel and insufficient air.
- (d) An ionic hydride is composed of the hydride anion and an active metal cation; it is a stoichiometric compound. Metallic hydrides are composed of hydrogen and less active metals. It actually consists of hydrogen atoms in the voids present in the metallic lattice. It is a nonstoichiometric compound.
- 4.** (a)  $O_3$ , ozone (b)  $N_2O$ , dinitrogen monoxide (nitrous oxide)
- (c)  $KO_2$ , potassium superoxide (d)  $CaH_2$ , calcium hydride
- (e)  $Mg_3N_2$ , magnesium nitride (f)  $K_2CO_3$ , potassium carbonate
- (g)  $NH_4H_2PO_4$ , ammonium dihydrogen phosphate
- 5.** (a)  $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$  and  $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2O(g)$
- (b) coke: almost pure C (c) urea:  $CO(NH_2)_2$  (d) limestone: principally  $CaCO_3$
- (e) a mixture of  $CO(g)$  and  $H_2(g)$ , produced by steam reforming of a hydrocarbon.
- 6.** (a)  $NO_2$  has N in O.S. = +4. (b)  $KO_2$  has O in O.S. = -1/2.
- (c)  $N_2O$  has N in O.S. = +1. (d)  $CaH_2$  has H in O.S. = -1. (e) CO has C in O.S. = +2.

7. (a) Small quantities of  $O_2(g)$  can be prepared either by the electrolysis of water, or by the gentle heating of  $KClO_3(s)$  in the presence of a  $MnO_2(s)$  catalyst.



- (b) Small quantities of  $N_2O(g)$  can be produced by the thermal decomposition of ammonium nitrate.

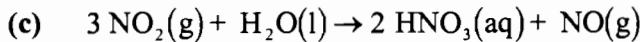
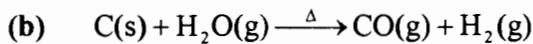


- (c) Small quantities of  $H_2(g)$  can be produced by the reaction of a moderately active metal with a strong acid:  $Zn(s) + 2 HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

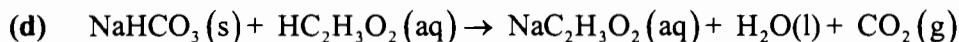
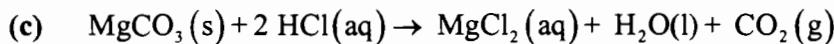
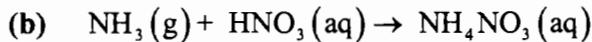
- (d) Small quantities of  $CO_2(g)$  can be produced by the reaction of a metal carbonate with a strong acid.  $CaCO_3(s) + 2 HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

8. For a reagent to be an oxidizing agent, it must have atoms that can be easily reduced (to a lower oxidation state).  $H_2$  and  $NH_3$  are not oxidizing reagents as they are in their lowest common oxidation states for the two elements (0 and -3, for H and N, respectively). Both  $NO_2$  and  $NO$  have the potential to be oxidizing agents (N in the +4 and +2 oxidation states respectively).  $NO_2$  would be the best oxidizing agent as nitrogen in this compound is in a higher oxidation state and, as we have seen in this chapter, it can be reduced to  $NO$  (e.g. see equations 8.8 and 8.9).

9. (a)  $LiH(s) + H_2O(l) \rightarrow Li^+(aq) + OH^-(aq) + H_2(g)$

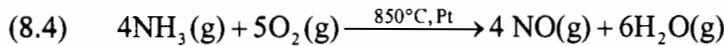


10. (a)  $Mg(s) + 2 HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

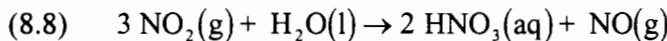


11. Aqueous sulfuric acid is  $H_2SO_4(aq)$ ; aqueous ammonia is  $NH_3(aq)$ . The equation for their complete neutralization is:  $H_2SO_4(aq) + 2 NH_3(aq) \rightarrow (NH_4)_2SO_4(aq)$

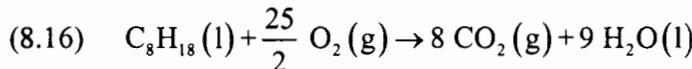
12. We can identify oxidizing and reducing agents by changes in oxidation state. The oxidation state of one element in an oxidizing agent is lowered, while the oxidation state of one element in a reducing agent is raised.



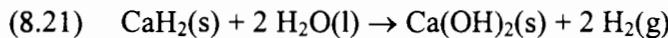
The oxidation state of N is -3 on the left- and +2 on the right-hand side of this equation; the O.S. of N increases.  $\text{NH}_3(\text{g})$  is the reducing agent. The oxidation state of O is 0 on the left- and -2 on the right-hand side of this equation; the O.S. of O decreases.  $\text{O}_2(\text{g})$  is the oxidizing agent.



The oxidation state of N is +4 on the left- and +5 in  $\text{HNO}_3(\text{aq})$  on the right-hand side of this equation; the O.S. of N increases.  $\text{NO}_2(\text{g})$  is the reducing agent. The oxidation state of N is +4 on the left- and +2 in  $\text{NO}(\text{g})$  on the right-hand side of this equation; the O.S. of O decreases.  $\text{NO}_2(\text{g})$  is also the oxidizing agent. This is a disproportionation reaction.

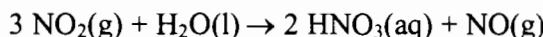


The oxidation state of C is 2.25 on the left- and +4 on the right-hand side of this equation; the O.S. of C increases.  $\text{C}_8\text{H}_{18}(\text{l})$  is the reducing agent. The oxidation state of O is 0 on the left- and -2 on the right-hand side of this equation; the O.S. of oxygen decreases.  $\text{O}_2(\text{g})$  is the oxidizing agent.

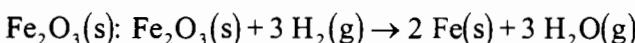


The oxidation state for H in  $\text{CaH}_2(\text{s})$  is -1 and in  $\text{H}_2(\text{g})$  it is 0. Consequently,  $\text{CaH}_2(\text{s})$  is the reducing agent (H is oxidized in the process). The oxidation state for H in  $\text{H}_2\text{O}(\text{l})$  is +1 and in  $\text{H}_2(\text{g})$  it is 0. Consequently,  $\text{H}_2\text{O}(\text{l})$  is the oxidizing agent (H is reduced in the process).

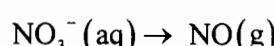
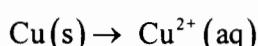
13. The third step in the Ostwald process is a disproportionation reaction ( $\text{N}^{4+} \rightarrow \text{N}^{2+}$  and  $\text{N}^{5+}$ ):



14. The oxide of iron with an oxidation state of +3 is



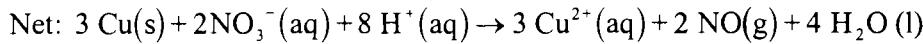
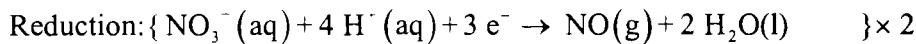
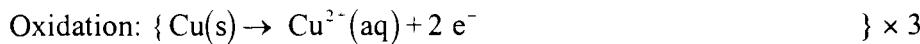
15. We assume that copper is oxidized to copper(II) ion. The skeleton half-equations are as follows.



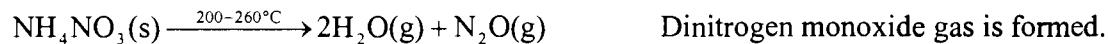
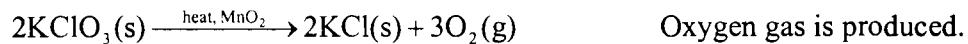
The nitrogen-containing half-reaction is balanced in two steps, first balance for O then for H.



The two half-equations then are balanced for charge using electrons and combined to produce the net ionic equation. Finally, nitrate spectator ions are added to give the balanced equation.



16. The gaseous thermal decomposition product is given as the last product in each of these chemical equations.



17. (a) The basic causes of photochemical smog are high temperature combustion processes, notably those associated with automobile engines (aircraft and industrial processes also contribute to this problem).
- (b) Ozone layer depletion results from two major sources: (1) Nitrogen monoxides produced by combustion reactions (supersonic jets operating in the stratosphere) or from natural sources ( $\text{NO}_2$  producing bacteria) and (2) chlorofluorocarbons (CFC's) which have been inadvertently released into the atmosphere. CFCs are particularly worrisome as they have a very long lifetime in the atmosphere.
- (c) The major cause of global warming is increased levels of carbon dioxide ( $\text{CO}_2$ ) resulting from the burning of carbon-containing fuels and deforestation of tropical regions.
18. Catalytic converters are basically smog control devices on newer automobiles. Catalytic converters have an oxidation catalyst that oxidizes CO and hydrocarbons to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . It may also have a reduction catalyst that reduces NO to  $\text{N}_2$ . The catalysts involved with these processes are generally platinum or palladium metal operating at relatively high temperature.
19. He is found in natural gas deposits principally because alpha particles are produced during natural radioactive decay processes. These alpha particles are  ${}^4\text{He}$  nuclei; they obtain two electrons from the surrounding material to become helium atoms. This gaseous helium then accumulates with the natural gas trapped beneath the earth. Although other noble gases are produced by radioactive decay—notably  ${}^{40}\text{Ar}$ —they are not produced in the large quantities that helium is.

- 20.** Replacing petroleum products with hydrogen as a fuel for transportation has the following advantages and disadvantages.

Advantages: Eventual decline of supplies of fossil fuels requires finding alternative energy sources. Hydrogen would provide an essentially pollution free exhaust and more efficient fuel. Range of supersonic aircraft could be increased and hypersonic planes become a real possibility.

Disadvantages: Sources of hydrogen gas are relatively expensive along with high storage cost for the gas. Very low temperatures are required for hydrogen storage ( $\text{bp} = -253^\circ\text{C}$ ). Hydrogen must be maintained out of the contact with oxygen or air (explosive mixtures).

## EXERCISES

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### The Atmosphere

- 21.** We assume that the gases in the atmosphere obey the ideal gas law,  $PV = nRT$ . Then the amount in moles of a particular gas will be given by  $n = \frac{PV}{RT}$ . Since all of the gases in the mixture are at the same temperature and subjected to the same total pressure, their amounts in moles are proportional to their volumes, with the same proportionality constant ( $P/RT$ ) for each gas in the mixture. Therefore, volume percents and mole percents will be the same.

### Nitrogen

- 23.** (a) The Haber-Bosch process is the principal artificial method of fixing atmospheric nitrogen.  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
- (b) The 1<sup>st</sup> step of the Ostwald process:  $4\text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \xrightarrow{850^\circ\text{C}, \text{Pt}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- (c) The 2<sup>nd</sup> and 3<sup>rd</sup> steps of the process:  $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$   
 $3 \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$

- 25.** Decomposition of  $\text{HNO}_3(\text{l})$ :  $\text{HNO}_3(\text{l}) \rightarrow \text{N}_2\text{O}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

Although this equation can be balanced by the half-reaction method, it also can be balanced by inspection. First notice that all of the N is present in  $\text{N}_2\text{O}_4(\text{g})$  in the products. This implies that there are two  $\text{HNO}_3(\text{aq})$ :  $2 \text{HNO}_3(\text{l}) \rightarrow \text{N}_2\text{O}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ . With this addition, N and H are balanced, and we need to only consider balancing oxygen. There are 6 O's on the left and 7 O's on the right, an imbalance that can be corrected either by making 1/2 the coefficient of  $\text{O}_2(\text{g})$  or by doubling all of the other coefficients and leaving the  $\text{O}_2(\text{g})$  coefficient alone:  $4 \text{HNO}_3(\text{l}) \rightarrow 2 \text{N}_2\text{O}_4(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

27. We recall that 1 mol of gas occupies 22.414 L at STP.

$$\begin{aligned}\text{mass N}_2 &= 9.39 \times 10^{11} \text{ ft}^3 \times \left( \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{1 \text{ mol N}_2}{22.414 \text{ L}} \times \frac{28.01 \text{ g N}_2}{1 \text{ mol}} \\ &\quad \times \frac{1 \text{ kg}}{1000 \text{ g}} = 3.32 \times 10^{10} \text{ kg N}_2\end{aligned}$$

29.  $75 \times 10^9 \text{ gal} \times \frac{15 \text{ miles}}{1 \text{ gal}} \times \frac{5 \text{ g}}{1 \text{ mile}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 6 \times 10^9 \text{ kg of nitrogen oxides released.}$

## Oxygen

31. (a)  $2\text{HgO(s)} \xrightarrow{\Delta} 2\text{Hg(l)} + \text{O}_2(\text{g})$  (b)  $2\text{KClO}_4(\text{s}) \xrightarrow{\Delta} 2\text{KClO}_3(\text{s}) + \text{O}_2(\text{g})$

33. We first write the formulas of the four substances:  $\text{N}_2\text{O}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_4\text{O}_6$ ,  $\text{CO}_2$ . The one constant in all these substances is oxygen. If we compare amounts of substance with the same amount (in moles) of oxygen, the one with the smallest mass of the other element will have the highest percent oxygen.

3 mol  $\text{N}_2\text{O}_4$  contains 12 mol O and 6 mol N:  $6 \times 14.0 = 84.0 \text{ g N}$

4 mol  $\text{Al}_2\text{O}_3$  contains 12 mol O and 8 mol Al:  $8 \times 27.0 = 216 \text{ g Al}$

2 mol  $\text{P}_4\text{O}_6$  contains 12 mol O and 8 mol P:  $8 \times 31.0 = 248 \text{ g P}$

6 mol  $\text{CO}_2$  contains 12 mol O and 6 mol C:  $6 \times 12.0 = 72.0 \text{ g C}$

Thus, of the oxides listed,  $\text{CO}_2$  contains the largest percent oxygen by mass.

35. Recall that fraction by volume and fraction by pressure are numerically equal. Additionally, one atmosphere pressure is equivalent to 760 mmHg. We combine these two facts.

$$P\{\text{O}_3\} = 760 \text{ mmHg} \times \frac{0.04 \text{ mmHg of O}_3}{10^6 \text{ mmHg of atmosphere}} = 3 \times 10^{-5} \text{ mmHg}$$

37. The electrolysis reaction is  $2\text{H}_2\text{O(l)} \xrightarrow{\text{electrolysis}} 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ . In this reaction, 2 moles of  $\text{H}_2(\text{g})$  are produced for each mole of  $\text{O}_2(\text{g})$ , by the law of combining volumes, we would expect the volume of hydrogen to be twice the volume of oxygen produced. (Actually the volumes are not exactly in the ratio of 2:1 because of the different solubilities of oxygen and hydrogen in water.)

## The Noble Gases

39. First we use the ideal gas law to determine the amount in moles of argon.

$$n = \frac{PV}{RT} = \frac{145 \text{ atm} \times 55 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 299 \text{ K}} = 3.25 \times 10^2 \text{ mol Ar}$$

$$\text{L air} = 3.25 \times 10^2 \text{ mol Ar} \times \frac{22.414 \text{ L Ar STP}}{1 \text{ mol Ar}} \times \frac{100.000 \text{ L air}}{0.934 \text{ L Ar}} = 7.8 \times 10^5 \text{ L air}$$

41. 1 mol of the mixture at STP occupies a volume of 22.414 L. It contains 0.79 mol He and 0.21 mol O<sub>2</sub>.

$$\text{STP density} = \frac{\text{mass}}{\text{volume}} = \frac{0.79 \text{ mol He} \times \frac{4.003 \text{ g He}}{1 \text{ mol He}} + 0.21 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2}}{22.414 \text{ L}} = 0.44 \text{ g/L}$$

25°C is a temperature higher than STP. This condition increases the 1.00-L volume that contains 0.44 g of the mixture at STP. We calculate the expanded volume with the combined gas law.

$$V_{\text{final}} = 1.00 \text{ L} \times \frac{(25 + 273.2) \text{ K}}{273.2 \text{ K}} = 1.09 \text{ L} \quad \text{final density} = \frac{0.44 \text{ g}}{1.09 \text{ L}} = 0.40 \text{ g/L}$$

## Carbon

43. (a)  $2 \text{C}_6\text{H}_{14}(\text{l}) + 19 \text{O}_2(\text{g}) \rightarrow 12 \text{CO}_2(\text{g}) + 14 \text{H}_2\text{O}(\text{l})$   
 (b)  $\text{PbO}(\text{s}) + \text{CO}(\text{g}) \xrightarrow{\text{heat}} \text{Pb}(\text{s}) + \text{CO}_2(\text{g})$   
 (c)  $2 \text{KOH}(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{K}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 (d)  $\text{MgCO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

45. The reaction referred to is exemplified by



the action of hydrochloric acid on calcium carbonate. Notice that no oxidation states change in this reaction; it is a double displacement reaction followed by the decomposition of "H<sub>2</sub>CO<sub>3</sub>(aq)". Since the carbon dioxide produced in this reaction is not formed from elemental carbon or by the oxidation of a carbon-containing compound, it cannot be partially oxidized. Thus, no CO(g) will form.

47. The combustion reaction:  $\text{C}_8\text{H}_{18}(\text{l}) + 25/2 \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{l})$

First compute the enthalpy change for combustion.

$$\Delta H^\circ = 8\Delta H_f^\circ[\text{CO}_2(\text{g})] + 9\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - [\Delta H_f^\circ[\text{C}_8\text{H}_{18}(\text{l})] + \frac{25}{2}\Delta H_f^\circ[\text{O}_2(\text{g})]]$$

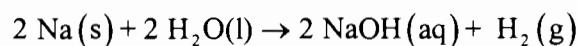
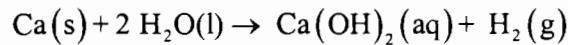
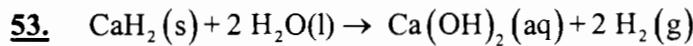
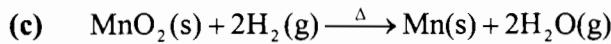
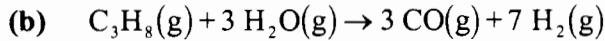
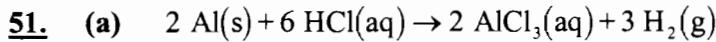
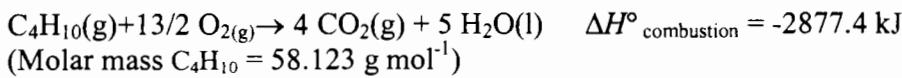
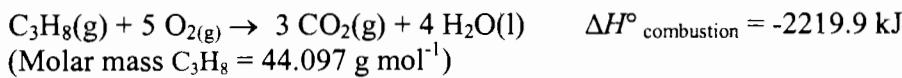
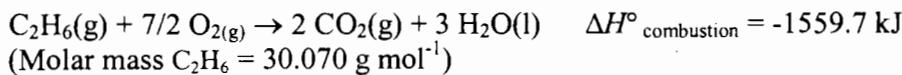
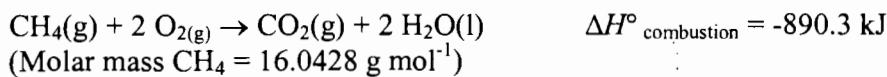
$$\Delta H^\circ = 8(-393.5) + 9(-285.8) - (-250.0) - 25/2(0.00) = -5470 \text{ kJ/mol C}_8\text{H}_{18}$$

Then determine the heat produced from each gallon of gasoline.

$$\begin{aligned} \text{heat produced} &= 1.00 \text{ gal} \times \frac{3.785 \text{ L}}{1 \text{ gal}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.703 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.23 \text{ g C}_8\text{H}_{18}} \times \frac{5470 \text{ kJ}}{1 \text{ mol C}_8\text{H}_{18}} \\ &= 1.27 \times 10^5 \text{ kJ of heat} \quad (\text{Note that } \Delta H = -1.27 \times 10^5 \text{ kJ}) \end{aligned}$$

## Hydrogen

**49.** The four reactions of interest are: (Note:  $\Delta H^\circ_{\text{combustion}} = \sum \Delta H^\circ_{\text{f, products}} - \sum \Delta H^\circ_{\text{f, reactants}}$ )



(a) The reaction that produces the largest volume of  $\text{H}_2(\text{g})$  per liter of water also produces the largest amount of  $\text{H}_2(\text{g})$  per mole of water used. All three reactions use two moles of water and the reaction with  $\text{CaH}_2(\text{s})$  produces the most  $\text{H}_2(\text{g})$ .

(b) We can compare three reactions that produce the same amount of hydrogen; the one that requires the smallest mass of solid produces the greatest amount of  $\text{H}_2$  per gram of solid. The amount of hydrogen we choose is 2 moles, which means that we compare 1 mol  $\text{CaH}_2$  (42.09 g) with 2 mol Ca (80.16 g) and with 4 mol Na (91.96 g). Clearly  $\text{CaH}_2$  produces the greatest amount of  $\text{H}_2$  per gram of solid.

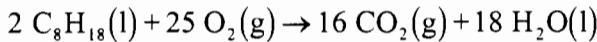
**55.** Greatest mass percent hydrogen:

The atmosphere is mostly  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$  with only a trace of hydrogen containing gas molecules. Seawater is  $\text{H}_2\text{O}(\text{l})$ , natural gas is  $\text{CH}_4(\text{g})$  and ammonia is  $\text{NH}_3(\text{g})$ . Each of these compounds have one non-hydrogen atom, each of which have approximately the same mass ( $\sim 14 \pm 2 \text{ g mol}^{-1}$ ). Since  $\text{CH}_4$  has the highest hydrogen atom to non-hydrogen atom ratio, this molecule has the greatest mass percent hydrogen.

## FEATURE PROBLEMS

- 71.** (a) An engine with a fuel-lean mixture will produce large proportions of nitrogen oxides since there is a large amount of air (which contains nitrogen and oxygen) compared to the fuel. On the other hand, an engine with a fuel-rich mixture will produce unburned fuel (RH) and carbon monoxide, because of the lack of oxygen.

- (b) First we balance the combustion reaction.



$$\frac{\text{air}}{\text{fuel}} = \frac{25 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} \times \frac{100 \text{ mol air}}{20.946 \text{ mol O}_2} \times \frac{28.95 \text{ g}}{1 \text{ mol air}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.2 \text{ g C}_8\text{H}_{18}} = 15 : 1$$

We used the average molar mass of air from Exercise 42.

- 72.** (a) The  $\text{N}_2(\text{g})$  extracted from liquid air has some  $\text{Ar}(\text{g})$  mixed in. Only  $\text{O}_2(\text{g})$  was removed from liquid air in the oxygen-related experiments.
- (b) Because of the presence of  $\text{Ar}(\text{g})$  [39.95 g/mol], the  $\text{N}_2(\text{g})$  [28.01 g/mol] from liquid air will have a greater density than  $\text{N}_2(\text{g})$  from nitrogen compounds.
- (c) Magnesium will react with nitrogen  $[3 \text{Mg}(\text{s}) + \text{N}_2(\text{g}) \rightarrow \text{Mg}_3\text{N}_2(\text{s})]$  but not with Ar. Thus, magnesium reacts with all the nitrogen in the mixture, but leaves the relatively inert Ar(g) unreacted.
- (d) The “nitrogen” remaining after oxygen is extracted from each mole of air (Rayleigh’s mixture) contains  $(0.78084 + 0.00934) = 0.79018 \text{ mol}$  and has the mass calculated below.

$$\text{mass of gaseous mixture} = (0.78084 \times 28.013 \text{ g/mol N}_2) + (0.00934 \times 39.948 \text{ g/mol Ar})$$

$$\text{mass of gaseous mixture} = 21.874 \text{ g N}_2 + 0.373 \text{ g Ar} = 22.247 \text{ g mixture.}$$

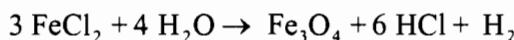
Then, the molar mass of the mixture can be computed:  $22.247 \text{ g mixture} / 0.79018 \text{ mol} = 28.154 \text{ g/mol}$ . Since the STP molar volume of an ideal gas is 22.414 L, we can compute the two densities.

$$d(\text{N}_2) = \frac{28.013 \text{ g/mol}}{22.414 \text{ L/mol}} = 1.2498 \text{ g/mol} \quad d(\text{mixture}) = \frac{28.154 \text{ g/mol}}{22.414 \text{ L/mol}} = 1.2561 \text{ g/mol}$$

These densities differ by 0.50%.

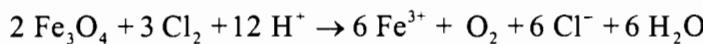
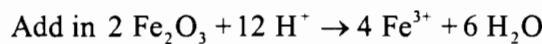
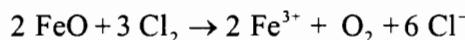
73. The goal is to demonstrate that the three reactions result in the decomposition of water as the net reaction: Net:  $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$  First balance each equation.

(1)  $3 \text{FeCl}_2 + 4 \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{HCl} + \text{H}_2$  Balance by inspection. Notice that there are 3 Fe and 4 O on the right-hand side. Then balance Cl.



(2)  $\text{Fe}_3\text{O}_4 + \text{HCl} + \text{Cl}_2 \rightarrow \text{FeCl}_3 + \text{H}_2\text{O} + \text{O}_2$  Try the half-equation method.

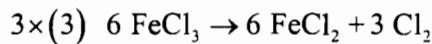
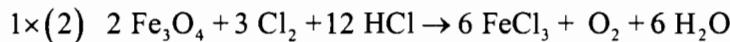
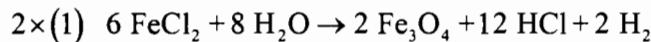
$\text{Cl}_2 + 2 \text{e}^- \rightarrow 2 \text{Cl}^-$  But realize that  $\text{Fe}_3\text{O}_4 = \text{Fe}_2\text{O}_3 \cdot \text{FeO}$ ; only iron(II) needs to be oxidized.  $2 \text{FeO} \rightarrow 2 \text{Fe}^{3+} + \text{O}_2 + 6 \text{e}^-$  Now combine the two half-equations.



And 12  $\text{Cl}^-$  spectators:  $2 \text{Fe}_3\text{O}_4 + 3 \text{Cl}_2 + 12 \text{HCl} \rightarrow 6 \text{FeCl}_3 + \text{O}_2 + 6 \text{H}_2\text{O}$

(3)  $\text{FeCl}_3 \rightarrow \text{FeCl}_2 + \text{Cl}_2$  by inspection  $2 \text{FeCl}_3 \rightarrow 2 \text{FeCl}_2 + \text{Cl}_2$

One strategy is to consider each of the three equations and the net equation. Only equation (1) produces hydrogen; run it twice. Only equation (2) produces oxygen; run it once. Equation (3) can balance out the  $\text{Cl}_2$  required by equation (2); run it three times.




---

Net:  $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$

# CHAPTER 9

## ELECTRONS IN ATOMS

### PRACTICE EXAMPLES

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**1A** Use  $c = \lambda \nu$ , solve for frequency.  $\nu = \frac{2.9979 \times 10^8 \text{ m/s}}{690 \text{ nm}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 4.34 \times 10^{14} \text{ Hz}$

**1B** Wavelength and frequency are related through the equation  $c = \lambda \nu$ , which can be solved for either one.

$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{91.5 \times 10^6 \text{ s}^{-1}} = 3.28 \text{ m} \quad \text{Note that } \text{Hz} = \text{s}^{-1}$$

**2A** The relationship  $\nu = c / \lambda$  can be substituted into the equation  $E = h\nu$  to obtain  $E = hc / \lambda$ . This energy, in J/photon, can then be converted to kJ/mol.

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js photon}^{-1} \times 2.998 \times 10^8 \text{ ms}^{-1}}{230 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ = 520 \text{ kJ/mol}$$

With a similar calculation one finds that 290 nm corresponds to 410 kJ/mol. Thus, the energy range is from 400 to 520 kJ/mol, respectively.

**2B** The equation  $E = h\nu$  is solved for frequency and the two frequencies are calculated.

$$\nu = \frac{E}{h} = \frac{3.056 \times 10^{-19} \text{ J / photon}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s / photon}} \quad \nu = \frac{E}{h} = \frac{4.414 \times 10^{-19} \text{ J / photon}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s / photon}} \\ = 4.612 \times 10^{14} \text{ Hz} \quad = 6.662 \times 10^{14} \text{ Hz}$$

To determine color, we calculate the wavelength of each frequency and compare it with *text* Figure 9-3.

$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{4.612 \times 10^{14} \text{ Hz}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} \quad \lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{6.662 \times 10^{14} \text{ Hz}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} \\ = 650 \text{ nm} \quad \text{orange} \quad = 450 \text{ nm} \quad \text{indigo}$$

The colors of the spectrum that are not absorbed are what we see when we look at a plant: blue, green, and yellow. The plant appears green.

**3A** We solve the Rydberg equation for  $n$  to see if we obtain an integer.

$$n = \sqrt{n^2} = \sqrt{\frac{-R_H}{E_n}} = \sqrt{\frac{-2.179 \times 10^{-18} \text{ J}}{-2.69 \times 10^{-20} \text{ J}}} = \sqrt{81.00} = 9.00 \quad \text{Thus, } E_9 = -2.69 \times 10^{-20} \text{ J}$$

**3B** It is not likely that an atomic radius would be precisely equal to an arbitrary unit of length, but let us see how close the radii are.  $1 \text{ nm} = 1000 \text{ pm}$ , so we solve the following for  $n$ .

$$1000 \text{ pm} = n^2 53 \text{ pm} \quad n = \sqrt{\frac{1000}{53}} = 4.3$$

We see that no radius is exactly 1 nm. The closest:

$$r_4 = 4^2 a_0 = 16 \times 0.053 \text{ nm} = 0.85 \text{ nm} \quad r_5 = 5^2 a_0 = 25 \times 0.053 \text{ nm} = 1.3 \text{ nm}$$

**4A** We first determine the energy difference, and then the wavelength of light corresponding to that energy.

$$\Delta E = R_H \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 2.179 \times 10^{-18} \text{ J} \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 4.086 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{4.086 \times 10^{-19} \text{ J}} = 4.862 \times 10^{-7} \text{ m} = 486.2 \text{ nm}$$

**4B** The longest wavelength light results from the transition that spans the smallest difference in energy. Since all Lyman series emissions end with  $n_f = 1$ , the smallest energy transition has  $n_i = 2$ . From this, we obtain the value of  $\Delta E$ .

$$\Delta E = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.179 \times 10^{-18} \text{ J} \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = -1.634 \times 10^{-18} \text{ J}$$

From this energy emitted, we can obtain the wavelength of the emitted light:  $\Delta E = hc / \lambda$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{1.634 \times 10^{-18} \text{ J}} = 1.216 \times 10^{-7} \text{ m} = 121.6 \text{ nm} = 1216 \text{ angstroms}$$

**5A**

$$\left. \begin{array}{l} E_f = \frac{-Z^2 \times R_H}{n_f^2} = \frac{-4^2 \times 2.179 \times 10^{-18} \text{ J}}{3^2} \\ E_f = -3.874 \times 10^{-18} \text{ J} \\ \\ E_i = \frac{-Z^2 \times R_H}{n_i^2} = \frac{-4^2 \times 2.179 \times 10^{-18} \text{ J}}{5^2} \\ E_i = -1.395 \times 10^{-18} \text{ J} \end{array} \right\} \begin{array}{l} \Delta E = E_f - E_i \\ \Delta E = (-3.874 \times 10^{-18} \text{ J}) - (-1.395 \times 10^{-18} \text{ J}) \\ \Delta E = -2.479 \times 10^{-18} \text{ J} \end{array}$$

To determine the wavelength, use  $E = h\nu = \frac{hc}{\lambda}$ ; Rearrange for  $\lambda$ :

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ Js}) \left( 2.998 \times 10^8 \frac{\text{m}}{\text{s}} \right)}{2.479 \times 10^{-18} \text{ J}} = 8.013 \times 10^{-8} \text{ m} = 80.13 \text{ nm}$$

**5B** Since  $E = \frac{-Z^2 \times R_H}{n^2}$ , the transitions are related to  $Z^2$ , hence, if the frequency is 16 times

$$\text{greater, then the value of the ratio } \frac{Z^2(\text{?-atom})}{Z^2(\text{H-atom})} = \frac{Z^2}{1^2} = 16$$

We can easily see  $Z^2 = 16$  or  $Z = 4$  corresponding to a Be nucleus.  
The hydrogen-like ion must be  $\text{Be}^{3+}$ .

**6A** Superman's de Broglie wavelength is given by the relationship  $\lambda = h / m\nu$

$$\lambda = \frac{h}{m\nu} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{91 \text{ kg} \times \frac{1}{5} \times 2.998 \times 10^8 \text{ m/s}} = 1.21 \times 10^{-43} \text{ m}$$

**6B** The de Broglie wavelength is given by  $\lambda = h / m\nu$  which can be solved for  $\nu$ .

$$\nu = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{1.673 \times 10^{-27} \text{ kg} \times 0.0100 \times 10^{-9} \text{ m}} = 3.96 \times 10^4 \text{ m/s}$$

We used the facts that  $1 \text{ J} = \text{kg m}^2 \text{s}^{-2}$ ,  $1 \text{ nm} = 10^{-9} \text{ m}$  and  $1 \text{ g} = 10^{-3} \text{ kg}$

**7A**  $p = (91 \text{ kg})(5.996 \times 10^7 \text{ m s}^{-1}) = 5.46 \times 10^9 \text{ kg m s}^{-1}$

$$\Delta p = (0.015)(5.46 \times 10^9 \text{ kg m s}^{-1}) = 8.2 \times 10^7 \text{ kg m s}^{-1}$$

$$\Delta x = \frac{h}{4\pi \Delta p} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{(4\pi)(8.2 \times 10^7 \frac{\text{kg m}}{\text{s}})} = 6.4 \times 10^{-43} \text{ m}$$

**7B**  $24 \text{ nm} = 2.4 \times 10^{-8} \text{ m} = \Delta x = \frac{h}{4\pi \Delta p} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{(4\pi)(\Delta p)}$

Solve for  $\Delta p$ :  $\Delta p = 2.2 \times 10^{-27} \text{ kg m s}^{-1}$

$$(\Delta\nu)(m) = \Delta p = 2.2 \times 10^{-27} \text{ kg m s}^{-1} = (\Delta\nu)(1.67 \times 10^{-27} \text{ kg}) \quad \text{Hence, } \Delta\nu = 1.3 \text{ m s}^{-1}$$

**8A** The value of  $\ell$  can range from 0 to  $n-1$ ; in this case,  $\ell=0$  is acceptable. The value of  $m_\ell$  is integral and ranges from  $-\ell$  to  $+\ell$ ; in this case,  $m_\ell=0$  is acceptable.

Yes, an orbital can have  $n=3$ ,  $\ell=0$ , and  $m_\ell=0$ .

**8B** The first restriction is that  $\ell$  must be an integer smaller than  $n$ . This restricts  $\ell$  to the values: 2, 1, and 0. The second restriction is that the absolute value of  $m_\ell$  must be an integer equal to or smaller than  $\ell$ . This further restricts  $\ell$ , and the only allowed values are:  $\ell = 2$  and  $\ell = 1$ .

**9A** The magnetic quantum number,  $m_\ell$ , is not reflected in the orbital designation. Because  $\ell = 1$ , this is a  $p$  orbital. Because  $n = 3$ , the designation is  $3p$ .

**9B** The H-atom orbitals  $3s$ ,  $3p$  and  $3d$  are degenerate. Therefore, the 9 quantum number combinations are:

$n$	$\ell$	$m_\ell$
3s	3	0
3p	3	1
3d	3	2

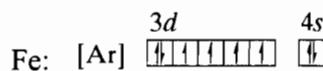
-1,0,+1  
-2,-1,0,+1,+2

**10A** We can simply sum the exponents to obtain the number of electrons in the neutral atom and thus the atomic number of the element.  $Z = 2 + 2 + 6 + 2 + 6 + 2 + 2 = 22$ , which is the atomic number for Ti.

**10B** Iodine has an atomic number of 53. The first 36 electrons have the same electron configuration as Kr:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ . The next two electrons go into the  $5s$  subshell ( $5s^2$ ), then 10 electrons fill the  $4d$  subshell ( $4d^{10}$ ), accounting for a total of 48 electrons. The last five electrons partially fill the  $5p$  subshell ( $5p^5$ ).

The electron configuration of I is therefore  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$ . Each iodine atom has ten  $3d$  electrons and one unpaired  $5p$  electron.

**11A** Iron has 26 electrons, of which 18 are accounted for by the [Ar] configuration. Beyond [Ar] there are two  $4s$  electrons and six  $3d$  electrons, as shown in the following orbital diagram.



**11B** Bismuth has 83 electrons, of which 54 are accounted for by the [Xe] configuration. Beyond [Xe] there are two  $6s$  electrons, fourteen  $4f$  electrons, ten  $5d$  electrons, and three  $6p$  electrons, as shown in the following orbital diagram.



- 12A** (a) Tin is in the 5<sup>th</sup> period, hence, five electronic shells are filled or partially filled.  
(b) The 3p subshell was filled with Ar; there are six 3p electrons in an atom of Sn.  
(c) The electron configuration of Sn is [Kr] 4d<sup>10</sup>5s<sup>2</sup>5p<sup>2</sup>. There are no 5d electrons.  
(d) Both of the 5p electrons are unpaired; there are two unpaired electrons in a Sn atom.
- 12B** (a) The 3d subshell was filled at Zn; each Y atom has ten 3d electrons.  
(b) Ge is in the 4p row; each germanium atom has two 4p electrons.  
(c) We would expect each Au atom to have ten 5d electrons and one 6s electron. Each Au atom should have one unpaired electron.

## REVIEW QUESTIONS

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1. (a)  $\lambda$  is the symbol for wavelength, which is the distance between like features (two peaks, for instance) of successive waves.  
(b)  $\nu$  is the symbol for frequency, which is the number of times that a particular feature of successive waves (such as a peak) passes a fixed point per unit time, e.g. per second.  
(c)  $h$  is the symbol for Planck's constant, which relates the energy and frequency of radiation:  $E = h\nu$ .  
(d)  $\Psi$  is the symbol for the wavefunction, which is the function that contains all the information known about an electron within a given atomic or molecular system.  
(e) The principal quantum number,  $n$ , is related to both the distance of an electron from the nucleus and to the electron's energy.
2. (a) The atomic (line) spectrum is the result of atoms being energized and then radiating energy as they lose that energy and return to lower energy states. Since only certain energy levels are permitted for each atom, the energies radiated are definite, giving rise to light of only certain wavelengths, or lines in the spectrum.  
(b) The photoelectric effect occurs when light (*photo-*) shining on a surface causes electrons (*-electric*) to be emitted from that surface.  
(c) A matter wave refers to the wave properties associated with matter.  
(d) The Heisenberg uncertainty principle states that it is impossible to simultaneously determine the position and linear momentum of a particle to any desired degree of precision.  
(e) Electron spin is that property of electrons that makes them appear as if they were spinning, or rotating, on an axis. Electrons can spin in only one of two states: clockwise (spin up) or counterclockwise (spin down).  
(f) The Pauli exclusion principle states that two electrons in an atom do not share the same four quantum numbers.

3. (a) The frequency of radiation is the number of oscillations that occur per unit time (as the radiation is observed passing a fixed point), the wavelength is the distance between two wave peaks on successive waves.
- (b) Ultraviolet light is radiation that has wavelengths just a bit shorter than those of visible light. Infrared light has wavelengths just a bit longer than visible light.
- (c) A continuous spectrum is visible light of all wavelengths that has been spread out by a prism or a grating. A discontinuous spectrum is light of only certain wavelengths, such as light emitted from an atomic species that has been excited.
- (d) A traveling wave is one whose wave peaks move past a given point as time passes, such as waves in the ocean. A standing wave is one whose nodes remain fixed, such as sound waves in an organ pipe or the waves in a violin string.
- (e) A quantum number is one of the four (principal, orbital, magnetic, spin) definite values that are used to specify the properties of an electron in an atom. An orbital is a region of space in which there is a good chance of finding an electron.
- (f) *spdf* notation specifies the electron configuration of an atom by giving the principal and orbital quantum numbers of electrons, grouped into subshells. An orbital diagram places each electron of an atom, symbolized as an arrow, into a space that represents an orbital.
- (g) An *s*-block element is one in Group 1A or Group 2A. A *p*-block element is one in Group 3A, 4A, 5A, 6A, 7A, or 8A.
- (h) A main-group element is an element in one of the “A” groups, i.e., the *s* block or the *p* block. A transition element is one in a “B” group, that is a *d*-block element. (Sometimes *f*-block elements, also called inner-transition elements, are included as transition elements as well.)

4. (a) length (nm) =  $1625 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 162.5 \text{ nm}$
- (b) length ( $\mu\text{m}$ ) =  $3880 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}} \times \frac{10^6 \mu\text{m}}{1 \text{ m}} = 0.388 \mu\text{m}$
- (c) length (nm) =  $7.27 \times 10^{-3} \text{ m} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 7.27 \times 10^6 \text{ nm}$
- (d) length (m) =  $546 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 5.46 \times 10^{-7} \text{ m}$
- (e) length (nm) =  $1.12 \text{ cm} \times \frac{1 \text{ m}}{10^2 \text{ cm}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 1.12 \times 10^7 \text{ nm}$
- (f) length (cm) =  $2.6 \times 10^4 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}} \times \frac{10^2 \text{ cm}}{1 \text{ m}} = 2.6 \times 10^{-4} \text{ cm}$

5. (a)  $\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{6.8 \times 10^{12} \text{ s}^{-1}} = 4.4 \times 10^{-5} \text{ m, infrared}$

(b)  $\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{9.8 \times 10^{15} \text{ s}^{-1}} = 3.1 \times 10^{-8} \text{ m, ultraviolet}$

(c)  $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{2.54 \times 10^7 \text{ s}^{-1}} = 11.8 \text{ m, radio}$

(d)  $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.07 \times 10^8 \text{ s}^{-1}} = 2.80 \text{ m, radio}$

6. The wavelength is the distance between successive peaks. Thus,  $4 \times 1.17 \text{ nm} = \lambda = 4.68 \text{ nm}$ .

7. (a)  $\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{4.68 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 6.41 \times 10^{16} \text{ Hz}$

(b)  $E = h\nu = 6.626 \times 10^{-34} \text{ J s} \times 6.41 \times 10^{16} \text{ Hz} = 4.25 \times 10^{-17} \text{ J}$

8. (a) The velocity of electromagnetic radiation in a vacuum, the speed of light, is a universal constant.
- (b) The wavelength of electromagnetic radiation is inversely proportional to its frequency:  $\lambda = c / \nu$ .
- (c) The energy per mole of electromagnetic radiation is directly proportional to its frequency:  $E = N_A h\nu$ .

9. (a)  $\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = 6.9050 \times 10^{14} \text{ s}^{-1}$

(b)  $\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{7^2} \right) = 7.5492 \times 10^{14} \text{ s}^{-1}$

$$\lambda = \frac{2.9979 \times 10^8 \text{ m/s}}{7.5492 \times 10^{14} \text{ s}^{-1}} = 3.9711 \times 10^{-7} \text{ m} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 397.11 \text{ nm}$$

(c)  $\nu = \frac{3.00 \times 10^8 \text{ m}}{380 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 7.89 \times 10^{14} \text{ s}^{-1} = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$

$$0.250 - \frac{1}{n^2} = \frac{7.89 \times 10^{14} \text{ s}^{-1}}{3.2881 \times 10^{15} \text{ s}^{-1}} = 0.240 \quad \frac{1}{n^2} = 0.250 - 0.240 = 0.010 \quad n = 10$$

10. The frequencies of hydrogen emission lines in the infrared region of the spectrum other than the visible region would be predicted by replacing the constant "2" in the Balmer equation by the variable  $m$ , where  $m$  is an integer smaller than  $n : m = 3, 4, \dots$

The resulting equation is  $\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$

11. (a)  $E = h\nu = 6.626 \times 10^{-34} \text{ J s} \times 8.62 \times 10^{15} \text{ s}^{-1} = 5.71 \times 10^{-18} \text{ J / photon}$

$$(b) E_m = 6.626 \times 10^{-34} \text{ J s} \times 1.53 \times 10^{14} \text{ s}^{-1} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 61.0 \text{ kJ/mol}$$

12. (a)  $\nu = \frac{E}{h} = \frac{4.18 \times 10^{-21} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 6.31 \times 10^{12} \text{ s}^{-1} = 6.31 \times 10^{12} \text{ Hz}$

$$(b) E = h\nu = \frac{hc}{\lambda}; \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m/s}}{215 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}}} = 5.57 \times 10^{-7} \text{ m} = 557 \text{ nm}$$

13.  $\Delta E = -2.179 \times 10^{-18} \text{ J} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -2.179 \times 10^{-18} \text{ J} \left( \frac{1}{3^2} - \frac{1}{5^2} \right) = -1.550 \times 10^{-19} \text{ J}$

$$E_{\text{photon emitted}} = 1.550 \times 10^{-19} \text{ J} = h\nu \quad \nu = \frac{E}{h} = \frac{1.550 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 2.339 \times 10^{14} \text{ s}^{-1}$$

14. The electron (a), has the longest wavelength. De Broglie's equation ( $\lambda = h/m\nu$ ) indicates that, if the velocity is constant, the wavelength is inversely proportional to the mass. Thus, the particle with the least mass will have the longest wavelength. Of the four particles given, the *electron* (a) is the least massive.

15. (a)  $m_\ell = 0, \pm 1$  Because  $\ell = 1$  and  $|m_\ell|$  must be  $\leq \ell$ .

- (b)  $\ell = 1, 2, 3$   $\ell$  must be less than  $n$  (which equals 4) and also must be  $\geq |m_\ell|$ , and  $m_\ell = -1$ .

- (c)  $n = 2, 3, \dots$   $n$  must be greater than  $\ell$  (which equals 1 in this case).

16. (a)  $4s$  has  $n = 4$   $\ell = 0$  (b)  $3p$  has  $n = 3$   $\ell = 1$

- (c)  $5f$  has  $n = 5$   $\ell = 3$  (d)  $3d$  has  $n = 3$   $\ell = 2$



(c) Te has 52 electrons, 16 more than the noble gas Kr. Te has two unpaired electrons.  
 $[\text{Kr}] \ 4d \begin{array}{|c|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array} \ 5s \begin{array}{|c|} \hline \uparrow \\ \hline \end{array} \ 4p \begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \uparrow \\ \hline \end{array}$

(d) Al has 13 electrons, 3 more than the noble gas Ne. One unpaired electron.  
 $[\text{Ne}] \ 3s \begin{array}{|c|} \hline \uparrow \\ \hline \end{array} \ 3p \begin{array}{|c|c|c|} \hline \uparrow & & \\ \hline \end{array}$

21. (a) Main group metals include those in Groups 1A and 2A, along with Al, Ga, In, Tl, Sn, Pb, Bi and Po.
- (b) Main group nonmetals are: H, F, Cl, Br, I, O, S, Se, N, P, C, and B.
- (c) Noble gases are He, Ne, Ar, Kr, Xe, and Rn.
- (d) The *d*-block elements are those in Groups 1B, 2B, 3B, 4B, 5B, 6B, 7B, and 8B.
- (e) The inner transition elements include those with atomic numbers from  $Z = 58$  (Ce) through  $Z = 71$  (Lu) and those from  $Z = 90$  (Th) through  $Z = 103$  (Lr).

22. Base the prediction of each electron configuration upon the configuration of the preceding noble gas.

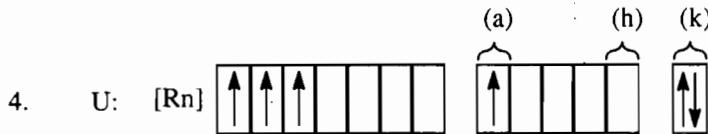
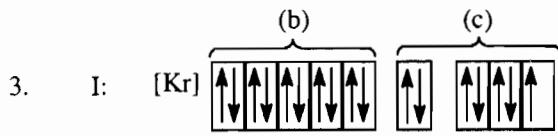
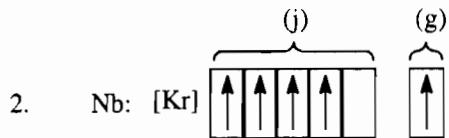
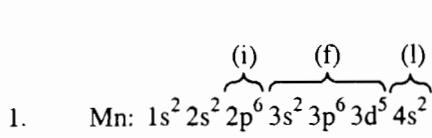
		prediction	from the text Appendix
(a)	In:	$[\text{Kr}] \ 4d^{10} 5s^2 5p^1$	in group 13
(b)	Cd:	$[\text{Kr}] \ 4d^{10} 5s^2$	in group 12
(c)	Sb:	$[\text{Kr}] \ 4d^{10} 5s^2 5p^3$	in group 15
(d)	Au:	$[\text{Xe}] \ 4f^{14} 5d^9 6s^2$	in group 11
			$[\text{Kr}] \ 4d^{10} 5s^2 5p^1$
			$[\text{Kr}] \ 4d^{10} 5s^2$
			$[\text{Kr}] \ 4d^{10} 5s^2 5p^3$
			$[\text{Xe}] \ 4f^{14} 5d^{10} 6s^1$

The predictions exactly match the given electron configurations for the first three atoms; for Au, the configuration  $[\text{Xe}]4f^{14}5d^{10}6s^1$  is the one actually adopted because it is a more stable arrangement.

23. (a) K is in group 1(1A) and in the fourth period. Elements in group 1 have an  $s^1$  outer electron configuration; those in the fourth period are filling the 4th principal quantum level. Thus K has one  $4s$  electron.
- (b) I is in group 17(7A) ( $s^2 p^5$  outer electron configuration) and in the 5th period (5th principal quantum level). I has five  $5p$  electrons.
- (c) Zn is in group 12 [ $(n-1)d^{10} n s^2$  outer electron configuration] and in the 4th period ( $n = 4$ ). Zn has ten  $3d$  electrons.
- (d) S is in group 16  $[n s^2 n p^4]$  and in the 3rd period. The  $2p^6$  electron configuration was complete with the preceding noble gas (Ne). S has six  $2p$  electrons.
- (e) Pb follows the lanthanide series in which fourteen  $4f$  electrons were added. Pb has fourteen  $4f$  electrons.

- (f) Ni is in the  $d$ -block of elements, two from the end. It therefore has eight  $d$  electrons. It also is in the fourth period, so these eight  $d$  electrons are  $3d$  electrons. Ni has eight  $3d$  electrons.

24.



## EXERCISES

## Electromagnetic Radiation

25. (a) TRUE Since frequency and wavelength are inversely related to each other, radiation of shorter wavelength has higher frequency.  
(b) FALSE Light of wavelengths between 390 nm and 790 nm is visible to the eye.  
(c) FALSE All electromagnetic radiation has the same speed in vacuum.  
(d) TRUE The wavelength of an X-ray is approximately 0.1 nm.

27. Convert all lengths into meters. (a)  $5.9 \times 10^{-6}$  m, (b)  $1.13 \times 10^{-3}$  m, (c)  $8.60 \times 10^{-8}$  m, (d)  $6.92 \times 10^{-6}$  m. The light having the highest frequency is (c) since it has the shortest wavelength.

29. The speed of light is used to convert the distance into an elapsed time.

$$\text{time} = 93 \times 10^6 \text{ mi} \times \frac{5280 \text{ ft}}{1 \text{ mi}} \times \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in.}} \times \frac{1 \text{ s}}{3.00 \times 10^{10} \text{ cm}} \times \frac{1 \text{ min}}{60 \text{ s}} = 8.3 \text{ min}$$

## Atomic Spectra

31. The longest wavelength component has the lowest frequency (and the smallest energy).

$$\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 4.5668 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{4.5668 \times 10^{14} \text{ s}^{-1}} = 6.5646 \times 10^{-7} \text{ m} \\ = 656.46 \text{ nm}$$

$$\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 6.1652 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{6.1652 \times 10^{14} \text{ s}^{-1}} = 4.8626 \times 10^{-7} \text{ m} \\ = 486.26 \text{ nm}$$

$$\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = 6.9050 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{6.9050 \times 10^{14} \text{ s}^{-1}} = 4.3416 \times 10^{-7} \text{ m} \\ = 434.16 \text{ nm}$$

$$\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{6^2} \right) = 7.3069 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{7.3069 \times 10^{14} \text{ s}^{-1}} = 4.1028 \times 10^{-7} \text{ m} \\ = 410.28 \text{ nm}$$

33. First we determine the frequency of the radiation, and then match it with the Balmer equation.

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s} \times \frac{10^9 \text{ nm}}{1 \text{ m}}}{389 \text{ nm}} = 7.71 \times 10^{14} \text{ s}^{-1} = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \\ \left( \frac{1}{2^2} - \frac{1}{n^2} \right) = \frac{7.71 \times 10^{14} \text{ s}^{-1}}{3.2881 \times 10^{15} \text{ s}^{-1}} = 0.234 = 0.2500 - \frac{1}{n^2} \quad \frac{1}{n^2} = 0.016 \quad n = 7.9 \approx 8$$

## Quantum Theory

35. (a) Combine  $E = h\nu$  and  $c = \nu\lambda$  to obtain  $E = hc/\lambda$

$$E = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{474 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 4.19 \times 10^{-19} \text{ J / photon}$$

$$(b) \quad E_m = 4.19 \times 10^{-19} \frac{\text{J}}{\text{photon}} \times 6.022 \times 10^{23} \frac{\text{photons}}{\text{mol}} = 2.52 \times 10^5 \text{ J/mol}$$

- 37.** The easiest way to answer this question is to convert all (b) through (d) into nanometers. The radiation with the smallest wavelength will have the greatest energy per photon while the radiation with the largest wavelength has the smallest amount of energy per photon.

(a)  $6.62 \times 10^2 \text{ nm}$

(b)  $2.1 \times 10^{-5} \text{ cm} \times \frac{1 \times 10^7 \text{ nm}}{1 \text{ cm}} = 2.1 \times 10^2 \text{ nm}$

(c)  $3.58 \mu\text{m} \times \frac{1 \times 10^3 \text{ nm}}{1 \mu\text{m}} = 3.58 \times 10^3 \text{ nm}$

(d)  $4.1 \times 10^{-6} \text{ m} \times \frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} = 4.1 \times 10^3 \text{ nm}$

So,  $2.1 \times 10^{-5} \text{ nm}$  radiation, by virtue of possessing the smallest wavelength in the set, has the greatest energy per photon. Conversely, since  $4.1 \times 10^3 \text{ nm}$  has the largest wavelength, it possesses the least amount of energy per photon.

- 39.** Notice that energy and wavelength are inversely related:  $E = \frac{hc}{\lambda}$ . Therefore radiation that is 100 times as energetic as radiation with a wavelength of 988 nm will have a wavelength one hundredth as long: 9.88 nm. The frequency of this radiation is:

$$v = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{9.88 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 3.03 \times 10^{16} \text{ s}^{-1}$$

From Figure 9-3, this is ultraviolet radiation.

## The Photoelectric Effect

**41. (a)**  $E = hv = 6.63 \times 10^{-34} \text{ J s} \times 9.96 \times 10^{14} \text{ s}^{-1} = 6.60 \times 10^{-19} \text{ J/photon}$

- (b)** Indium will display a photoelectric effect when exposed to ultraviolet light since ultraviolet light has a maximum frequency of  $1 \times 10^{16} \text{ s}^{-1}$ , which is above the threshold frequency of indium. It will not display a photoelectric effect when exposed to infrared light since the maximum frequency of infrared light is  $\sim 3 \times 10^{14} \text{ s}^{-1}$ , which is below the threshold frequency of indium.

## The Bohr Atom

**43. (a)** radius =  $n^2 a_0 = 6^2 \times 0.53 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 1.9 \text{ nm}$

**(b)**  $E_n = -\frac{R_H}{n^2} = -\frac{2.179 \times 10^{-18} \text{ J}}{6^2} = -6.053 \times 10^{-20} \text{ J}$

45. (a)  $\nu = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{4^2} - \frac{1}{7^2} \right) = 1.384 \times 10^{14} \text{ s}^{-1}$

(b)  $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.384 \times 10^{14} \text{ s}^{-1}} = 2.166 \times 10^{-6} \text{ m} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 2166 \text{ nm}$

(c) This is infrared radiation.

47. (a) According to the Bohr model, the radii of allowed orbits in a hydrogen atom are given by; where  $n = 1, 2, 3 \dots$  and  $a_0 = 5.3 \times 10^{-11} \text{ m}$  (0.53 Å or 53 pm) so,  
 $r_4 = (4)^2 (5.3 \times 10^{-11} \text{ m}) = 8.5 \times 10^{-10} \text{ m}$

(b) Here we want to see if there is an allowed orbit at  $r = 4.00 \text{ \AA}$ . To answer this question we will employ the equation  $r_n = n^2 a_0$ :  $4.00 \text{ \AA} = n^2 (0.53 \text{ \AA})$  or  $n = 2.75 \text{ \AA}$   
 Since  $n$  is not a whole number, we can conclude that the hydrogen atom does not orbit at a radius of  $4.00 \text{ \AA}$  (i.e., such an orbit is forbidden by selection rules).

(c) The energy level for the  $n = 8$  orbit is calculated using the equation

$$E_n = \frac{-2.179 \times 10^{-18} \text{ J}}{n^2} \quad E_8 = \frac{-2.179 \times 10^{-18} \text{ J}}{8^2} = -3.405 \times 10^{-20} \text{ J} \text{ (relative to } E_\infty = 0 \text{ J})$$

(d) Here we need to determine if  $2.500 \times 10^{-17} \text{ J}$  corresponds to an allowed orbit in the

hydrogen atom. Once again we will employ the equation  $E_n = \frac{-2.179 \times 10^{-18} \text{ J}}{n^2}$

$$2.500 \times 10^{-17} \text{ J} = \frac{-2.179 \times 10^{-18} \text{ J}}{n^2} \text{ or } n^2 = \frac{-2.179 \times 10^{-18} \text{ J}}{2.500 \times 10^{-17} \text{ J}} \text{ hence, } n = 0.2952$$

Because  $n$  is not a whole number,  $2.500 \times 10^{-17} \text{ J}$  is not an allowed energy state for an electron in a hydrogen atom.

49. If infrared light is produced, the quantum number of the final state must have a lower value (be of lower energy) than the quantum number of the initial state. First we compute the frequency of the transition being considered (from  $\nu = c / \lambda$ ), and then solve for the final quantum number.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{2170 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 1.38 \times 10^{14} \text{ s}^{-1} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{n^2} - \frac{1}{7^2} \right) = 3.289 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{n^2} - \frac{1}{7^2} \right)$$

$$\left( \frac{1}{n^2} - \frac{1}{7^2} \right) = \frac{1.38 \times 10^{14} \text{ s}^{-1}}{3.289 \times 10^{15} \text{ s}^{-1}} = 0.0419_6 \quad \frac{1}{n^2} = 0.0419_6 + \frac{1}{7^2} = 0.0623_7 \quad n = 4$$

## Wave-Particle Duality

51. The de Broglie equation is  $\lambda = h / mv$ . This means that, for a given wavelength to be produced, a lighter particle would have to be moving faster. Thus, electrons would have to move faster than protons to display matter waves of the same wavelength.

**53.** 
$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{\left(145 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}}\right) \left(168 \text{ km/h} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1000 \text{ m}}{1 \text{ km}}\right)} = 9.79 \times 10^{-35} \text{ m}$$

The diameter of a nucleus approximates  $10^{-15} \text{ m}$ , far larger than this wavelength.

## The Heisenberg Uncertainty Principle

- 55.** The Bohr model is a deterministic model of an atom. It implies that the position of the electron is exactly known at any time in the future, once that position is known at the present. The distance of the electron from the nucleus also is exactly known, as is its energy. And finally, the velocity of the electron in its orbit is exactly known. All of these exactly known quantities—position, distance from nucleus, energy, and velocity—can't, according to the Heisenberg uncertainty principle, be known with great precision simultaneously.

**57.** 
$$\Delta v = \left(\frac{1}{100}\right)(0.1) \left(2.998 \times 10^8 \frac{\text{m}}{\text{s}}\right) = 2.998 \times 10^5 \text{ m/s} \quad m = 1.673 \times 10^{-27} \text{ kg}$$

$$\Delta p = m\Delta v = (1.673 \times 10^{-27} \text{ kg})(2.998 \times 10^5 \text{ m/s}) = 5.0 \times 10^{-22} \text{ kg m s}^{-1}$$

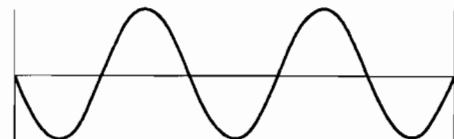
$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34} \text{ Js}}{(4\pi)(5.0 \times 10^{-22} \frac{\text{kg m}}{\text{s}})} = \sim 1 \times 10^{-13} \text{ m} \quad (\sim 100 \text{ times the diameter of a nucleus})$$

- 59.** electron mass =  $9.109 \times 10^{-31} \text{ kg}$ ,  $\lambda = 0.53 \text{ \AA}$  ( $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ ) hence  $\lambda = 0.53 \times 10^{-10} \text{ m}$

$$\lambda = \frac{h}{mv} \text{ or } v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.109 \times 10^{-31} \text{ kg})(0.53 \times 10^{-10} \text{ m})} = 1.4 \times 10^7 \text{ m s}^{-1}$$

## Wave Mechanics

- 61.** A sketch of this situation is presented at right. We see that 2.50 waves span the space of the 42 cm. Thus, the length of each wave is obtained by equating:  $2.50\lambda = 42 \text{ cm}$ , giving  $\lambda = 17 \text{ cm}$ .



- 63.** The second overtone has three half-wavelengths within the string. We can find the wavelength for the second overtone by using the equation l: string length =  $\frac{n\lambda}{2}$ , which gives the result:  $24 \text{ in} = \frac{3\lambda}{2}$ ,  $\lambda_{\text{second overtone}} = 16 \text{ inches}$

**65.** The differences between Bohr orbits and wave mechanical orbitals are given below.

- (a) The first difference is that of shape. Bohr orbits, as originally proposed, are circular (later Sommerfeld proposed elliptical orbits). Orbitals, on the other hand, are spherical; or shaped like two tear drops or two squashed spheres; or shaped like four tear drops meeting at their points.
  - (b) Bohr orbits are planar pathways, while orbitals are three-dimensional regions of space in which there is a high probability of finding electrons.
  - (c) The electron in a Bohr orbit has a definite trajectory. Its position and velocity are known at all times. The electron in an orbital, however, does not have a well-known position or velocity. In fact, there is a small but definite probability that the electron may be found outside the boundaries generally drawn for the orbital.
- Orbits and orbitals are similar in that the radii of Bohr orbits correspond to the distance from the nucleus in an orbital at which the electron is found with high probability.

## Quantum Numbers and Electron Orbitals

**67.** Answer (a) is incorrect because the values of  $m_s$  may be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . Answers (b) and (d) are incorrect because the value of  $\ell$  may be any integer  $\geq |m_\ell|$ , and less than  $n$ . Thus, answer (c) is correct.

**69.** (a)  $n = 5 \quad \ell = 1 \quad m_\ell = 0$  designates a  $5p$  orbital. ( $\ell = 1$  for all  $p$  orbitals.)

(b)  $n = 4 \quad \ell = 2 \quad m_\ell = -2$  designates a  $4d$  orbital. ( $\ell = 2$  for all  $d$  orbitals.)

(c)  $n = 2 \quad \ell = 0 \quad m_\ell = 0$  designates a  $2s$  orbital. ( $\ell = 0$  for all  $s$  orbitals.)

**71.** (a) Just one electron can have  $n = 3, \ell = 2, m_\ell = 0$ , and  $m_s = +1/2$ . Four quantum numbers completely designate an electron.

(b) These three quantum numbers designate an orbital, which can hold two electrons. Two electrons can have the three quantum numbers  $n = 3, \ell = 2, m_\ell = 0$ .

(c) These two quantum numbers designate the  $3d$  subshell, which contains five orbitals, with the possibility of two electrons in each. Ten electrons can have the two quantum numbers  $n = 3, \ell = 2$ .

(d)  $n = 3$  designates the shell that contains the  $3d$  subshell that has five orbitals, the  $3p$  subshell with three orbitals, and the  $3s$  subshell with one orbital. Each of these nine orbitals in the shell can hold two electrons, for a total of 18 electrons.

(e) The first two quantum numbers designate the  $3d$  subshell, which has five orbitals. Each orbital can accommodate one electron with spin up. Five electrons can have the quantum numbers  $n = 3, \ell = 2, m_\ell = 1/2$ .

## The Shapes of Orbitals and Radial Probabilities

- 73.** The wavefunction for the 2s orbital of a hydrogen atom is:

$$\psi_{2s} = \frac{1}{4} \left( \frac{1}{2\pi a_0^3} \right)^{1/2} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}}$$

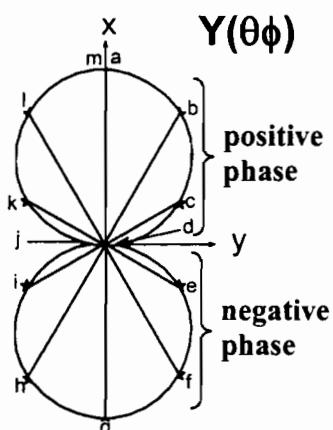
Where  $r = 2a_0$ , the  $\left( 2 - \frac{r}{a_0} \right)$  term becomes zero, thereby making  $\psi_{2s} = 0$ . At this point the

wave function has a radial node (i.e. the electron density is zero). The finite value of  $r$  is  $2a_0$  at the node, which is equal to  $2 \times 53$  pm or 106 pm. Thus at 106 pm, there is a nodal surface with zero electron density.

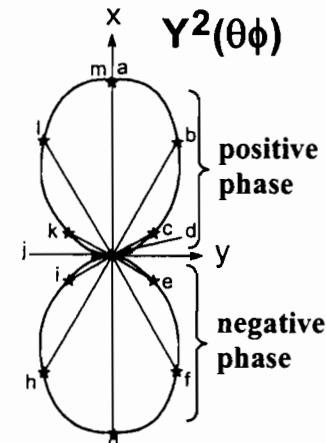
- 75.** The angular part of the  $2p_y$  wavefunction is  $Y(\theta\phi)_{py} = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi$ . The two lobes of the  $2p_y$  orbital lie in the  $xy$  plane and perpendicular to this plane is the  $xz$  plane. For all points in the  $xz$  plane  $\phi = 0$ , and since the sine of  $0^\circ$  is zero, this means that the entire  $xz$  plane is a node. Thus, the probability of finding a  $2p_y$  electron in the  $xz$  plane is zero.

- 77/79.** The  $2p_x$  orbital  $Y(\theta\phi) = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi$ ; Note: in the  $xy$  plane  $\theta = 90^\circ$  and  $\sin\theta = 1$

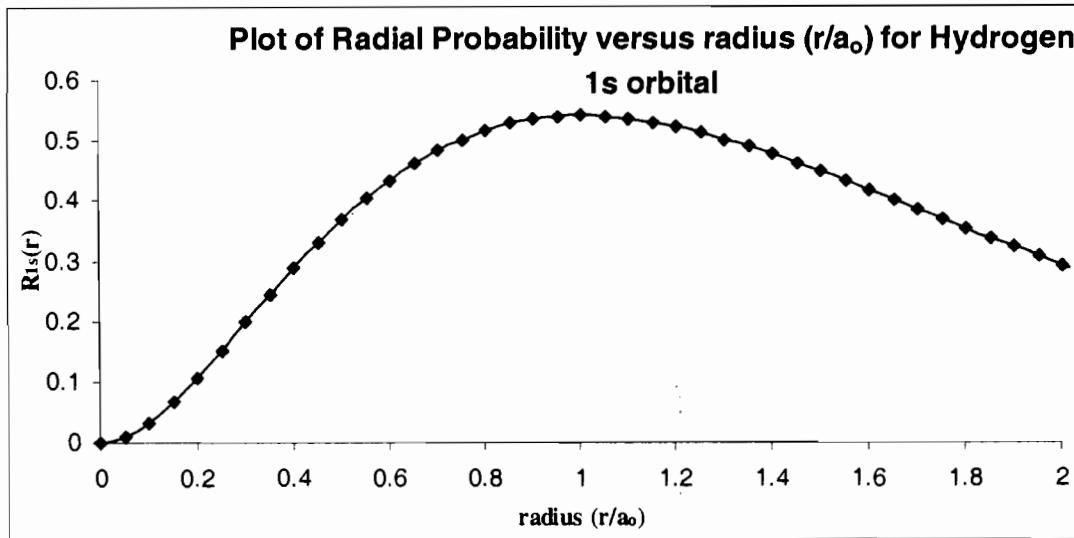
Plotting in the  $xy$  plane requires that we vary only  $\phi$



Point	Angle (°)	$Y(\theta\phi)$	$Y^2(\theta\phi)$
a	0	0.4886	0.2387
b	30	0.4231	0.1790
c	60	0.2443	0.0597
d	90	0.000	0.000
e	120	-0.2443	0.597
f	150	-0.4231	0.1790
g	180	-0.4886	0.2387
h	210	-0.4231	0.1790
i	240	-0.2443	0.0597
j	270	0.000	0.000
k	300	0.2443	0.0597
l	330	0.4231	0.1790
m	360	0.4886	0.2387



81. A plot of radial probability distribution versus  $r/a_0$  for a  $H_{1s}$  orbital shows a maximum at 1.0 (that is,  $r = a_0$ ). The plot is shown below:



## Electron Configurations

83. Configuration (b) is correct for phosphorus. The reason why each other configuration is incorrect follows.
- The two electrons in the  $3s$  subshell must have opposed spins, or different values of  $m_s$ .
  - The three  $3p$  orbitals must each contain one electron, before a pair of electrons is placed in any one of these orbitals.
  - The three unpaired electrons in the  $3p$  subshell must all have the same spin, either all spin up or all spin down.
85. We write the correct electron configuration first in each case.
- P:  $[\text{Ne}]3s^2 3p^3$  There are 3 unpaired electrons in each P atom.
  - Br:  $[\text{Ar}]3d^{10} 4s^2 4p^5$  There are ten  $3d$  electrons in an atom of Br.
  - Ge:  $[\text{Ar}]3d^{10} 4s^2 4p^2$  There are two  $4p$  electrons in an atom of Ge.
  - Ba:  $[\text{Xe}]6s^2$  There are two  $6s$  electrons in an atom of Ba.
  - Au:  $[\text{Xe}]4f^{14} 5d^9 6s^2$  There are fourteen  $4f$  electrons in an atom of Au.
- 87.
- N is the third element in the  $p$ -block of the second period. It has three  $2p$  electrons.
  - Rb is the first element in the  $s$ -block of the *fifth* period. It has two  $4s$  electrons.
  - As is in the  $p$ -block of the fourth period. The  $3d$  subshell is filled with ten electrons, but no  $4d$  electrons have been added.

- (d) Au is in the *d*-block of the sixth period; the *4f* subshell is filled. Au has fourteen *4f* electrons.
- (e) Pb is the second element in the *p*-block of the sixth period; it has two *6p* electrons. Since these two electrons are placed in separate *6p* orbitals, they are unpaired. There are two unpaired electrons.
- (f) Group 4A of the periodic table is the group with the elements C, Si, Ge, Sn, and Pb. This group currently has five named elements.
- (g) The sixth period begins with the element Cs ( $Z = 55$ ) and ends with the element Rn ( $Z = 86$ ). This period is 32 elements long.
- 89.** Since the periodic table is based on electron structure, two elements in the same group (Pb and element 114) should have similar electron configurations.
- (a) Pb: [Xe]  $4f^{14} 5d^{10} 6s^2 6p^2$       (b) 114: [Rn]  $5f^{14} 6d^{10} 7s^2 7p^2$

## FEATURE PROBLEMS

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- 112.** By carefully scanning the diagram, we note that there are no spectral lines in the area of 304 nm and 309 nm, nor at 318 nm, and 327 nm. Likewise, there are none between 435 and 440 nm. We conclude that V is absent.

There are spectral lines that correspond to each of the Cr spectral lines—between 355 nm and 362 nm, and between 425 nm and 430 nm. Cr is present.

There are no spectral lines close to 403 nm; Mn is absent.

There are spectral lines at about 344 nm, 358 nm, 372 nm, 373 nm, and 386 nm. Fe is present.

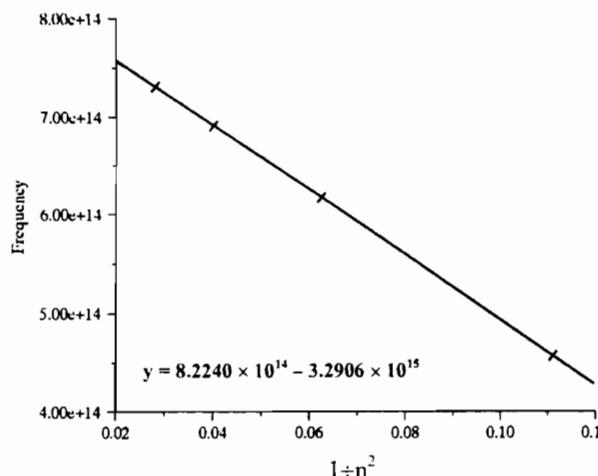
There are spectral lines at 341 nm, 344 nm to 352 nm, and 362 nm. Ni is present.

There are spectral lines between 310 and 315 nm and at about 415 nm. Another element is present.

Thus, Cr, Fe, and Ni are present. V and Mn are absent. There is an additional element present.

- 113.** The equation of a straight line is  $y = mx + b$ , where  $m$  is the slope of the line and  $b$  is its y-intercept. The Balmer equation is  $\nu = 3.2881 \times 10^{15} \text{ Hz} \left( \frac{1}{2^2} - \frac{1}{n^2} \right) = \frac{c}{\lambda}$ . In this equation, one plots  $\nu$  on the vertical axis, and  $1/n^2$  on the horizontal axis. The slope is  $b = -3.2881 \times 10^{15} \text{ Hz}$  and the intercept is  $3.2881 \times 10^{15} \text{ Hz} \div 2^2 = 8.2203 \times 10^{14} \text{ Hz}$ . The plot of the data of Figure 9.9 follows.

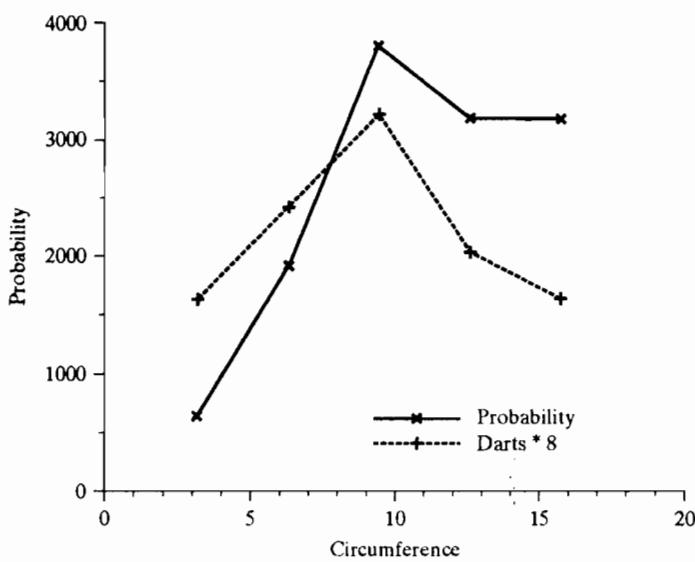
$\lambda$	656.3 nm	486.1 nm	434.0 nm	410.1 nm
$\nu$	$4.568 \times 10^{14} \text{ Hz}$	$6.167 \times 10^{14} \text{ Hz}$	$6.908 \times 10^{14} \text{ Hz}$	$7.310 \times 10^{14} \text{ Hz}$
$n$	3	4	5	6



We see the slope ( $-3.2906 \times 10^{15}$ ) and the y-intercept ( $8.2240 \times 10^{14}$ ) are almost exactly what we had predicted from the Balmer equation.

- 114.** This graph differs from the one involving  $\psi^2$  in Figure 9-18(a) because this graph factors in the volume of the thin shell. Figure 9-18(a) simply is a graph of the probability of finding an electron at a distance  $r$  from the nucleus. But the graph that accompanies this problem multiplies that radial probability by the volume of the shell that is a distance  $r$  from the nucleus. The volume of the shell is the thickness of the shell (a very small value  $dr$ ) times the area of the shell ( $4\pi r^2$ ). Close to the nucleus, the area is very small because  $r$  is very small. Therefore, the relative probability also is very small near the nucleus; there just isn't enough volume to contain the electrons.
- What we plot is the product of the number of darts times the circumference of the outer boundary of the scoring ring. (probability = number  $\times$  circumference)

darts	200	300	400	250	200
score	"50"	"40"	"30"	"20"	"10"
radius	1.0	2.0	3.0	4.0	5.0
circumference	3.14	6.28	9.42	12.6	15.7
probability	628	1884	3768	3150	3140



The graph of “probability” is close to the graph that accompanies this problem, except that the dart board is two-dimensional, while the atom is three-dimensional. This added dimension means that the volume close to the nucleus is relatively much smaller than is the area close to the center. The other difference, of course, is that it is harder for darts to get close to the center, while electrons are attracted to the nucleus.

- 115. (a)** First we calculate the range of energies for the incident photons used in the absorption experiment. Remember:  $E_{\text{photon}} = h\nu$  &  $\nu = c/\lambda$ . At one end of the range,  $\lambda = 100 \text{ nm}$ .

$$\text{Therefore, } \nu = 2.998 \times 10^8 \text{ m s}^{-1} \div (1.00 \times 10^{-7} \text{ m}) = 2.998 \times 10^{15} \text{ s}^{-1}$$

$$\text{So } E_{\text{photon}} = 6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^{15} \text{ s}^{-1}) = 1.98 \times 10^{-18} \text{ J}$$

At the other end of the range,  $\lambda = 1000 \text{ nm}$ .

$$\text{Therefore, } \nu = 2.998 \times 10^8 \text{ m s}^{-1} \div 1.00 \times 10^{-6} \text{ m} = 2.998 \times 10^{14} \text{ s}^{-1}$$

$$\text{So } E_{\text{photon}} = 6.626 \times 10^{-34} \text{ J s} (2.998 \times 10^{14} \text{ s}^{-1}) = 1.98 \times 10^{-19} \text{ J.}$$

Next, we will calculate what excitations are possible using photons with energies between  $1.98 \times 10^{-18} \text{ J}$  and  $1.98 \times 10^{-19} \text{ J}$  and the electron initially residing in the  $n = 1$  level. These “orbit transitions” can be found with the equation

$$\Delta E = E_f - E_i = -2.179 \times 10^{-18} \left( \frac{1}{(1)^2} - \frac{1}{(n_f)^2} \right) \text{ For the lowest energy photon}$$

$$1.98 \times 10^{-19} \text{ J} = -2.179 \times 10^{-18} \left( \frac{1}{(1)^2} - \frac{1}{(n_f)^2} \right) \text{ or } 0.0904 = 1 - \frac{1}{(n_f)^2}$$

From this  $-0.9096 = -\frac{1}{(n_f)^2}$  and  $n_f = 1.05$

Thus, the lowest energy photon is not capable of promoting the electron above the  $n = 1$  level. For the highest energy level:

$$1.98 \times 10^{-18} \text{ J} = -2.179 \times 10^{-18} \left( \frac{1}{(1)^2} - \frac{1}{(n_f)^2} \right) \quad \text{or} \quad 0.9114 = 1 - \frac{1}{(n_f)^2}$$

From this  $-0.0886 = -\frac{1}{(n_f)^2}$  and  $n_f = 3.35$  Thus, the highest energy photon can promote a groundstate electron to both the  $n = 2$  and  $n = 3$  levels. This means that we would see two lines in the absorption spectrum, one corresponding to the  $n = 1 \rightarrow n = 2$  transition and the other to the  $n = 1 \rightarrow n = 3$  transition.

$$\text{Energy for the } n = 1 \rightarrow n = 2 \text{ transition} = -2.179 \times 10^{-18} \left( \frac{1}{(1)^2} - \frac{1}{(2)^2} \right) = 1.634 \times 10^{-18} \text{ J}$$

$$\nu = \frac{1.634 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 2.466 \times 10^{15} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{2.466 \times 10^{15} \text{ s}^{-1}} = 1.215 \times 10^{-7} \text{ m}$$

$$\lambda = 121.5 \text{ nm}$$

Thus, we should see a line at 121.5 nm in the absorption spectrum.

$$\text{Energy for the } n = 1 \rightarrow n = 3 \text{ transition} = -2.179 \times 10^{-18} \left( \frac{1}{(1)^2} - \frac{1}{(3)^2} \right) = 1.937 \times 10^{-18} \text{ J}$$

$$\nu = \frac{1.937 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 2.923 \times 10^{15} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{2.923 \times 10^{15} \text{ s}^{-1}} = 1.025 \times 10^{-7} \text{ m}$$

$$\lambda = 102.5 \text{ nm}$$

Consequently, the second line should appear at 102.6 nm in the absorption spectrum.

- (b) An excitation energy of  $1230 \text{ kJ mol}^{-1}$  to  $1240 \text{ kJ mol}^{-1}$  works out to  $2 \times 10^{-18} \text{ J}$  per photon. This amount of energy is sufficient to raise the electron to the  $n = 4$  level. Consequently, six lines will be observed in the emission spectrum. The calculation for each emission line is summarized below:

$$E_{4 \rightarrow 1} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{1^2} - \frac{1}{4^2} \right) = 3.083 \times 10^{15} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{3.083 \times 10^{15} \text{ s}^{-1}} = 9.724 \times 10^{-8} \text{ m}$$

$$\lambda = 97.2 \text{ nm}$$

$$E_{4 \rightarrow 2} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 6.167 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{6.167 \times 10^{14} \text{ s}^{-1}} = 4.861 \times 10^{-7} \text{ m}$$

$$\lambda = 486.1 \text{ nm}$$

$$E_{4 \rightarrow 3} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{3^2} - \frac{1}{4^2} \right) = 1.599 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{1.599 \times 10^{14} \text{ s}^{-1}} = 1.875 \times 10^{-6} \text{ m}$$

$$\lambda = 1875 \text{ nm}$$

$$E_{3 \rightarrow 2} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 2.924 \times 10^{15} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{2.924 \times 10^{15} \text{ s}^{-1}} = 1.025 \times 10^{-7} \text{ m}$$

$$\lambda = 102.5 \text{ nm}$$

$$E_{2 \rightarrow 1} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = 4.568 \times 10^{14} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{4.568 \times 10^{14} \text{ s}^{-1}} = 6.563 \times 10^{-7} \text{ m}$$

$$\lambda = 656.3 \text{ nm}$$

$$E_{1 \rightarrow 0} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{1}{0^2} - \frac{1}{1^2} \right) = 2.467 \times 10^{15} \text{ s}^{-1} \quad \lambda = \frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{2.467 \times 10^{15} \text{ s}^{-1}} = 1.215 \times 10^{-7} \text{ m}$$

$$\lambda = 121.5 \text{ nm}$$

- (c) The number of lines observed in the two spectra is not the same. The absorption spectrum has two lines while the emission spectrum has six lines. Notice that the 102.5 nm and 1021.5 nm lines are present in both spectra. This is not surprising since the energy difference between each level is the same whether it is probed by emission or absorption spectroscopy.

116. (a) The wavelength associated with each Helium-4 atom must be close to 100 pm ( $1.00 \times 10^{-10} \text{ m}$ ) in order for diffraction to take place. To find the necessary velocity for the He atoms, we need to employ the de Broglie equation:  $\lambda = \frac{h}{mv}$ .

Rearrange to give  $v = \frac{h}{m\lambda}$  where:

$$\lambda = 1.00 \times 10^{-10} \text{ m}, h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1} \text{ and } m_{\text{neutron}} = 6.696 \times 10^{-27} \text{ kg.}$$

$$\text{So, } v = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1}}{6.696 \times 10^{-27} \text{ kg} (1.00 \times 10^{-10} \text{ m})} = 9.90 \times 10^2 \text{ m s}^{-1}$$

- (b) The de Broglie wavelength for the beam of protons would be too small for any diffraction to occur. Instead, most of the protons would simply pass through the film of gold and have little or no interaction with the constituent gold atoms. Keep in mind, however, that some of the protons will end up being deflected or bounced back by passing too close to a nucleus or by colliding with a gold nucleus head on, respectively.

# CHAPTER 10

## THE PERIODIC TABLE AND SOME ATOMIC PROPERTIES

### PRACTICE EXAMPLES

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- 1A** Atomic size decreases left to right through a period, and bottom to top in a family. We expect the smallest elements to be in the upper right corner of the periodic table. S is the element closest to the upper right corner and should have the smallest atom.

$$S = 104 \text{ pm} \quad As = 121 \text{ pm} \quad I = 133 \text{ pm}$$

- 1B** From the periodic table inside the front cover, we see that Na is in the same period as Al (period 3), but in a different group from K, Ca, and Br (period 4), which might predict that Na and Al are about the same size. However, there is a substantial decrease in size as one moves from left to right in a period due to an increase in effective nuclear charge, enough such that Ca should be about the same size as Na. Table 10-1 shows:

$$227 \text{ pm for K} < 197 \text{ pm for Ca} \approx 184 \text{ pm for Na} < 143 \text{ pm for Al} < 114 \text{ pm for Br}$$

- 2A**  $Ti^{2+}$  and  $V^{3+}$  are isoelectronic; the one with higher positive charge should be smaller:  $V^{3+} < Ti^{2+}$ .  $Sr^{2+}$  and  $Br^-$  are isoelectronic; again, the one with higher positive charge should be smaller:  $Sr^{2+} < Br^-$ . In addition  $Ca^{2+}$  and  $Sr^{2+}$  both are ions of Group 2A; the one of lower atomic number should be smaller:  $Ca^{2+} < Sr^{2+} < Br^-$ . Finally, we know that the size of atoms decreases left to right across a period; we expect size of like-charged ions to follow the same trend:  $Ti^{2+} < Ca^{2+}$ . Summarized below:

$$V^{3+}(64 \text{ pm}) < Ti^{2+}(86 \text{ pm}) < Ca^{2+}(100 \text{ pm}) < Sr^{2+}(113 \text{ pm}) < Br^-(196 \text{ pm})$$

- 2B**  $Br^-$  clearly is larger than As since  $Br^-$  is an anion in the same period as As. In turn, As is larger than N since both are in the same group, with As lower down in the group. As also should be larger than P, which is larger than  $Mg^{2+}$ , an ion smaller than N. All that remains is to note that Cs is a truly large atom, one of the largest in the periodic table. The As atom should be in the middle. Data from Table 10-1 are:

$$65 \text{ pm for } Mg^{2+} < 70 \text{ pm for N} < 125 \text{ pm for As} < 196 \text{ pm for } Br^- < 265 \text{ pm for Cs}$$

- 3A** Ionization increases from bottom to top of a group and from left to right through a period. The first ionization energy of K is less than that of Mg and the first ionization energy of S is less than that of Cl. We would suppose also that the first ionization energy of Mg is smaller than that of S, because Mg is a metal.

$$K(418.8 \text{ kJ/mol}) < Mg(737.7 \text{ kJ/mol}) < S(1000 \text{ kJ/mol}) < Cl(1251.1 \text{ kJ/mol})$$

- 3B** We would expect an alkali metal (Rb) or an alkaline earth metal (Sr) to have a low first ionization energy and nonmetals (e.g. Br) to have relatively high first ionization energies. Metalloids (such as Sb and As) should have intermediate ionization energies. Since the first ionization energy for As is larger than that for Sb, the first ionization energy of Sb should be in the middle. Data that were used to produce Figure 10-9 include the following (in kJ/mol): 403 for Rb, 549 for Sr, 834 for Sb, 947 for As, and 1140 for Br.
- 4A** Cl and Al must be paramagnetic, since they each have an odd number of electrons. The electron configurations of  $K^+$  ([Ar]) and  $O^{2-}$  ([Ne]) are those of the nearest noble gas; because all electrons are paired, they are diamagnetic. In Zn: [Ar]  $3d^{10}4s^2$  all electrons are paired; the atom is diamagnetic. **4B** The electron configuration of Cr is [Ar]  $3d^54s^1$ ; it has six unpaired electrons. The electron configuration of  $Cr^{2+}$  is [Ar]  $3d^4$ ; it has four unpaired electrons. The electron configuration of  $Cr^{3+}$  is [Ar]  $3d^3$ ; it has three unpaired electrons. Thus, of the two ions,  $Cr^{2+}$  has the greater number of unpaired electrons.
- 5A** We expect the melting point of bromine to be close to the average of those of chlorine and iodine: estimated melting point of  $Br_2 = \frac{172\text{ K} + 387\text{ K}}{2} = 280\text{ K}$ . The actual melting point is 266 K.
- 5B** If the boiling point of  $I_2$  (458 K) is the average of the boiling points of  $Br_2$  (349 K) and  $At_2$ , then  $458\text{ K} = (349\text{ K} + ?)/2$   $? = 2 \times 458\text{ K} - 349\text{ K} = 567\text{ K}$   
The estimated boiling point of molecular astatine is about 570 K.

## REVIEW QUESTIONS

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1. **(a)** Two isoelectronic species (an atom and an ion, or two ions) have the same number of electrons.  
**(b)** The valence electrons in an atom are those that have the highest principal quantum number. They also are the ones furthest from the nucleus and thus on the outside of the atom. Because they are the electrons that other atoms “see”, they are most important in determining the atom’s chemical behavior.  
**(c)** A metal is an element that is relatively easily oxidized. Most elements are metals. In the periodic table, all of the transition elements are metals, as well as the lanthanides and actinides. In addition, metals are the representative elements in group 1(1A) and group 2(2A), as well as Al, Ga, In, Tl, Sn, Pb, Bi and Po.  
**(d)** A nonmetal is an element that is relatively easily reduced. In the periodic table, nonmetals are at the right and include H, F, Cl, Br, I, O, S, Se, N, P, C and B.  
**(e)** A metalloid is an element that is relatively easy to oxidize or to reduce. That is, their behavior is between that of metals and of nonmetals. Metalloids include Si, Ge, As, Sb, Te and At.

2. (a) The periodic law is, like all natural laws, a summary of experimental observations. It states that a given property of elements varies periodically when the elements are arranged in order of increasing atomic number.
- (b) Ionization energy is the quantity of energy that, when added to a gaseous atom (or ion), will remove an electron.
- (c) Electron affinity is the energy change that occurs when an electron is added to a gaseous atom (or ion). Since the electron affinity process usually is exothermic for atoms, most atomic electron affinities are negative.
- (d) Paramagnetism, the result of a species having one or more unpaired electrons, is the small attraction of that species into a magnetic field. It is not nearly as strong as the more familiar property of ferromagnetism.
3. (a) Lanthanide elements are *f*-block elements in which the  $4f$ -subshell is filling: Ce through Lu. Actinide elements are in which the  $5f$ -subshell is filling: Th through Lr.
- (b) A covalent radius is the radius of an atom that is bonded covalently to another. For example, one half the internuclear distance in  $\text{Cl}_2$  is the covalent radius of chlorine. A metallic radius is half the shortest internuclear distance in a crystal of solid metal.
- (c) The atomic number of an atom equals the number of protons in the nucleus and thus the positive charge of the nucleus. The effective nuclear charge is the positive charge experienced by the outermost electrons. Intervening electrons of inner shells cancel much of the nuclear charge out.
- (d) Ionization energy is the energy that is needed to remove an electron from a gaseous atom (or ion). Electron affinity is the energy change that occurs when an electron is added to a gaseous atom (or ion).
- (e) A paramagnetic species has one or more unpaired electrons and is drawn towards a magnetic field. A diamagnetic species has all electrons paired and is slightly repelled by a magnetic field.
4. The pairs of elements that are “out of order” based on their atomic masses are presented here, together with their atomic numbers. The periodic table lists elements in order of increasing atomic number, not increasing atomic mass. For one of these pairs there is a further explanation. Most of the Ar in the atmosphere is thought to result from the radioactive decay of  $^{40}\text{K}$ , a nuclide of that once was more plentiful than it is now.

Element	Ar	K	Te	I	Co	Ni
Z	18	19	52	53	27	28
At. mass (u)	39.948	39.098	127.60	126.9045	58.9332	58.693

Element	Th	Pa	Pu	Am	Sg	Bh
Z	90	91	94	95	106	107
At. mass (u)	232.0381	231.0359	244	243	263	262

5. (a) The number of protons in the nucleus of  $^{119}_{50}\text{Sn}$  equals the atomic number: 50 protons.
- (b) The number of neutrons in the nucleus is the difference between the mass number and the atomic number of the nuclide:  $119 - 50 = 69$  neutrons.
- (c) Sn is in Group 14 of the fifth period of the periodic table. The  $4d$  subshell completed filling with element 47 (Ag). Thus, there are ten  $4d$  electrons in Sn.
- (d) The  $3s$  subshell is filled. Sn has two  $3s$  electrons.
- (e) The outer (valence) electron configuration of Sn is  $5s^2 5p^2$ . Sn has two  $5p$  electrons.
- (f) There are four electrons in the shell of highest principal quantum number ( $n = 5$ ) in an atom of Sn.

6. In the literal sense, isoelectronic means having the same number of electrons. (In another sense, not used in the text, it means having the same electron configuration.) We determine the total number of electrons and the electron configuration for each species and make our decisions based on this information.

$\text{Fe}^{2+}$	24 electrons	$[\text{Ar}] 3d^6$	$\text{Sc}^{3+}$	18 electrons	$[\text{Ar}]$
$\text{Ca}^{2+}$	18 electrons	$[\text{Ar}]$	$\text{F}^-$	10 electrons	$[\text{He}] 2s^2 2p^6$
$\text{Co}^{2+}$	25 electrons	$[\text{Ar}] 3d^7$	$\text{Co}^{3+}$	24 electrons	$[\text{Ar}] 3d^6$
$\text{Sr}^{2+}$	36 electrons	$[\text{Ar}] 3d^{10} 4s^2 4p^6$	$\text{Cu}^+$	28 electrons	$[\text{Ar}] 3d^{10}$
$\text{Zn}^{2+}$	28 electrons	$[\text{Ar}] 3d^{10}$	$\text{Al}^{3+}$	10 electrons	$[\text{He}] 2s^2 2p^6$

Species with the same number of electrons and the same electron configuration are the following.  $\text{Fe}^{2+}$  and  $\text{Co}^{3+}$      $\text{Sc}^{3+}$  and  $\text{Ca}^{2+}$      $\text{F}^-$  and  $\text{Al}^{3+}$      $\text{Zn}^{2+}$  and  $\text{Cu}^+$

7. Isoelectronic species must have the same number of electrons, and each element has a different atomic number, atoms of different elements cannot be isoelectronic. Two different cations may be isoelectronic, as may two different anions, or an anion and a cation. An example would be two anions (or two cations, or an anion and a cation) that have the electron configuration of a nearby noble gas, such as:  $\text{O}^{2-}$  and  $\text{F}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , or  $\text{F}^-$  and  $\text{Na}^+$ .

8. (a) The most nonmetallic element is the one farthest to the right and the top (with the exception of the noble gases). This is the element fluorine.
- (b) The transition elements are those with incomplete  $d$  subshells, or those which can form ions with incomplete  $d$  subshells. Scandium ( $[\text{Ar}] 3d^1 4s^2$ ) is the transition element with the smallest atomic number.
- (c) The metalloids are defined as the elements in Groups 14 – 17 (4A - 7A) that are adjacent to the stair-step diagonal line in the periodic table, except for Al and Po; that is, Si, Ge, As, Sb, Te and At. Of these 6 elements, only Si ( $Z = 14$ ) has an atomic number exactly midway between those of two noble gases, Ne ( $Z = 10$ ) and Ar ( $Z = 18$ ).

9. In general, atomic size in the periodic table increases from top to bottom for a group and increases from right to left through a period, as indicated in Figures 10-4 and 10-8. The larger element is indicated first, followed by the reason for making the choice.
- (a) Te: Te is to the left of Br and also in the period below that of Br in the 4th period.
- (b) K: K is to the left of Ca within the same period, Period 4.
- (c) Cs: Cs is both below and to the left of Ca in the periodic table.
- (d) N: N is to the left of O within the same period, Period 2.
- (e) P: P is both below and to the left of O in the periodic table.
- (f) Au: Au is both below and to the left of Al in the periodic table.
10. An Al atom is larger than a F atom since Al is both below and to the left of F in the periodic table. As is larger than Al, since As is below Al in the periodic table. (Even though As is to the right of Al, we would not conclude that As is smaller than Al, since increases in size down a group are more pronounced than decreases in size across a period (from left to right). A  $\text{Cs}^+$  ion is isoelectronic with an  $\text{I}^-$  ion, and in an isoelectronic series, anions are larger than cations; thus  $\text{I}^-$  is larger than  $\text{Cs}^+$ .  $\text{I}^-$  also is larger than As, since I is below As in the periodic table (and increases in size down a group are more pronounced than those across a period). Finally, N is larger than F, since N is to the left of F in the periodic table. Therefore, we conclude that F is the smallest species listed and  $\text{I}^-$  is the largest. In fact, with the exception of  $\text{Cs}^+$ , we can rank the species in order of decreasing size.  $\text{I}^- > \text{As} > \text{Al} > \text{N} > \text{F}$  and also  $\text{I}^- > \text{Cs}^+$
11. Ionization energy in the periodic table decreases from top to bottom for a group, and increases from left to right for a period, as summarized in Figure 10-9. Cs has the lowest ionization energy; it is furthest to the left and nearest to the bottom of the periodic table. Next comes Sr, followed by As, then S, and finally F, the most nonmetallic element in the group (and in the periodic table). Thus, the elements listed in order of increasing ionization energy are:  $\text{Cs} < \text{Sr} < \text{As} < \text{S} < \text{F}$
12. (a) The first element in a group has the smallest atoms. In Group 14 this is C.
- (b) The atom in a period with the largest atoms is furthest to the left. In the fifth period this is Rb.
- (c) The bottom element in a group has atoms with the lowest first ionization energy. In Group 17 this is At (or I if we do not wish to consider radioactive elements).
13. First we convert the mass of Na given to an amount in moles of Na. Then we compute the energy needed to ionize this much Na.

$$\text{Energy} = 1.00 \text{ mg Na} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{495.8 \text{ kJ}}{1 \text{ mol Na}} = 0.0216 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 21.6 \text{ J}$$

- 14.** (a) The most metallic element is the one closest to the lower left-hand corner. This is the element Ba.
- (b) The most nonmetallic element is the one closest to the upper right-hand corner, the element S.
- (c) There are two distinct metals in this group, Ba and Ca; they have the lowest ionization energies. There is one distinct nonmetal, S; it has the highest ionization energy. The remaining two elements, As and Bi, are a metalloid and a metal, respectively. The metalloid has a higher ionization energy than does the metal. Bi has the intermediate value of ionization energy of the five elements listed.
- 15.** Metallic character decreases from left to right and from bottom to top in the periodic table. Thus, in order of decreasing metallic character the elements listed are: Rb > Ca > Sc > Fe > Te > Br > O > F The difficulty in establishing this series is in placing the elements Te and Br. First, the metal Fe is more metallic than the nonmetal Te. Further, Te clearly is more metallic than the halogen Br. Finally, we only need to recognize that Cl and O have approximately the same nonmetallic character, and Br clearly is more metallic than is Cl.
- 16.** Paramagnetism indicates unpaired electrons, which in turn are often associated with partially filled subshells. First we write the electron configurations of the elements, and then those of the ions. From those electron configurations, we determine whether the species is paramagnetic or diamagnetic.

K	[Ar] 4s <sup>1</sup>	K <sup>+</sup> [Ar]	diamagnetic, all subshells filled.
Cr	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>	Cr <sup>3+</sup> [Ar] 3d <sup>3</sup>	paramagnetic.
Zn	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>	Zn <sup>2+</sup> [Ar] 3d <sup>10</sup>	diamagnetic, all subshells filled.
Cd	[Kr] 4d <sup>10</sup> 5s <sup>2</sup>		diamagnetic, all subshells filled.
Co	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>	Co <sup>3+</sup> [Ar] 3d <sup>6</sup>	paramagnetic.
Sn	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	Sn <sup>2+</sup> [Kr] 4d <sup>10</sup> 5s <sup>2</sup>	diamagnetic, all subshells filled.
Br	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>		paramagnetic

- 17.** (a) 6. Tl's electron configuration [Xe] 4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup>6p<sup>1</sup> has one *p* electron in its outermost shell.
- (b) 8. Z = 70 identifies the element as Yb, an *f*-block of the periodic table, an inner transition element.
- (c) 5. Ni has the electron configuration [Ar] 4s<sup>2</sup>3d<sup>8</sup>. It also is a *d*-block element.
- (d) 1. An *s*<sup>2</sup> outer electron configuration, with the underlying configuration of a noble gas, is characteristic of elements of group 2(2A), the alkaline earth elements.
- (e) 2. The element in the fifth period and Group 15 is Sb, a metalloid.
- (f) 4 and 6. The element in the fourth period and Group 16 is Se, a nonmetal. (Note, B is a nonmetal with electron configuration 1s<sup>2</sup>2s<sup>2</sup>2p<sup>1</sup> (having one *p* electron in the shell of highest *n*) 6. is also a possible answer)

18. We expect periodic properties to be functions of atomic number/position.

Element, atomic number He, 2 Ne, 10 Ar, 18 Kr, 36 Xe, 54 Rn, 86

Boiling point, K 4.2 K 27.1 K 87.3 K 119.7 K 165 K

A simple method to determine the boiling point of Radon is to expect that the boiling point of xenon (165 K) is the average of the boiling points of radon and krypton (120 K).

$$165 \text{ K} = (120 \text{ K} + ?)/2 \quad ? = 2 \times 165 \text{ K} - 120 \text{ K} = 210 \text{ K} = \text{b.p. of radon (211 tabulated)}$$

## EXERCISES

### The Periodic Law

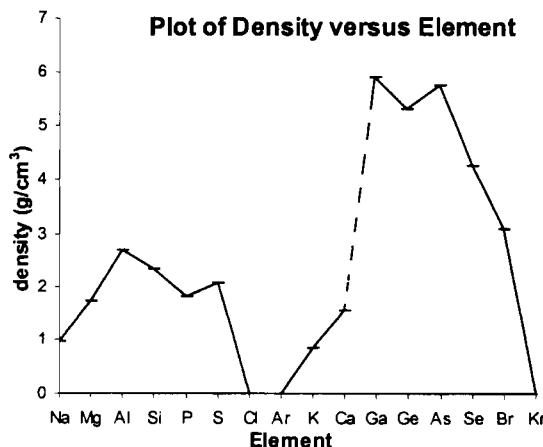
19. Element 114 will be a metal in the same group as Pb, element 82 (18 cm<sup>3</sup>/mol); Sn, element 50 (18 cm<sup>3</sup>/mol); and Ge, element 32 (14 cm<sup>3</sup>/mol). We note that the atomic volume of Pb and Sn are essentially equal, probably due to the lanthanide contraction. If there is also an actinide contraction, element 114 will have an atomic volume of 18 cm<sup>3</sup> / mol. If there is no actinide contraction, we would predict a molar volume of ~ 22 cm<sup>3</sup> / mol. This need to estimate atomic volume is what makes the value for density inaccurate.

$$\text{density} \left( \frac{\text{g}}{\text{cm}^3} \right) = \frac{298 \frac{\text{g}}{\text{mol}}}{18 \frac{\text{cm}^3}{\text{mol}}} = 16 \frac{\text{g}}{\text{cm}^3}$$

$$\text{density} \left( \frac{\text{g}}{\text{cm}^3} \right) = \frac{298 \frac{\text{g}}{\text{mol}}}{22 \frac{\text{cm}^3}{\text{mol}}} = 14 \frac{\text{g}}{\text{cm}^3}$$

21. A plot of density versus element is given below (table only shows a few elements used in the plot. Density clearly is a periodic property for these two periods of main group elements. It rises, falls a bit, rises again, and falls back to the axis, in both cases.

Element	Z	Density, g/cm <sup>3</sup>
Na	11	0.968
Mg	12	1.738
Al	13	2.699
Si	14	2.336
P	15	1.823
S	16	2.069
Cl	17	0.0032
Ar	18	0.0018
K	19	0.856
Ca	20	1.550
Ga	31	5.904
Ge	32	5.323
As	33	5.778
Se	34	4.285
Br	35	3.100
Kr	36	0.0037

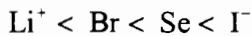


## The Periodic Table

- 23.** Mendeleev arranged elements in the periodic table in order of increasing atomic weight. Of course, atomic masses with non-integral values are permissible. Hence, there always is room for an added element between two elements that already are present in the table. On the other hand, Moseley arranged elements in order of increasing atomic number. Only integral (whole number) values of atomic number are permitted. Thus, when elements with all possible integral values in a certain range have been discovered, no new elements are possible in that range.
- 25.** (a) The noble gas following radon ( $Z = 86$ ) will have an atomic number of  $(86 + 32 =) 118$ .
- (b) The alkali metal following francium ( $Z = 87$ ) will have an atomic number of  $(87 + 32 =) 119$ .
- (c) The mass number of radon ( $A = 222$ ) is  $(222 \div 86) = 2.58$  times its atomic number. The mass number of Lr ( $A = 262$ ) is  $(262 \div 103) = 2.54$  times its atomic number. Thus, we would expect the mass numbers, and hence approximate atomic masses of elements 118 and 119 to be about 2.5 times their atomic numbers, that is,  $A_{118} \approx 298$  u and  $A_{119} \approx 295$  u.

## Atomic Radii and Ionic Radii

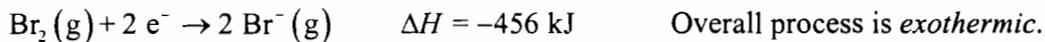
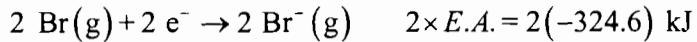
- 27.** The reason why the sizes of atoms do not simply increase with atomic number is because electrons often are added successively to the same subshell. These electrons do not fully screen each other from the nuclear charge (they do not effectively get between each other and the nucleus). Consequently, as each electron is added to a subshell and the nuclear charge increases by one unit, all of the electrons in this subshell are drawn more closely into the nucleus.
- 29.** (a) The smallest atom in Group 13 is the first: B
- (b) Po is in the sixth period, and is larger than the others, which are rewritten in the following list from left to right in the fifth period, that is, from largest to smallest: Sr, In, Sb, Te. Thus, Te is the smallest of the elements given.
- 31.** Ions can be isoelectronic without having noble-gas electron configurations. An example is  $\text{Cu}^+$  and  $\text{Zn}^{2+}$ , which both have the electron configuration  $[\text{Ar}]3d^{10}$ .
- 33.**  $\text{Li}^+$  is the smallest; it not only is in the second period, but also is a cation.  $\text{I}^-$  is the largest, an anion in the 5th period. Next largest is Se in the previous (the 4th) period. We expect Br to be smaller than Se because it is both to the right of Se and in the same period.



## Ionization Energies; Electron Affinities

35. The second ionization energy for an atom ( $I_2$ ) cannot be smaller than the first ionization energy ( $I_1$ ) for the same atom. The reason is that, when the first electron is removed it is being taken away from a species with a charge of  $1+$ . On the other hand, when the second electron is removed, it is being taken from a species with a charge of  $2+$ . Since the force between two charged particles is proportional to  $q_+q_- / r^2$  ( $r$  is the distance between the particles), the higher the charge, the more difficult it will be to remove an electron.
37. There are four third-shell electrons in each atom of silicon. In Table 10.4, the values for the ionization energies of these four electrons are listed in kJ/mol. Thus, the energy needed to ionize all four electrons from a mole of silicon atoms is given by:  

$$\text{Energy} = (786.5 + 1577 + 3232 + 4356) \text{ kJ} = 9952 \text{ kJ}$$
39. The electron affinity of bromine is  $-324.6 \text{ kJ/mol}$  (Figure 10-10). We use Hess's law to determine the heat of reaction for  $\text{Br}_2(\text{g})$  becoming  $\text{Br}^-(\text{g})$ .



41. The reasoning here is similar to that for the answer to Exercise 35. In both cases, an electron is being removed from an atom with a neon electron configuration. But in the case of  $\text{Na}^+$ , the electron is being removed from a species with a  $2+$  charge, while in the case of Ne, the electron is being removed from a species with a  $1+$  charge. The more highly charged the resulting species is, the more difficult it is to produce it by removing an electron.

## Magnetic Properties

43. Three of the ions have noble gas electron configurations and thus have no unpaired electrons:  $\text{F}^-$  is  $1s^2 2s^2 2p^6$        $\text{Ca}^{2+}$  and  $\text{S}^{2-}$  are  $[\text{Ne}]3s^2 3p^6$   
 Only  $\text{Fe}^{2+}$  has unpaired electrons. Its electron configuration is  $[\text{Ar}]3d^6$ .
45. All atoms with an odd number of electrons must be paramagnetic. There is no way to pair all of the electrons up if there is an odd number of electrons. Many atoms with an even number of electrons are diamagnetic, but some are paramagnetic. The one of lowest atomic number is carbon ( $Z = 6$ ), which has two unpaired  $p$ -electrons producing the paramagnetic behavior:  $[\text{He}] 2s^2 2p^2$ .

## Predictions Based on the Periodic Table

- 47.** (a) Elements that one would expect to exhibit the photoelectric effect with visible light should be ones that have a small value of their first ionization energy. Based on Figure 10-9, the alkali metals have the lowest first ionization potentials: Cs, Rb, and K are three suitable metals. Metals that would not exhibit the photoelectric effect with visible light are those that have high values of their first ionization energy. Again from Figure 10-9, Zn, Cd, and Hg seem to be three metals that would not exhibit the photoelectric effect with visible light.
- (b) From Figure 10-1, we notice that the atomic (molar) volume increases for the solid forms of the noble gases as we travel down the group (the data points just before the alkali metal peaks). But it seems to increase less rapidly than the molar mass. This means that the density should increase with atomic mass, and Rn should be the densest solid in the group. We expect densities of liquids to follow the same trend as densities of solids.
- (c) To estimate the first ionization energy of fermium, we note in Figure 10-9 that the ionization energies of the lanthanides (following the Cs valley) are approximately the same. We expect similar behavior of the actinides, and estimate a first ionization energy of about +600 kJ/mol.
- (d) We can estimate densities of solids from the information in Figure 10-1. Radium has  $Z = 88$  and an approximate atomic volume of  $40 \text{ cm}^3/\text{mol}$ . Then we use the molar mass of radium to determine its density:

$$\text{density} = \frac{1 \text{ mol}}{40 \text{ cm}^3} \times \frac{226 \text{ g Ra}}{1 \text{ mol}} = 5.7 \text{ g/cm}^3$$

- 49.** (a) From Figure 10-1, the atomic (molar) volume of Al is  $10 \text{ cm}^3/\text{mol}$  and that for In is  $15 \text{ cm}^3/\text{mol}$ . Thus, we predict  $12.5 \text{ cm}^3/\text{mol}$  as the molar volume for Ga. Then we compute the expected density for Ga.

$$\text{density} = \frac{1 \text{ mol Ga}}{12.5 \text{ cm}^3} \times \frac{68 \text{ g Ga}}{1 \text{ mol Ga}} = 5.4 \text{ g/cm}^3$$

- (b) Since Ga is in group 13 (3A) (Gruppe III on Mendeleev's table), the formula of its oxide should be  $\text{Ga}_2\text{O}_3$ . We use Mendeleev's molar masses to determine the molar mass for  $\text{Ga}_2\text{O}_3$ . Molar mass =  $2 \times 68 \text{ g Ga} + 3 \times 16 \text{ g O} = 184 \text{ g Ga}_2\text{O}_3$
- $$\% \text{ Ga} = \frac{2 \times 68 \text{ g Ga}}{184 \text{ g Ga}_2\text{O}_3} \times 100\% = 74\%(\text{Ga});$$

- 51.** (a) Size increases down a group and from right to left in a period. Ba is closest to the lower left corner of the periodic table and thus has the largest size.
- (b) Ionization energy decreases down a group and from right to left in a period. Although Pb is closest to the bottom of its group, Sr is farthest left in its period (and only one period above Pb). Sr should have the lowest first ionization energy.

- (c) Electron affinity becomes more negative from left to right in a period and from bottom to top in a group. Cl is closest to the upper right in the periodic table and has the most negative (smallest) electron affinity.
- (d) The number of unpaired electrons can be determined from the orbital diagram for each species.

F	[He] $2s^2 2p^5$	1 unpaired $e^-$	N	[He] $2s^2 2p^3$	3 unpaired $e^-$
$S^{2-}$	[Ne] $3s^2 3p^6$	0 unpaired $e^-$	$Mg^{2+}$	[He] $2s^2 2p^6$	0 unpaired $e^-$
$Sc^{3+}$	[Ne] $3s^2 3p^6$	0 unpaired $e^-$	$Ti^{3+}$	[Ar] $3d^1$	1 unpaired $e^-$

Thus, N has the largest number of unpaired electrons.

## FEATURE PROBLEMS

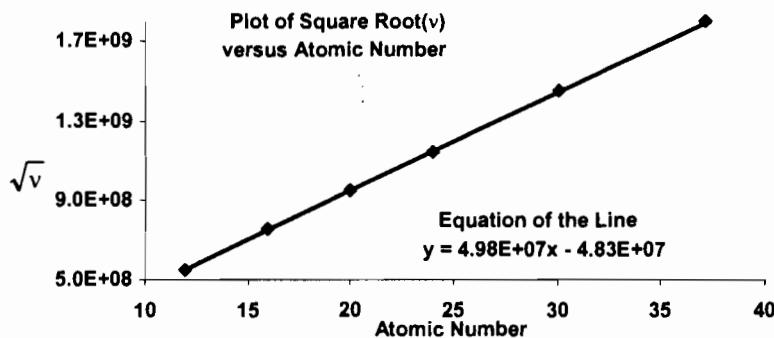
72. (a) The work function is the energy required for an electron to escape the solid surface of an element.
- (b) Work functions tend to decrease down a group and increase across a period in the periodic table. The work function increases across the periodic table from left to right following the steady increase in effective nuclear charge. As one proceeds down a given group, the principle quantum number increases and so does the distance of the outer electrons from the nucleus. The further the electrons are from the nucleus, the more easily they can be removed from the solid surface of the element, and hence, the smaller will be the value of the work function for the element.
- (c) Through the process of interpolation, one would predict that the work function for potassium should fall somewhere close to 3.9. The published value for the work function of potassium is 3.69 (CRC handbook). Had we been provided more information on the nature of the bonding in each of these metals, and had we been told what type of crystalline lattice each metal adopts, we would have been able to come up with a more accurate estimate of the work function.
- (d) The periodic trends in work function closely follow those in ionization energy. This should come as no surprise since both ionization and the work function involve the loss of electrons from neutral atoms.
73. The Moseley equation,  $v = A(Z - B)^2$ , where  $v$  is the frequency of the emitted X-ray radiation,  $Z$  is the atomic number and  $A$  and  $B$  are constants, relates the frequency of emitted X-rays to the nuclear charge for the atoms that make up the target of the cathode ray tube. X-rays are emitted by the element after one of its K-level electrons has been knocked out of the atom by collision with a fast moving electron. In this question, we have been asked to determine the values for the constants  $A$  and  $B$ . The simplest way to find these values is to plot  $\sqrt{v}$  vs.  $Z$ . This plot provides  $\sqrt{A}$  as the slope and  $-\sqrt{A}(B)$  as the y-intercept. Starting with  $v = A(Z - B)^2$ , we first take the square root of both sides. This affords  $\sqrt{v} = \sqrt{A}(Z - B)$ . Multiplying out this expression gives  $\sqrt{v} = \sqrt{A}(Z) - \sqrt{A}(B)$ . This expression follows the equation of a straight line  $y = mx + b$ , where  $y = \sqrt{v}$ ,  $m = \sqrt{A}$ ,  $x = Z$  and  $b = -\sqrt{A}(B)$ . So a plot of  $\sqrt{v}$  vs.  $Z$  will provide us with  $A$  and  $B$ .

B, after a small amount of mathematical manipulation. Before we can construct the plot we need to convert the provided X-ray wavelengths into their corresponding frequencies. For instance, Mg has an X-ray wavelength = 987 pm. The corresponding frequency for this radiation =  $c/\lambda$ , hence,

$$\nu = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{9.87 \times 10^{-10} \text{ m}} = 3.04 \times 10^{17} \text{ s}^{-1}$$

Performing similar conversions on the rest of the data allows for the construction of the following table and plot (below).

(Z)	$\sqrt{\nu}$
12	$5.51 \times 10^8$
16	$7.48 \times 10^8$
20	$9.49 \times 10^8$
24	$1.14 \times 10^9$
30	$1.45 \times 10^9$
37	$1.80 \times 10^9$



The slope of the line is  $4.98 \times 10^7 = \sqrt{A}$  and the y-intercept is  $-4.83 \times 10^7 = -\sqrt{A}$  (B).

$$\text{Thus, } A = 2.30 \times 10^{15} \text{ Hz and } B = \frac{-4.83 \times 10^7}{-4.98 \times 10^7} = 0.970$$

According to Bohr's theory, the frequencies that correspond to the lines in the emission

$$\text{spectra are given by the equation: } (3.2881 \times 10^{15} \text{ s}^{-1}) \left( \frac{1}{(n_i)^2} - \frac{1}{(n_f)^2} \right),$$

where  $(3.2881 \times 10^{15} \text{ s}^{-1})$  represents the frequency for the lowest energy photon that is capable of completely removing (ionizing) an electron from a hydrogen atom in its groundstate. The value of A (calculated in this question) is close to the Rydberg frequency  $(3.2881 \times 10^{15} \text{ s}^{-1})$ , so it is probably the equivalent term in the Moseley equation. The constant B, which is close to unity, could represent the number of electrons left in the K shell after one K-shell electron has been ejected by a cathode ray. Thus, one can think of B as representing the screening afforded by the remaining electron in the K-shell. Of course screening of the nucleus is only possible for those elements with  $Z > 1$ .

- 74. (a)** The table provided in this question shows the energy changes associated with the promotion of the outermost valence electron of sodium into the first four excited states above the highest occupied ground state atomic orbital. In addition, we have been told that the energy needed to completely remove one mole of  $3s$  electrons from one mole of sodium atoms in the ground state is 496 kJ. The ionization energy for each excited state can be found by subtracting the “energy quanta” entry for the excited state from 496 kJ mol<sup>-1</sup>.

$$\text{e.g., for } [\text{Ne}]3p^1, \text{ the 1}^{\text{st}} \text{ ionization energy} = 496 \frac{\text{kJ}}{\text{mol}} - 203 \frac{\text{kJ}}{\text{mol}} = 293 \frac{\text{kJ}}{\text{mol}}$$

Thus, the rest of the ionization energies are:

$$[\text{Ne}]4s^1, = 496 \text{ kJ mol}^{-1} - 308 \text{ kJ mol}^{-1} = 188 \text{ kJ mol}^{-1}$$

$$[\text{Ne}]3d^1, = 496 \text{ kJ mol}^{-1} - 349 \text{ kJ mol}^{-1} = 147 \text{ kJ mol}^{-1}$$

$$[\text{Ne}]4p^1, = 496 \text{ kJ mol}^{-1} - 362 \text{ kJ mol}^{-1} = 134 \text{ kJ mol}^{-1}$$

- (b)**  $Z_{\text{eff}}$  (the effective nuclear charge) for each state can be found by using the equation:

$$\text{Ionization Energy in kJ mol}^{-1} (\text{I.E.}) = \frac{A(Z_{\text{eff}})^2}{n^2}$$

Where  $n$  = starting principle quantum level for the electron that is promoted out of the atom and  $A = 1.3121 \times 10^3 \text{ kJ mol}^{-1}$  (Rydberg constant).

$$\text{For } [\text{Ne}]3p^1 \text{ (n = 3)} \quad 2.93 \times 10^2 \text{ kJ mol}^{-1} = \frac{1.3121 \times 10^3 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{3^2} \quad Z_{\text{eff}} = 1.42$$

$$\text{For } [\text{Ne}]4s^1 \text{ (n = 4)} \quad 1.88 \times 10^2 \text{ kJ mol}^{-1} = \frac{1.3121 \times 10^3 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4^2} \quad Z_{\text{eff}} = 1.51$$

$$\text{For } [\text{Ne}]3d^1 \text{ (n = 3)} \quad 1.47 \times 10^2 \text{ kJ mol}^{-1} = \frac{1.3121 \times 10^3 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{3^2} \quad Z_{\text{eff}} = 1.00$$

$$\text{For } [\text{Ne}]4p^1 \text{ (n = 4)} \quad 1.34 \times 10^2 \text{ kJ mol}^{-1} = \frac{1.3121 \times 10^3 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4^2} \quad Z_{\text{eff}} = 1.28$$

- (c)  $\bar{r}_{nl}$ , which is the average distance of the electron from the nucleus for a particular orbital, can be calculated with the equation:

$$\bar{r}_{nl} = \frac{n^2 a_0}{Z_{\text{eff}}} \left( 1 + \frac{1}{2} \left( 1 - \frac{\ell(\ell+1)}{n^2} \right) \right) \quad \text{Where} \quad a_0 = 52.9 \text{ pm},$$

$n = \text{principal quantum number}$

$\ell = \text{angular quantum number for the orbital}$

$$\text{For } [\text{Ne}]3p^1 \text{ (} n = 3, \ell = 1 \text{)} \quad \bar{r}_{3p} = \frac{3^2 (52.9 \text{ pm})}{1.42} \left( 1 + \frac{1}{2} \left( 1 - \frac{1(1+1)}{3^2} \right) \right) = 466 \text{ pm}$$

$$\text{For } [\text{Ne}]4s^1 \text{ (} n = 4, \ell = 0 \text{)} \quad \bar{r}_{4s} = \frac{4^2 (52.9 \text{ pm})}{1.51} \left( 1 + \frac{1}{2} \left( 1 - \frac{0(0+1)}{4^2} \right) \right) = 823 \text{ pm}$$

$$\text{For } [\text{Ne}]3d^1 \text{ (} n = 3, \ell = 2 \text{)} \quad \bar{r}_{3d} = \frac{3^2 (52.9 \text{ pm})}{1.00} \left( 1 + \frac{1}{2} \left( 1 - \frac{2(2+1)}{3^2} \right) \right) = 555 \text{ pm}$$

$$\text{For } [\text{Ne}]4p^1 \text{ (} n = 4, \ell = 1 \text{)} \quad \bar{r}_{4p} = \frac{4^2 (52.9 \text{ pm})}{1.28} \left( 1 + \frac{1}{2} \left( 1 - \frac{1(1+1)}{4^2} \right) \right) = 950 \text{ pm}$$

- (d) The results from the  $Z_{\text{eff}}$  calculations show that the greatest effective nuclear charge is experienced by the  $4s$  orbital ( $Z_{\text{eff}} = 1.51$ ). Next are the two  $p$ -orbitals,  $3p$  and  $4p$ , which come in at 1.42 and 1.28 respectively. Coming in last is the  $3d$  orbital, which has a  $Z_{\text{eff}} = 1.00$ . These results are precisely in keeping with what we would expect. First of all, only the  $s$ -orbital penetrates all the way to the nucleus. Both the  $p$ - and  $d$ -orbitals have nodes at the nucleus. Also  $p$ -orbitals penetrate more deeply than do  $d$ -orbitals. Recall that the more deeply an orbital penetrates (i.e. the closer the orbital is to the nucleus), the greater is the effective nuclear charge felt by the electrons in that orbital. It follows then that the  $4s$  orbital will experience the greatest effective nuclear charge and that the  $Z_{\text{eff}}$  values for the  $3p$  and  $4p$  orbitals should be larger than the  $Z_{\text{eff}}$  for the  $3d$  orbital.

The results from the  $\bar{r}_{nl}$  calculations for the four excited state orbitals show that the largest orbital in the set is the  $4p$  orbital. This is exactly as expected because the  $4p$  orbital is highest in energy and hence, on average furthest from the nucleus. The  $4s$  orbital has an average position closer to the nucleus because it experiences a larger effective nuclear charge. The  $3p$  orbital, being lowest in energy and hence on average closest to the nucleus, is the smallest orbital in the set. The  $3p$  orbital has an average position closer to the nucleus than the  $3d$  orbital (which is in the same principle quantum level), because it penetrates more deeply into the atom.

75. (a) First of all, we need to find the ionization energy (I.E.) for the process:

$F^-(g) \rightarrow F(g) + e^-$ . To accomplish this, we need to calculate  $Z_{\text{eff}}$  for the species in the left hand column and plot the number of protons in the nucleus against  $Z_{\text{eff}}$ . By extrapolation, we can estimate the first ionization energy for  $F(g)$ . The electron affinity for F is equal to the first ionization energy of  $F^-$  multiplied by minus one (i.e., by reversing the ionization reaction, one can obtain the electron affinity).

For  $Ne(g) \rightarrow Ne^+(g) + e^-$  (I.E. = 2080 kJ mol<sup>-1</sup>; n = 2; 10 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 2080 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 2.518$$

For  $Na^+(g) \rightarrow Na^{2+}(g) + e^-$  (I.E. = 4565 kJ mol<sup>-1</sup>; n = 2; 11 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 4565 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 3.730$$

For  $Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^-$  (I.E. = 7732 kJ mol<sup>-1</sup>; n = 2; 12 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 7732 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 4.855$$

For  $Al^{3+}(g) \rightarrow Al^{4+}(g) + e^-$  (I.E. = 11,577 kJ mol<sup>-1</sup>; n = 2; 13 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 11,577 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 5.941$$

A plot of the points (10, 2.518), (11, 3.730), (12, 4.855), (13, 5.941) gives a straight line that follows the equation:  $Z_{\text{eff}} = 1.1394(Z) - 8.8421$

For  $F^-$ ,  $Z = 9$ ; so  $Z_{\text{eff}} = 1.1394(9) - 8.8421 = 1.413$  and  $n = 2$ . Hence,

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (1.413)^2}{4} = 654.5 \text{ kJ mol}^{-1} \text{ for } F^-$$

The Electron affinity for F must equal the reverse of the first ionization energy or -654.5 kJ. The actual experimental value found for the first electron affinity of F is -328 kJ/mol.

- (b) Here, we will use the same method of solution as we did for part (a). To find the electron affinity for the process:  $O(g) + e^- \rightarrow O^-(g)$ , we first need to calculate the I.E. for  $O^-(g)$ . This is available from a plot of the number of protons in the nucleus vs.  $Z_{\text{eff}}$  for the four species in the central column.

For  $F(g) \rightarrow F^+(g) + e^-$  (I.E. = 1681 kJ mol<sup>-1</sup>; n = 2; 9 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 1681 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 2.264$$

For  $Ne^+(g) \rightarrow Ne^{2+}(g) + e^-$  (I.E. = 3963 kJ mol<sup>-1</sup>; n = 2; 10 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 3963 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 3.476$$

For  $Na^{2+}(g) \rightarrow Na^{3+}(g) + e^-$  (I.E. = 6912 kJ mol<sup>-1</sup>; n = 2; 11 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 6912 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 4.590$$

For  $Mg^{3+}(g) \rightarrow Mg^{4+}(g) + e^-$  (I.E. = 10,548 kJ mol<sup>-1</sup>; n = 2; 12 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 10,548 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 5.671$$

A plot of the points (9, 2.264), (10, 3.476), (11, 4.590), (12, 5.671), gives a straight line that follows the equation:  $Z_{\text{eff}} = 1.134(Z) - 7.902$

For  $O^-$ , Z = 8; so  $Z_{\text{eff}} = 1.134(8) - 7.902 = 1.170$  and n = 2. Hence,

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (1.179)^2}{4} = 449 \text{ kJ mol}^{-1} \text{ for } O^-$$

The Electron affinity for O must equal the reverse of the first ionization energy, or - 449 kJ. Again we will use the same method of solution as was used for part (a). To find the electron affinity for the process:  $N(g) + e^- \rightarrow N^-(g)$ , we first need to calculate the I.E. for  $N^-(g)$ . This is accessible from a plot of the number of protons in the nucleus vs.  $Z_{\text{eff}}$  for the four species in the last column.

For  $O(g) \rightarrow O^+(g) + e^-$  (I.E. = 1314 kJ mol<sup>-1</sup>; n = 2; 8 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 1314 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 2.001$$

For  $F^+(g) \rightarrow F^{2+}(g) + e^-$  (I.E. = 3375 kJ mol<sup>-1</sup>; n = 2; 9 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 3375 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 3.208$$

For  $\text{Ne}^{2+}(\text{g}) \rightarrow \text{Ne}^{3+}(\text{g}) + \text{e}^-$  (I.E. = 6276 kJ mol<sup>-1</sup>; n = 2; 10 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 6276 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 4.374$$

For  $\text{Na}^{3+}(\text{g}) \rightarrow \text{Na}^{4+}(\text{g}) + \text{e}^-$  (I.E. = 9,540 kJ mol<sup>-1</sup>; n = 2; 11 protons)

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (Z_{\text{eff}})^2}{4} = 9,540 \text{ kJ mol}^{-1} \quad Z_{\text{eff}} = 5.393$$

A plot of the points (8, 2.001), (9, 3.204), (10, 4.374), (11, 5.393), gives a straight line that follows the equation:  $Z_{\text{eff}} = 1.1346(Z) - 7.0357$

For  $\text{N}^-$ ,  $Z = 7$ ; so  $Z_{\text{eff}} = 1.1346(7) - 7.0357 = 0.9065$  and  $n = 2$ . Hence,

$$\text{I.E. (kJ mol}^{-1}\text{)} = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (0.9065)^2}{4} = 269.6 \text{ kJ mol}^{-1} \text{ for N}^-$$

The Electron affinity for N must equal the reverse of the first ionization energy, or  $-269.6 \text{ kJ}$ .

- (c) For N, O and F, the additional electron ends up in a 2p orbital. In all three instances the nuclear charge is well shielded by the filled 2s orbital located below the 2p set of orbitals. As we proceed from N to F, electrons are placed, one by one, in the 2p subshell and these electrons do afford some additional shielding, but this extra screening is more than offset by the accompanying increase in nuclear charge. Thus, the increase in electron affinity observed upon moving from N via oxygen to fluorine is the result of the steady increase in  $Z_{\text{eff}}$  that occurs upon moving further to the right in the periodic table.
76. (a) An oxygen atom in the ground state has the valence shell configuration  $2s^2 2p^4$ . Thus there are a total of six electrons in the valence shell. The amount of shielding experienced by one electron in the valence shell is the sum of the shielding provided by the other five electrons in the valence shell and the shielding afforded by the two electrons in the filled 1s orbital below the valence shell. Shielding from electrons in the same shell contribute  $5 \times 0.35 = 1.75$  and the shielding from the electrons in the  $n = 1$  shell contributes  $2 \times 0.85 = 1.70$ . The total shielding is 3.45 ( $1.75 + 1.70$ ). For O,  $Z = 8$  hence,  $Z_{\text{eff}} = 8 - 3.45 = 4.55$ .

- (b) A ground state Cu atom has the valence shell configuration  $3d^94s^2$ . According to Slater's rules, the nine 3d electrons do not shield the 4s<sup>2</sup> electrons from the nucleus. Thus the total amount of shielding experienced by a 4s electron in Cu is:

$$\text{Shielding from the other 4s electron} = 1 \times 0.35 = 0.35$$

$$+ \text{shielding from the electrons in the } 3d \text{ subshell} = 9 \times 0.85 = 7.65$$

$$+ \text{shielding from the electrons in the } 3s/3p \text{ orbitals} = 8 \times 1.00 = 8.00$$

$$+ \text{shielding from the electrons in the } 2s/2p \text{ orbitals} = 8 \times 1.00 = 8.00$$

$$+ \text{shielding from the electrons in the } 1s \text{ orbital} = 2 \times 1.00 = \underline{2.00}$$

$$\text{Total shielding for the 4s electrons} = (0.35 + 7.65 + 8 + 8 + 2) = 26.00$$

$$\text{Copper has } Z = 29, \text{ so } Z_{\text{eff}} = 29 - 26.00 = 3.00$$

- (c) 3d electron in a ground state Cu atom will be shielded by the eight other 3d electrons and by the electrons in the lower principle quantum levels. Thus the total amount of shielding for a 3d electron is equal to

$$\text{shielding from the eight electrons in the } 3d \text{ subshell} = 8 \times 0.35 = 2.80$$

$$+ \text{shielding from the electrons in the } 3s/3p \text{ orbitals} = 8 \times 1.00 = 8.00$$

$$+ \text{shielding from the electrons in the } 2s/2p \text{ orbitals} = 8 \times 1.00 = 8.00$$

$$+ \text{shielding from the electrons in the } 1s \text{ orbital} = 2 \times 1 = \underline{2.00}$$

$$\text{Total shielding for the } 3d \text{ electrons} = (2.80 + 8.00 + 8.00 + 2.00) = 20.80$$

$$\text{Copper has } Z = 29, \text{ so } Z_{\text{eff}} = 29 - 20.80 = 8.2$$

- (d) To find  $Z_{\text{eff}}$  for the valence electron in each Group I element, we first calculate the screening constant for the electron.

$$\text{For H: } S = 0, \text{ so } Z_{\text{eff}} = Z \text{ and } Z = 1; \text{ thus } Z_{\text{eff}} = 1$$

$$\text{For Li: } S = 2(0.85) = 1.70 \text{ and } Z = 3; \text{ thus } Z_{\text{eff}} = 3 - 1.70 = 1.30$$

$$\text{For Na: } S = 8(0.85) + 2(1) = 8.80 \text{ and } Z = 11; \text{ thus } Z_{\text{eff}} = 11 - 8.80 = 2.20$$

$$\text{For K: } S = 8(0.85) + 8(1) + 2(1) = 16.80, Z = 19; \text{ thus } Z_{\text{eff}} = 19 - 16.80 = 2.20$$

$$\text{For Rb: } S = 8(0.85) + 10(1) + 8(1) + 8(1) + 2(1) = 34.80, Z = 37; \text{ thus } Z_{\text{eff}} = 37 - 34.80 = 2.20$$

$$\text{For Cs: } S = 8(0.85) + 10(1) + 8(1) + 10(1) + 8(1) + 8(1) + 2(1) = 52.80; Z = 55, \text{ Thus } Z_{\text{eff}} = 2.20$$

Based upon Slater's rules, we have found that the effective nuclear charge increases sharply between periods one and three and then stays at 2.20 for the rest of the alkali metal group. You may recall that the ionization energy for an element can be calculated by using the equation:

$$\text{I.E. (kJ mol}^{-1}) = \frac{1312.1 \frac{\text{kJ}}{\text{mol}} (\text{Z}_{\text{eff}})^2}{n^2} \quad \text{Where } n = \text{principal quantum number.}$$

By plugging the results from our  $Z_{\text{eff}}$  calculations into this equation, we would find that the ionization energy decreases markedly as we descend the alkali metal group, in spite of the fact that the  $Z_{\text{eff}}$  remains constant after Li. The reason that the ionization energy drops is, of course, because the value for  $n$  becomes larger as we move down the periodic table and, according to the ionization energy equation given above, larger  $n$  values translate into smaller ionization energies (this is because  $n^2$  appears in the denominator). Put another way, even though  $Z_{\text{eff}}$  remains constant throughout most of Group I, the valence s-electrons become progressively easier to remove as we move down the group because they are further and further from the nucleus. Of course, the further away an electron is from the nucleus, the weaker is its attraction to the nucleus and the easier it is to remove.

- (e) As was the case in part (d), to evaluate  $Z_{\text{eff}}$  for a valence electron in each atom, we must first calculate the screening experienced by the electron with Slater's rules

For Li:  $S = 2(0.85) = 1.70$  and  $Z = 3$ , thus  $Z_{\text{eff}} = 3 - 1.70 = 1.30$

For Be:  $S = 1(0.35) + 2(0.85) = 2.05$  and  $Z = 4$ ; thus  $Z_{\text{eff}} = 4 - 2.05 = 1.95$

For B:  $S = 2(0.35) + 2(0.85) = 2.40$  and  $Z = 5$ ; thus  $Z_{\text{eff}} = 5 - 2.40 = 2.60$

For C:  $S = 3(0.35) + 2(0.85) = 2.75$  and  $Z = 6$ ; thus  $Z_{\text{eff}} = 6 - 2.75 = 3.25$

For N:  $S = 4(0.35) + 2(0.85) = 3.10$  and  $Z = 7$ ; thus  $Z_{\text{eff}} = 7 - 3.10 = 3.90$

For O:  $S = 5(0.35) + 2(0.85) = 3.45$  and  $Z = 8$ ; thus  $Z_{\text{eff}} = 8 - 3.45 = 4.55$

For F:  $S = 6(0.35) + 2(0.85) = 3.80$  and  $Z = 9$ ; thus  $Z_{\text{eff}} = 9 - 3.80 = 5.20$

For Ne:  $S = 7(0.35) + 2(0.85) = 4.15$  and  $Z = 10$ ; thus  $Z_{\text{eff}} = 10 - 4.15 = 5.85$

The results from these calculations show that the  $Z_{\text{eff}}$  increases from left to right across the periodic table. Apart from small irregularities, the first ionization energies for the elements within a period also increase with increasing atomic number. Based upon our calculated  $Z_{\text{eff}}$  values, this is exactly the kind of trend for ionization energies that we would have anticipated. The fact is, a larger effective nuclear charge means that the outer electron(s) is/are held more tightly and this leads to a higher first ionization energy for the atom.

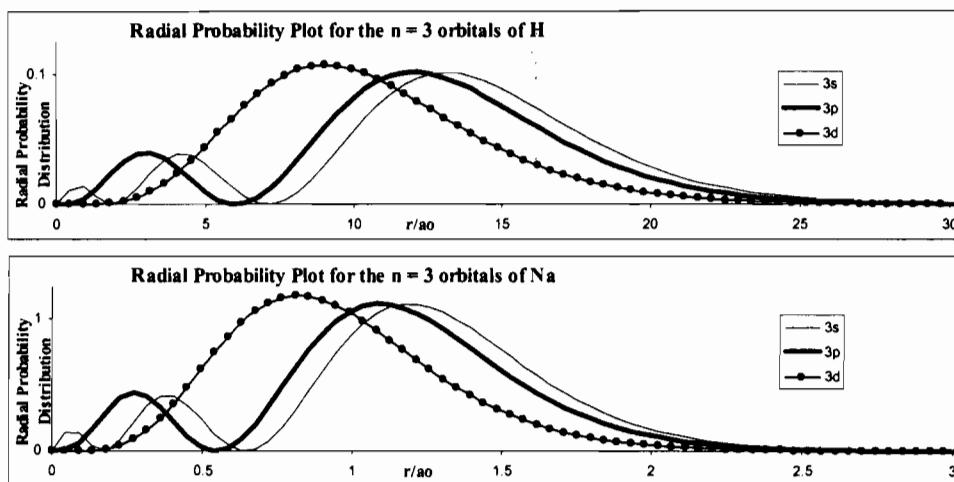
- (f) First we need to calculate the  $Z_{\text{eff}}$  values for an electron in the  $3s$ ,  $3p$  and  $3d$  orbitals of both a hydrogen atom and a sodium atom, by using Slater's rules. Since there is only one electron in a H atom, there is no possibility of shielding, and thus the effective nuclear charge for an electron in a  $3s$ ,  $3p$  or  $3d$  orbital of a H atom is one. The picture for Na is more complicated because it contains intervening electrons that shield the outermost electrons from the attractive power of the nucleus. The  $Z_{\text{eff}}$  calculations(based on Slater's Rules) for an electron in the i) the  $3s$  orbital, ii) the  $3p$  orbital, and iii) the  $3d$  orbital of a Na atom are shown below:

Na (3s electron;  $n = 3$ )  $Z_{\text{eff}} = 11.0 - [(8e^- \text{ in the } n = 2 \text{ shell} \times 0.85/e^-) + (2e^- \text{ in the } n = 1 \text{ shell} \times 1.00/e^-)] = [11.0 - 8.8] = 2.2$

Na (3p electron;  $n = 3$ ;  $e^-$  was originally in the 3s orbital))  $Z_{\text{eff}} = 11.0 - [(8e^- \text{ in the } n = 2 \text{ shell} \times 0.85/e^-) + (2e^- \text{ in the } n = 1 \text{ shell} \times 1.00/e^-)] = [11.0 - 8.8] = 2.2$

Na (3d electron;  $n = 3$ ;  $e^-$  was originally in the 3s orbital))  $Z_{\text{eff}} = 11.0 - [(8e^- \text{ in the } n = 2 \text{ shell} \times 1.00/e^-) + (2e^- \text{ in the } n = 1 \text{ shell} \times 1.00/e^-)] = [11.0 - 10.0] = 1.0$

Next, we insert these  $Z_{\text{eff}}$  values into their appropriate radial functions, which are gathered in Table 9.1, and use the results from these calculations to construct radial probability plots for an electron in the 3s, 3p and 3d orbitals of H and Na. The six plots that result are collected in the two figures presented below:



Notice that the 3s and 3p orbitals of sodium are much closer to the nucleus, on average, than the 3s and 3p orbitals of hydrogen. Because they are pulled more strongly towards the nucleus, the 3s and 3p orbitals of sodium end up being much smaller than the corresponding orbitals on hydrogen. Put another way, since the 3s and 3p electrons in sodium experience a larger effective nuclear charge, they are more tightly bound to the nucleus and, hence, are lower in energy than s and p electrons in the third principal shell of a hydrogen atom. If we want to express this in terms of shielding, we can say that the radial probability distributions for the 3s and 3p orbitals of sodium are smaller than those of hydrogen because the 3s and 3p orbitals of sodium are more poorly shielded. The graphs also show that the radial probability plot for the 3d orbital of a hydrogen atom is identical to that for a 3d orbital of a Na atom. This is what one would expect since a 3d electron in H and a 3d electron in Na both experience an effective nuclear charge of one.

# CHAPTER 11

## CHEMICAL BONDING I: BASIC CONCEPTS

### PRACTICE EXAMPLES

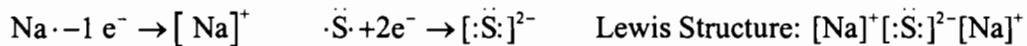
- 1A** Mg is in group 2(2A), and thus has 2 valence electrons and 2 dots in its Lewis symbol. Ge is in group 14(4A), and thus has 4 valence electrons and 4 dots in its Lewis symbol. K is in group 1(1A), and thus has 1 valence electron and 1 dot in its Lewis symbol. Ne is in group 18(8A), and thus has 8 valence electrons and 8 dots in its Lewis symbol.



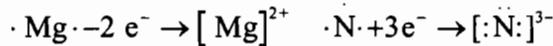
- 1B** Sn is in Family 4A, and thus has 4 electrons and 4 dots in its Lewis symbol. Br is in Family 7A with 7 valence electrons. Adding an electron produces an ion with 8 valence electrons. Tl is in Family 3A with 3 valence electrons. Removing an electron produces a cation with 2 valence electrons. S is in Family 6A with 6 valence electrons. Adding 2 electrons produces an anion with 8 valence electrons.



- 2A** The Lewis structure for the cation, the anion, and the compound follows the explanation.
- (a) Na loses one electron to form  $\text{Na}^+$ , while S gains two to form  $\text{S}^{2-}$ .

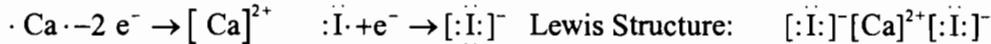


- (b) Mg loses two electrons to form  $\text{Mg}^{2+}$ , while N gains three to form  $\text{N}^{3-}$ .

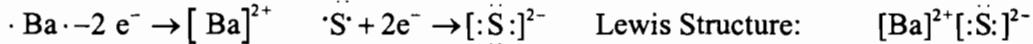


- 2B** Below each explanation are the Lewis structures for the cation, for the anion, and for the compound.

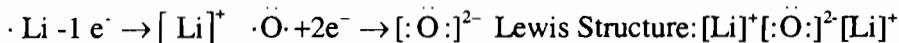
- (a) In order to acquire a noble-gas electron configuration, Ca loses two electrons, and I gains one, forming the ions  $\text{Ca}^{2+}$  and  $\text{I}^-$ . The formula of the compound is  $\text{CaI}_2$ .



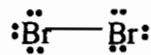
- (b) Ba loses two electrons and S gains two to acquire a noble-gas electron configuration, forming the ions  $\text{Ba}^{2+}$  and  $\text{S}^{2-}$ . The formula of the compound is  $\text{BaS}$ .



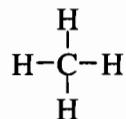
- (c)** Each Li loses one electron and each O gains two to attain a noble-gas electron configuration, producing the ions  $\text{Li}^+$  and  $\text{O}^{2-}$ . The formula of the compound is  $\text{Li}_2\text{O}$ .



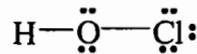
- 3A** In the  $\text{Br}_2$  molecule, the two Br atoms are joined by a single covalent bond. This bonding arrangement gives each Br atom a closed valence shell configuration that is equivalent to that for a Kr atom.



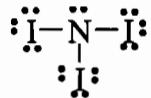
In  $\text{CH}_4$ , the carbon atom is covalently bonded to four hydrogen atoms. This arrangement gives the carbon atom a valence shell octet and each H atom a valence shell duet.



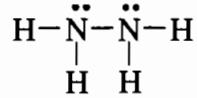
In  $\text{HOCl}$ , the hydrogen and chlorine atoms are attached to the central oxygen atom through single covalent bonds. This bonding arrangement provides each atom in the molecule with a closed valence shell.



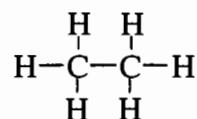
- 3B** The Lewis structure for  $\text{NI}_3$  is similar to that of  $\text{NH}_3$ . The central nitrogen atom is attached to each iodine atom by a single covalent bond. All of the atoms in this structure get a closed valence shell.



The Lewis diagram for  $\text{N}_2\text{H}_4$  has each nitrogen with one lone pair of electrons, two covalent bonds to hydrogen atoms and one covalent bond to the other nitrogen atom. With this arrangement, the nitrogen atoms complete their octets while the hydrogen atoms complete their duets.



In the Lewis structure for  $\text{C}_2\text{H}_6$ , each carbon atom shares four pairs of electrons with three hydrogen atoms and the other carbon atom. With this arrangement, the carbon atoms complete their octets while the hydrogen atoms complete their duets.



- 4A** The bond with the most ionic character is the one in which the two bonded atoms are the most different in their electronegativities. We find electronegativities in Table 11-2 and calculate  $\Delta\text{EN}$  for each bond.

Electronegativities:  $\text{H} = 2.1$   $\text{Br} = 2.8$   $\text{N} = 3.0$   $\text{O} = 3.5$   $\text{P} = 2.1$   $\text{Cl} = 3.0$

Bonds:  $\text{H}-\text{Br}$   $\text{N}-\text{H}$   $\text{N}-\text{O}$   $\text{P}-\text{Cl}$

$\Delta\text{EN}$  values:  $0.7$   $0.9$   $0.5$   $0.9$

Therefore, the  $\text{N}-\text{H}$  and  $\text{P}-\text{Cl}$  bonds are the most polar of the four bonds cited.

- 4B** The most polar bond is the one with the greatest electronegativity difference.

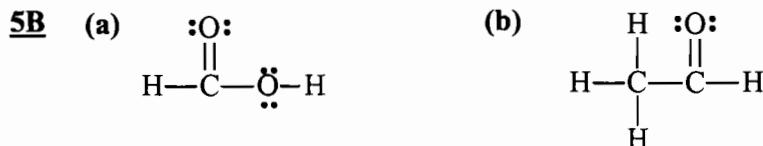
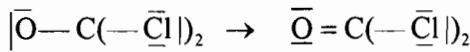
Electronegativities:  $\text{C} = 2.5$   $\text{S} = 2.5$   $\text{P} = 2.1$   $\text{O} = 3.5$   $\text{F} = 4.0$

Bonds:  $\text{C}-\text{S}$   $\text{C}-\text{P}$   $\text{P}-\text{O}$   $\text{O}-\text{F}$

$\Delta\text{EN}$  values:  $0.0$   $0.4$   $1.4$   $0.5$

Therefore, the  $\text{P}-\text{O}$  bond is the most polar of the four bonds cited.

- 5A** (a) C has 4 valence electrons and each S has 6 valence electrons:  $4 + (2 \times 6) = 16$  valence electrons or 8 pairs of valence electrons. We place C between two S, and use two electron pairs to hold the molecule together, one between C and each S. We complete the octet on each S with three electron pairs for each S. This uses six more electron pairs, for a total of eight electron pairs used.  $|\bar{S}—C—\bar{S}|$  But C does not have an octet. We correct this situation by moving one lone pair of each S into a bonding position between C and S.  $\bar{S} = C = \bar{S}$
- (b) C has 4 valence electrons, N has 5 valence electrons and hydrogen has 1 valence electron: Total number of valence electrons =  $4 + 5 + 1 = 10$  valence electrons or 5 pairs of valence electrons. We place C between H and N, and use two electron pairs to hold the molecule together, one between C and N, as well as one between C and H. We complete the octet on N using three lone pairs. This uses all five electron pairs.  $H—C—C—\bar{N}|$ . But C does not have an octet. We correct this situation by moving two lone pair from N into bonding position between C and N.  $H—C \equiv N|$
- (c) C has 4 valence electrons, each Cl has 7 valence electrons and oxygen has 6 valence electrons: Total number of valence electrons =  $4 + 2(7) + 6 = 24$  valence electrons or 12 pairs of valence electrons. We choose C as the central atom, and use three electron pairs to hold the molecule together, one between C and O, as well as one between C and each Cl. We complete the octet on Cl and O using three lone pairs. This uses all twelve electron pairs. But C does not have an octet. We correct this situation by moving one lone pair from O into bonding position between C and O.

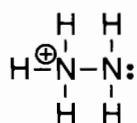


- 6A** (a) A plausible Lewis structure for the nitrosonium cation,  $NO^+$  is drawn below:



The nitrogen atom is triply bonded to the oxygen atom and both atoms in the structure possess a lone pair of electrons. This gives each atom an octet and a positive formal charge appears on the oxygen atom.

- (b) A plausible Lewis structure for  $N_2H_5^+$  is given below:

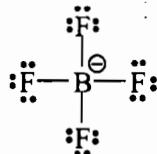


The two nitrogen atoms and the oxygen atom have each achieved an octet by keeping a pair of electrons for themselves while sharing three pairs of electrons with three other atoms. Each hydrogen atom has completed its duet by sharing a pair of electrons with either a nitrogen or an oxygen atom. A formal  $1+$  charge of has been assigned to the oxygen atom because it is bonded to three atoms (one more than its usual number) in this structure.

- (c) In order to achieve a noble gas configuration, oxygen gains two electrons, forming the stable dianion. The Lewis structure for  $O^{2-}$  is shown below.

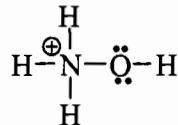


- 6B** (a) The most likely Lewis structure for  $BF_4^-$  is drawn below:



Four bonding pairs of electrons surround the central boron atom in this structure. This arrangement gives the boron atom a complete octet and a formal charge of  $1-$ . By virtue of being surrounded by three lone pairs and one bonding electron pair, each fluorine achieves a full octet.

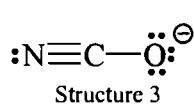
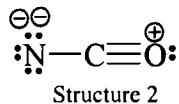
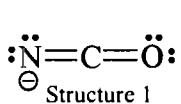
- (b) A plausible Lewis structural form for  $NH_3OH^+$ , the hydroxylammonium ion, has been provided below:



By sharing bonding electron pairs with three hydrogen atoms and the oxygen atom, the nitrogen atom acquires a full octet and a formal charge of  $1+$ . The oxygen atom shares one bonding electron pair with the nitrogen and a second bonding pair with a hydrogen atom.

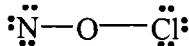
- (c) Three plausible resonance structures can be drawn for the isocyanate ion,  $NCO^-$ . The nitrogen contributes five electrons, the carbon four, oxygen six and one more electron is added to account for the negative charge, giving a total of 16 electrons or eight pairs of electrons. In the first resonance contributor, structure 1 below, the carbon atom is joined to the nitrogen and oxygen atoms by two double bonds thereby creating an octet for carbon. To complete the octet of nitrogen and oxygen, each atom is given a lone pair of electrons. Since nitrogen is sharing just two bonding pairs of electrons in this structure, it must be assigned a formal charge of  $1-$ . In structure 2, the carbon atom is again surrounded by four bonding pairs of electrons, but this time, the carbon atom forms a triple bond with oxygen and just a single bond with nitrogen. The octet for the nitrogen atom is closed with three lone pairs of electrons, while that for oxygen is closed with one lone pair of electrons. This

bonding arrangement necessitates giving nitrogen a formal charge of 2- and the oxygen atom a formal charge of 1+. In structure 3, which is the dominant contributor because it has a negative formal charge on oxygen (the most electronegative element in the anion), the carbon achieves a full octet by forming a triple bond with the nitrogen atom and a single bond with the oxygen atom. The octet for oxygen is closed with three lone pairs of electrons, while that for nitrogen is closed with one lone pair of electrons.

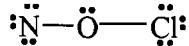


- 7A** The total number of valence electrons in  $\text{NOCl}$  is 18 (5 from nitrogen, 6 from oxygen and 7 from chlorine). Four electrons are used to covalently link the central oxygen atom to the terminal chlorine and nitrogen atoms in the implausible skeletal structure:  $\text{N}-\text{O}-\text{Cl}$ .

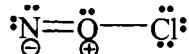
Next, we need to distribute the remaining electrons to achieve a noble gas electron configuration for each atom. Since four electrons were used to form the two covalent single bonds, fourteen electrons remain to be distributed. By convention, the valence shells for the terminal atoms are filled first. If we follow this convention, we can close the valence shells for both the nitrogen and the chlorine atoms with twelve electrons.



Oxygen is moved closer to a complete octet by placing the remaining pair of electrons on oxygen as a lone pair.

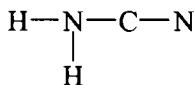


The valence shell for the oxygen atom can then be closed by forming a double bond between the nitrogen atom and the oxygen atom.

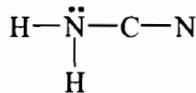


This structure obeys the requirement that all of the atoms end up with a filled valence shell, but is much poorer than the one derived in Example 11-7 because it has a positive formal charge on oxygen, which is the most electronegative atom in the molecule. In other words, this structure can be rejected on the grounds that it does not conform to the third rule for determining plausibility of a Lewis structure based on formal charges which states that "negative formal charges should appear on the most electronegative atom, while any positive formal charge should appear on the least electronegative atom".

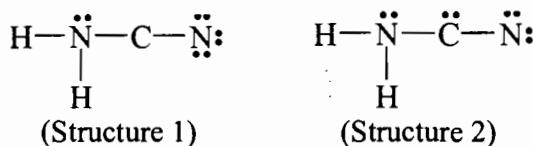
- 7B** There are a total of sixteen valence electrons in the cyanamide molecule (five from each nitrogen atom, four from carbon and one electron from each hydrogen atom). The formula has been written as  $\text{NH}_2\text{CN}$  to remind us that carbon, the most electropositive p-block element in the compound should be selected as the central atom in the skeletal structure.



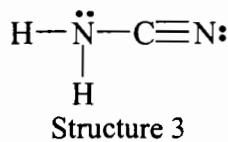
To construct this skeletal structure we use 8 electrons. Eight electrons remain to be added to the structure. Note: each hydrogen atom at this stage has achieved a duet by forming a covalent bond with the nitrogen atom in the  $\text{NH}_2$  group. The octet for the  $\text{NH}_2$  nitrogen is completed by giving it a lone pair of electrons.



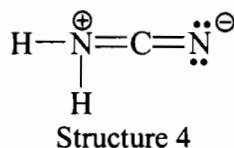
The remaining six electrons can then be given to the terminal nitrogen atom, affording structure 1, shown below. Alternatively, four electrons can be assigned to the terminal nitrogen atom and the last two electrons can be given to the central carbon atom, to produce structure 2 below:



The octet for the carbon atom in structure 1 can be completed by converting two lone pairs of electrons on the terminal nitrogen atom into two more covalent bonds to the central carbon atom.

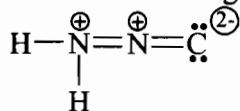


Each atom in structure 3 has a closed-shell electron configuration and a formal charge of zero. We can complete the octet for the carbon and nitrogen atoms in structure 1 by converting a lone pair of electrons on each nitrogen atom into a covalent bond to the central carbon atom.



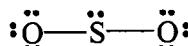
The resulting structure has a formal charge of 1- on the terminal nitrogen atom and a 1+ formal charge on the  $\text{NH}_2$  nitrogen atom.

Although both structures 3 and 4 both satisfy the octet and duet rules, structure 3 is the better of the two structures because it has no formal charges. A third structure which obeys the octet rule (depicted below), can be rejected on the grounds that it has formal charges of the same type (two 1+ formal charges) on adjacent atoms, as well as negative formal charges on carbon, which is not the most electronegative element in the molecule.

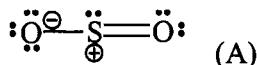


- 8A** The skeletal structure for  $\text{SO}_2$  has two terminal oxygen atoms bonded to a central sulfur atom. Sulfur has been selected as the central atom by virtue of it being the most electropositive atom in the molecule. It turns out that two different Lewis structures of

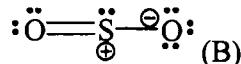
identical energy can be drawn on the skeletal structure described above. First we determine that  $\text{SO}_2$  has 18 valence electrons (6 from each atom). Four of the valence electrons must be used to covalently bond the three atoms together. The remaining 14 electrons are used to close the valence shell of each atom. Twelve electrons are used to give the terminal oxygen atoms a closed shell. The remaining two electrons ( $14 - 12 = 2$ ) are placed on the sulfur atom, affording the structure depicted below:



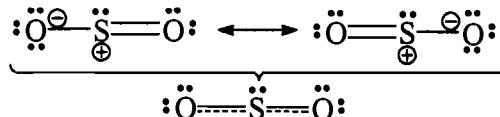
At this stage, the valence shells for the two oxygen atoms are closed, but the sulfur atom is two electrons short of a complete octet. If we complete the octet for sulfur by converting a lone pair of electrons on the right hand side oxygen atom into a sulfur-to-oxygen  $\pi$ -bond, we end up generating the resonance contributor (A) shown below:



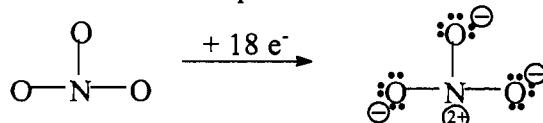
Notice that the structure has a positive formal charge on the sulfur atom (most electropositive element) and a negative formal charge on the left-hand oxygen atom. Remember that oxygen is more electronegative than sulfur, so these charges are plausible. The second completely equivalent contributor, (B), is produced by converting a lone pair on the left-most oxygen atom in the structure into a  $\pi$ -bond, resulting in conversion of a S-O single bond into a sulfur-oxygen double bond:



Neither structure is consistent with the observation that the two S-O bond lengths in  $\text{SO}_2$  are equal, and in fact, the true Lewis structure for  $\text{SO}_2$  is neither (A) or (B) but rather an equal blend of the two individual contributors called the resonance hybrid. (see below)

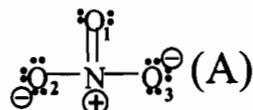


- 8B** The skeletal structure for the  $\text{NO}_3^-$  ion has three terminal oxygen atoms bonded to a central nitrogen atom. Nitrogen has been chosen as the central atom by virtue of it being the most electropositive atom in the ion. It turns out that three contributing resonance structures of identical energy can be derived from the skeletal structure described here. We begin the process of generating these three structures by counting the total number of valence electrons in the  $\text{NO}_3^-$  anion. The nitrogen atom contributes five electrons, each oxygen contributes six electrons and an additional electron must be added to account for the 1- charge on the ion. In total, we must account for 24 electrons. Six electrons are used to draw single covalent bonds between the nitrogen atom and each oxygen atom. The remaining 18 electrons are used to complete the octet for the three terminal oxygen atoms:

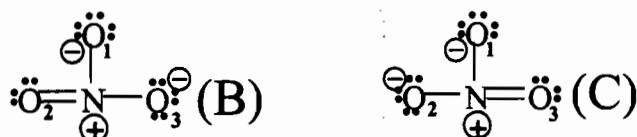


At this stage the valence shells for the oxygen atoms are filled, but the nitrogen atom is two electrons short of a complete octet. If we complete the octet for nitrogen by

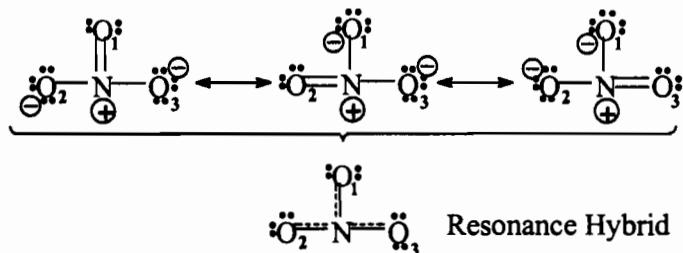
converting a lone pair on  $O_1$  into a nitrogen-to-oxygen  $\pi$ -bond, we end up generating resonance contributor (A):



Notice the structure has a 1+ formal charge on the nitrogen atom and a 1- on two of the oxygen atoms ( $O_2$  and  $O_3$ ). These formal charges are quite reasonable energetically. The second and third equivalent structures are generated similarly, by moving a lone pair from  $O_2$  to form a nitrogen to oxygen ( $O_2$ ) double bond, we end up generating resonance contributor (B), shown below. Likewise, by converting a lone pair from oxygen ( $O_3$ ) into a  $\pi$ -bond with the nitrogen atom, we end up generating resonance contributor (C), also shown below.

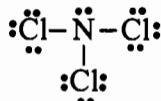


None of these individual structures ((A), (B) or (C)) correctly represents the actual bonding in the nitrate anion. The actual structure, called the resonance hybrid, is an average of all three structures (i.e.  $1/3(A) + 1/3(B) + 1/3(C)$ ):

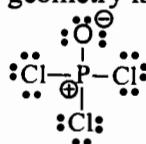


These three resonance forms give bond lengths approximately those of nitrogen-to-nitrogen double bonds.

- 9A** The Lewis structure of  $\text{NCl}_3$  has three Cl atoms bonded to N and one lone pair attached to N. These four electron groups around N produce a tetrahedral electron-group geometry. The fact that one of the electron groups is a lone pair means that the molecular geometry is trigonal pyramidal.



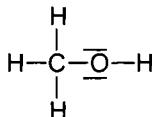
- 9B** The Lewis structure of  $\text{POCl}_3$  has three single P-Cl bonds and one P-O bond. These four electron groups around P produce a tetrahedral electron-group geometry. No lone pairs are attached to P and thus the molecular geometry is tetrahedral.



**10A** The Lewis structure of COS has one S doubly-bonded to C and an O doubly-bonded to C. There are no lone pairs attached to C. The electron-group and molecular geometries are the same: linear.  $|\overline{S} = C = \overline{O}|$

**10B** N is the central atom.  $|N \equiv N - \overline{O}|$  This gives an octet on each atom, a formal charge of 1+ on the central N, and a 1- on the O atom. There are two bonding pairs of electrons and no lone pairs on the central N atom. The  $N_2O$  molecule is linear.

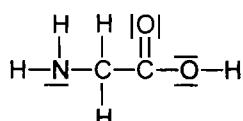
**11A** In the Lewis structure of methanol, each H atom contributes 1 valence electron, the C atom contributes 4, and the O atom contributes 6, for a total of  $(4 \times 1) + 4 + 6 = 14$  valence electrons, or 7 electron pairs. 4 electron pairs are used to connect the H atoms to the C and the O, 1 electron pair is used to connect C to O, and the remaining 2 electron pairs are lone pairs on O, completing its octet.



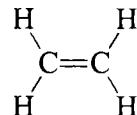
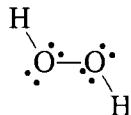
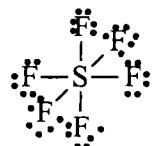
The resulting molecule has two central atoms. Around the C there are four bonding pairs, resulting in a tetrahedral electron-group geometry and molecular geometry. The H—C—H bond angles are 109.5° as are the H—C—O bond angles. Around the O there are two bonding pairs of electrons and two lone pairs, resulting in a tetrahedral electron-group geometry and a bent molecular shape around the O atom, with a C—O—H bond angle of slightly less than 109.5°.

**11B** The Lewis structure is drawn below. With four electron groups surrounding each, the electron-group geometries of N, the central C, and the right-hand O are all tetrahedral. The H—N—H bond angle and the H—N—C bond angles are almost the tetrahedral angle of 109.5°, made a bit smaller by the lone pair.

The H—C—N angles, the H—C—H angle and the H—C—C angles all are very close to 109.5°. The C—O—H bond angle is made somewhat smaller than 109.5° by the presence of two lone pairs on O. Three electron groups surround the right-hand C, making its electron-group and molecular geometries trigonal planar. The O—C—O bond angle and the O—C—C bond angles all are very close to 120°.

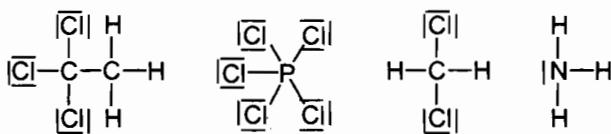


**12A** Lewis structures of the three molecules are drawn below. Around the S in the  $SF_6$  molecule are six bonding pairs of electrons, and no lone pairs. The molecule is octahedral; each of the S-F bond moments is cancelled by one on the other side of the molecule.



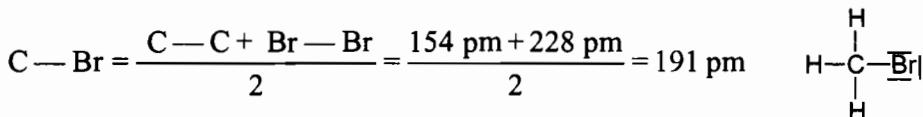
$\text{SF}_6$  is nonpolar. In  $\text{H}_2\text{O}_2$ , the molecular geometry around each O atom is bent; the bond moments do not cancel.  $\text{H}_2\text{O}_2$  is polar. Around each C in  $\text{C}_2\text{H}_4$  are three bonding pairs of electron; the molecule is planar around each C and planar overall. The polarity of each  $-\text{CH}_2$  group is cancelled by the polarity of the other  $\text{H}_2\text{C}-$  group.  $\text{C}_2\text{H}_2$  is nonpolar.

- 12B** Lewis structures of the four molecules are drawn below, we can consider the three C—H bonds and the one C—C bond to be non polar. The three C—Cl bonds are tetrahedrally oriented.



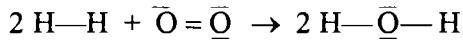
If there were a fourth C—Cl bond on the left-hand C, the bond dipoles would cancel out, producing a nonpolar molecule. Since it is not there, the molecule is polar. A similar argument is made for  $\text{NH}_3$ , where three tetrahedrally-oriented N—H polar bonds are not balanced by a fourth, and  $\text{CH}_2\text{Cl}_2$ , where two tetrahedrally oriented C—Cl bonds are not balanced by two others. This leaves nonpolar  $\text{PCl}_5$ , a symmetrical molecule in which bond dipoles cancel.

- 13A** The Lewis structure of  $\text{CH}_3\text{Br}$  has all single bonds. From Table 11.2 the length of a C—H bond is 110 pm. The length of a C—Br bond is not given in the table. A reasonable value is the average of the C—C and Br—Br bond lengths.



- 13B** In Table 11-2 the C—O bond length is 143 pm, while the C=O bond length is 120 pm, much closer to the experimental bond length in  $\text{CO}_2$ . In determining the Lewis structure, we begin with 4 valence electrons from C and 6 valence electrons from each of the two O atoms, for a total of  $4 + (2 \times 6) = 16$  valence electrons, or 8 pairs of electrons. Two of these eight pairs are used to attach the C atom to each O atom. The remaining 6 pairs complete the octet on each O atom, producing this Lewis structure:  $|\text{O}—\text{C}=\text{O}|$  This Lewis structure has two flaws: (1) There is no octet on C and (2) the carbon-to-oxygen bonds are single bonds, in contradiction to experimental evidence. If a lone pair of electrons from each O is shared with C, the following Lewis structure is produced, that overcomes both objections:  $|\text{O}=\text{C}=\text{O}|$

**14A** We first draw Lewis structures of all molecules involved.

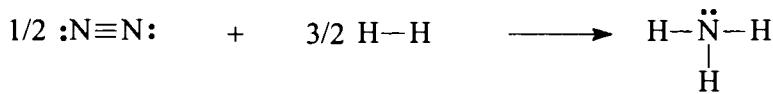


Break 1 O=O + 2H—H = 498 kJ/mol + (2 × 436 kJ/mol) = 1370 kJ/mol absorbed

Form 4H—O = (4 × 464 kJ/mol) = 1856 kJ/mol given off

Enthalpy change = 1370 kJ / mol – 1856 kJ / mol = –486 kJ / mol

**14B** The chemical equation, with Lewis structures is:



Energy required to break bonds =  $\frac{1}{2} \text{N} \equiv \text{N} + \frac{3}{2} \text{H—H}$

$$= (0.5 \times 946 \text{ kJ / mol}) + (1.5 \times 436 \text{ kJ / mol}) = 1.13 \times 10^3 \text{ kJ / mol}$$

Energy realized by forming bonds = 3 N—H =  $3 \times 389 \text{ kJ / mol} = 1.17 \times 10^3 \text{ kJ / mol}$

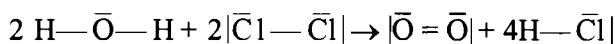
$$\Delta H = 1.13 \times 10^3 \text{ kJ / mol} - 1.17 \times 10^3 \text{ kJ / mol} = -4 \times 10^1 \text{ kJ / mol of NH}_3.$$

Thus,  $\Delta H_f = -4 \times 10^1 \text{ kJ / mol NH}_3$  (Appendix D value is  $\Delta H_f = -46.11 \text{ kJ / mol NH}_3$ )

**15A** The reaction with Lewis structures is  $\cdot \text{O}—\text{N} = \text{O} + \cdot \text{O} \rightarrow \text{N} = \text{O} + \text{O} = \text{O}$

The overall result seems to be converting a single N—O bond to a double O=O bond. Since we expect a double bond to be stronger than a single bond, we predict that the products will be more stable than the reactants and this reaction will be exothermic.

**15B** Double the chemical equation, as Lewis structures:



Energy required to break bonds =  $2 \text{Cl—Cl} + 4\text{H—O}$

$$= (2 \times 243 \text{ kJ / mol}) + (4 \times 464 \text{ kJ / mol}) = 2342 \text{ kJ / mol}$$

Energy realized by forming bonds = 1 O=O + 4 × H—Cl

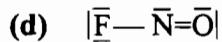
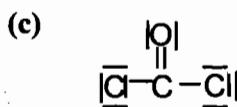
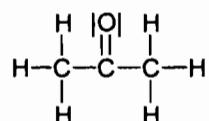
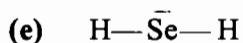
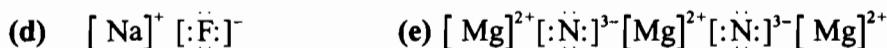
$$= 498 \text{ kJ / mol} + (4 \times 431 \text{ kJ / mol}) = 2222 \text{ kJ / mol}$$

$$\Delta H = \frac{1}{2}(2342 \text{ kJ / mol} - 2222 \text{ kJ / mol}) = +60 \text{ kJ / mol} \quad \text{The reaction is endothermic.}$$

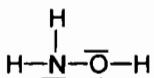
## REVIEW QUESTIONS

**Important Note:** In this and subsequent chapters, a lone pair of electrons in a Lewis structure is often shown as a line rather than a pair of dots. Thus, the Lewis structure of Be is Be| rather than Be:.

1. (a) Valence electrons are those in the highest principal quantum numbers, those in the outermost shell, furthest from the nucleus.  
(b) Electronegativity is a measure of the attraction that an atom in a compound has for the bonding electrons that its shares with other atoms.  
(c) Bond dissociation energy is the energy needed to break a mole of bonds of a given type.  
(d) A double covalent bond results when two pairs of electrons are shared by two atoms.  
(e) A coordinate covalent bond is formed when both electrons of a shared pair come originally from one of the bonded atoms.
2. (a) Formal charge is a measure of how many valence electrons surround an atom in a covalently bonded structure, compared with the number of valence electrons of the isolated atom.  
(b) Resonance occurs when the bonding in a molecule cannot be completely represented by one Lewis structure, but requires the “blending” of two or more contributing structures.  
(c) An expanded valence shell results when an atom uses empty, low-lying orbitals to accommodate more than eight electrons in its outermost electron shell.  
(d) Bond energy is the energy required to break a mole of bonds of a given type, averaged over all the compounds in which that type of bond appears.
3. (a) An ionic bond is the result of the attraction between a cation and an anion. A covalent bond results when two atoms share one or more pairs of electrons.  
(b) A bonding pair of electrons is a pair that is shared between two atoms. A lone pair resides on one atom only and is not shared between atoms.  
(c) Electron-group geometry describes the orientation of electron groups—bonding and lone pairs—around a central atom. Molecular geometry describes the orientation of bonding groups around the central atom.  
(d) A bond dipole moment is the result of the unequal sharing of bonding electrons between two atoms. The resultant dipole moment of a molecule is the vector sum of all of the individual bond dipole moments.  
(e) A polar molecule is one that has a net dipole moment, a slight overall separation of positive and negative charge. In a nonpolar molecule, there is no such net dipole moment.
4. (a)  $[\text{H:}]^-$       (b)  $:\text{Kr}:$       (c)  $[\cdot\text{Sn}\cdot]^{2+}$       (d)  $[\text{K}]^+$       (e)  $[\text{:Br:}]^-$   
(f)  $\cdot\text{Ge}\cdot$       (g)  $:\text{N}\cdot$       (h)  $\cdot\text{Ca}\cdot$       (i)  $[\text{:Se:}]^{2-}$       (j)  $[\text{Sc}]^{3+}$



8. (a)  $\text{H}-\text{H}-\bar{\text{N}}-\bar{\text{O}}-\text{H}$  has two bonds to (four electrons around) the second hydrogen, and only six electrons around the nitrogen. A better Lewis structure is



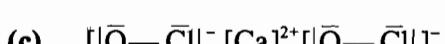
(b)  $|\bar{\text{O}}-\bar{\text{Cl}}-\bar{\text{O}}|$  has 20 valence electrons, whereas the molecule  $\text{ClO}_2$  has 19 valence electrons. This is a proper Lewis structure for the chlorite ion, although the brackets and the minus charge are missing. A plausible Lewis structure for the molecule  $\text{ClO}_2$  is  $|\bar{\text{O}}-\bar{\text{Cl}}-\bar{\text{O}}|$

(c)  $[\text{:C}=\text{N}:]^-$  has only six electrons around the C atom and two too few overall.

$[\text{C} \equiv \text{N}]^-$  is a more plausible Lewis structure for the cyanide ion.

(d)  $\text{Ca}-\bar{\text{O}}$  is improperly written as a covalent Lewis structure, although  $\text{CaO}$  is an ionic compound. In addition, there are only two electrons around the Ca atom.

$[\text{Ca}]^{2+} [\bar{\text{O}}]^{2-}$  is a more plausible Lewis structure for  $\text{CaO}$ .



**10.**

<b>(a)</b>	computations for:	H—	—C≡	≡ C
	no. valence $e^-$	1	4	4
	- no. lone-pair $e^-$	-0	-0	-2
	$-\frac{1}{2}$ no. bond-pair $e^-$	<u>-1</u>	<u>-4</u>	<u>-3</u>
	formal charge	0	0	-1

<b>(b)</b>	computations for:	=O	—O( $\times 2$ )	C
	no. valence $e^-$	6	6	4
	- no. lone-pair $e^-$	-4	-6	-0
	$-\frac{1}{2}$ no. bond-pair $e^-$	<u>-2</u>	<u>-1</u>	<u>-4</u>
	formal charge	-0	-1	0

<b>(c)</b>	computations for:	—H( $\times 7$ )	side C( $\times 2$ )	central C
	no. valence $e^-$	1	4	4
	- no. lone-pair $e^-$	-0	-0	-0
	$-\frac{1}{2}$ no. bond-pair $e^-$	<u>-1</u>	<u>-4</u>	<u>-3</u>
	formal charge	0	0	+1

- (d)** The formal charge on each I is 0,  
computed as follows:

$$\begin{aligned} \text{no. valence } e^- &= 7 \\ \text{-no. lone-pair } e^- &= -6 \\ \text{-} \frac{1}{2} \text{ no. bond-pair } e^- &= \underline{-1} \\ \text{formal charge} &= 0 \end{aligned}$$

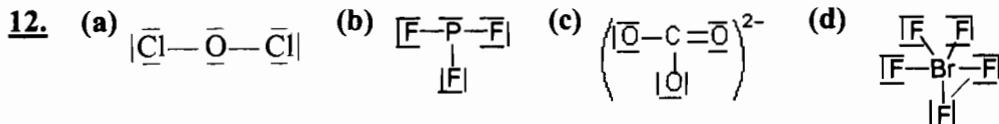
<b>(e)</b>	computations for:	=O	—O	=S—
	no. valence $e^-$	6	6	6
	- no. lone-pair $e^-$	-4	-6	-2
	$-\frac{1}{2}$ no. bond-pair $e^-$	<u>-2</u>	<u>-1</u>	<u>-3</u>
	formal charge	0	-1	+1

<b>(f)</b>	computations for:	=O	—O	=N—
	no. valence $e^-$	6	6	5
	- no. lone-pair $e^-$	-4	-6	-1
	$-\frac{1}{2}$ no. bond-pair $e^-$	<u>-2</u>	<u>-1</u>	<u>-3</u>
	formal charge	0	-1	+1

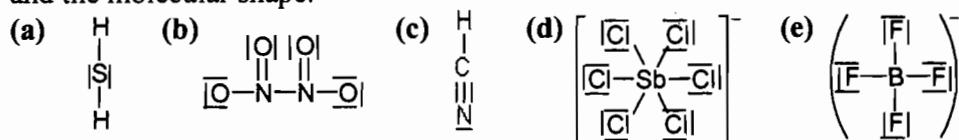
- 11.** Since electrons pair up (if at all possible) in plausible Lewis structures, we can get a very good indication if a species is paramagnetic if it has an odd number of (valence) electrons.

- |            |               |   |              |
|------------|---------------|---|--------------|
| <b>(a)</b> | $\text{OH}^-$ | $6 + 1 + 1 = 8$ valence electrons         | diamagnetic  |
| <b>(b)</b> | $\text{OH}$   | $6 + 1 = 7$ valence electrons             | paramagnetic |
| <b>(c)</b> | $\text{NO}_3$ | $5 + (3 \times 6) = 23$ valence electrons | paramagnetic |

- (d)  $\text{SO}_3$        $6 + (3 \times 6) = 24$  valence electrons      diamagnetic  
 (e)  $\text{SO}_3^{2-}$        $6 + (3 \times 6) + 2 = 26$  valence electrons      diamagnetic  
 (f)  $\text{HO}_2$        $1 + (2 \times 6) = 13$  valence electrons      paramagnetic



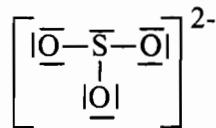
13. We first give all the Lewis structures. From each, we deduce the electron-group geometry and the molecular shape.



- (a)  $\text{H}_2\text{S}$       tetrahedral electron-group geometry, bent (angular) molecular geometry  
 (b)  $\text{N}_2\text{O}_4$       trigonal planar electron-group geometry around each N, planar molecule  
 (c)  $\text{HCN}$       linear electron-group geometry, linear molecular geometry  
 (d)  $\text{SbCl}_6^-$       octahedral electron-group geometry, octahedral geometry  
 (e)  $\text{BF}_4^-$       tetrahedral electron-group geometry, tetrahedral molecular geometry

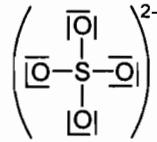
14. (a) In  $\text{SO}_2$ , there are a total of  $6 + (2 \times 6) = 18$  valence electrons, or 9 electron pairs. A plausible Lewis structure has two resonance forms, of which one is:  $\text{O} = \text{S} = \text{O}$ . This molecule is of the type  $\text{AX}_2\text{E}$ ; it has a trigonal planar electron-group geometry and a bent molecular shape.

- (b) In  $\text{SO}_3^{2-}$  the total number of valence electrons is  $2 + (3 \times 6) + 6 = 26$  valence electrons, or 13 electron pairs. A plausible Lewis structure is

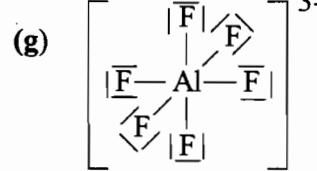
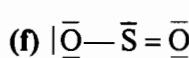
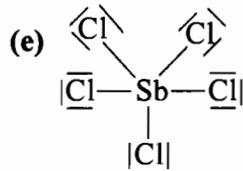
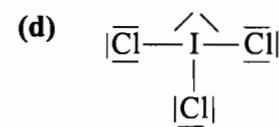
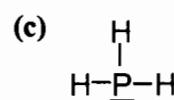
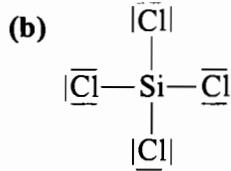


This molecule is of the type  $\text{AX}_3\text{E}$ ; it has a tetrahedral electron-group geometry and a trigonal pyramidal molecular shape.

- (c) In  $\text{SO}_4^{2-}$ , there are a total of  $2 + 6 + (4 \times 6) = 32$  valence electrons, or 16 electron pairs. There are several possible resonance forms, but a simple Lewis structure is provided (right). This ion is of the type  $\text{AX}_4^-$ ; it has a tetrahedral electron-group geometry and a tetrahedral shape.



15. In each case, a plausible Lewis structure is given first, followed by the  $\text{AX}_n\text{E}_m$  notation for each species followed by the electron-group geometry and, finally, the molecular geometry.



- (a) CO linear electron-group geometry, linear molecular geometry  
 (b)  $\text{SiCl}_4$  tetrahedral electron-group geometry, tetrahedral molecular geometry  
 (c)  $\text{PH}_3$  tetrahedral electron-group geometry, trigonal pyramidal molecular geometry  
 (d)  $\text{ICl}_3$  trigonal bipyramidal electron-group geometry, T-shape molecular geometry  
 (e)  $\text{SbCl}_5$  electron-group geometry and molecular geometry, trigonal bipyramidal  
 (f)  $\text{SO}_2$  trigonal planar electron-group geometry, bent molecular geometry  
 (g)  $\text{AlF}_6^{3-}$  octahedral electron-group geometry, octahedral geometry

16. bond  $\text{H}-\text{C}$   $\text{C}=\text{O}$   $\text{C}-\text{C}$   $\text{C}-\text{Cl}$

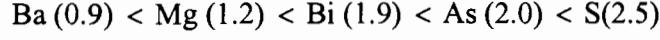
(a) bond length 110 120 154 178 pm

(b) bond energy 414 736 347 339 kJ/mol

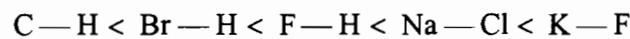
17. (c) is the longest bond. Single bonds are generally longer than multiple bonds. Of the two molecules with single bonds,  $\text{Br}_2$  is expected to have longer bonds than  $\text{BrCl}$ , since Br is larger than Cl. (a)  $|\text{O}=\text{O}|$  (b)  $|\text{N}\equiv\text{N}|$  (c)  $|\text{Br}-\text{Br}|$  (d)  $|\text{Br}-\text{Cl}|$

18. The reaction  $\text{O}_2 \rightarrow 2\text{O}$  is an endothermic reaction since it requires the breaking of the bond between two oxygen atoms without the formation of any bonds. Since bond breakage is endothermic, the entire process must be endothermic.

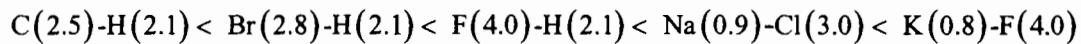
19. (a) The net result of this reaction involves breaking one mole of C—H bonds (which requires 414 kJ) and forming one mole of H—I bonds (which produces 297 kJ). Thus, this reaction is endothermic; a net infusion of energy is necessary.
- (b) The net result of this reaction, involves breaking one mol of H—H bonds (which requires 436 kJ) and one mol of I—I bonds (which requires 151 kJ), and forming two moles of H—I bonds (which produces  $2 \times 297 = 594$  kJ). Thus, this reaction is just barely exothermic.
20. Recall that electronegativity increases in the periodic table from lower left to upper right, and specifically that metals have lower electronegativities than do nonmetals, with metalloids having intermediate electronegativities. Based on these principles, the electronegativity of S is greater than that of As, which in turn is greater than that of Bi. The electronegativity of Ba is less than that of Mg. And finally, we would predict the electronegativity of Mg (a definite metal) to be less than that of Bi (somewhat metalloid in character). Thus, ranked in order of increasing electronegativity, these elements are: Ba < Mg < Bi < As < S, with Bi having the intermediate electronegativity of this group of five elements. The actual electronegativities are in parentheses:



21. Na—Cl and K—F both are bonds between a metal and a nonmetal; they have the largest ionic character, with the ionic character of K—F being greater than that of Na—Cl, both because K is more metallic (closer to the lower left of the periodic table) than Na and F is more nonmetallic (closer to the upper right) than Cl. The remaining three bonds are covalent bonds to H. Since H and C have about the same electronegativity (a fact you need to memorize), the H—C bond is the most covalent (or the least ionic). Br is somewhat more electronegative than is C, while F is considerably more electronegative than C, making the F—H bond the most polar of the three covalent bonds. Thus, ranked in order of increasing ionic character, these five bonds are:



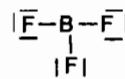
The actual electronegativity differences follow:



$$\Delta\text{EN} \quad = 0.4 \quad = 0.7 \quad = 1.9 \quad = 2.1 \quad = 3.2$$

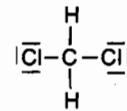
22. (a)  $\text{F}_2$  cannot possess a dipole moment, since both of the atoms in the diatomic molecule are the same. This means that there is no electronegativity difference between atoms, and hence no polar bonds.
- (b)  $|\overline{\text{O}}-\overset{\cdot}{\text{N}}=\overline{\text{O}}|$  Each nitrogen-to-oxygen bond in this molecule is polarized toward oxygen, the more electronegative element. The molecule is of the  $\text{AX}_2\text{E}$  category and hence is bent. Therefore the two bond dipoles do not cancel, and the molecule is polar.

- (c) Although each B—F bond is polarized toward F in this trigonal planar  $\text{AX}_3$  molecule these bond dipoles cancel. The molecule is nonpolar.

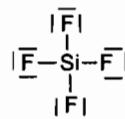


- (d)  $\text{H}-\overline{\text{Br}}$  The H—Br bond is polar toward Br, and this molecule is polar as well.

- (e) The H—C bonds are not polar, but the C—Cl bonds are, toward Cl. The molecular shape is tetrahedral ( $\text{AX}_4$ ) and thus these two C—Cl dipoles do not cancel each other; the molecule is polar.



- (f) Although each Si—F bond is polarized toward F, in this tetrahedral  $\text{AX}_4$  molecule these bond dipoles oppose and cancel each other; the molecule is nonpolar.

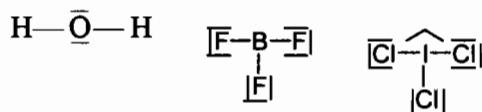


- (g)  $\overline{\text{O}}=\text{C}=\overline{\text{S}}$  In this linear molecule, the two bonds from carbon both are polarized away from carbon. But the C=O bond is more polar than the C=S bond, and hence the molecule is polar.

## EXERCISES

### Lewis theory

23. Hydrogen never has an octet of electrons in any of its compounds, but rather a pair (or duet, if you prefer). An example is the Lewis structure of  $\text{H}_2\text{O}$  (below). In many compounds in which the central atom is from the second period or higher, there are more than eight electrons around the central atom; an example of a compound with such an “expanded octet” is  $\text{ICl}_3$  (below). Finally, in some compounds, there are less than eight electrons around the central atom; one such “electron deficient” compound is  $\text{BF}_3$ .



25. (a)  $\text{Cs}^+[\text{:Br:}]^-$   $\text{CsBr}$ , cesium bromide (b)  $\text{H}-\overline{\text{Sb}}-\text{H}$   $\text{H}_3\text{Sb}$ , hydrogen antimonide



- (c)  $\begin{array}{c} \text{Cl} \quad \text{B} \quad \text{Cl} \\ | \quad \quad \quad || \\ \text{Cl} \quad \quad \quad \text{Cl} \end{array}$   $\text{BF}_3$ , boron trichloride (d)  $\text{Cs}^+[\text{:Cl:}]^-$   $\text{CsCl}$ , cesium chloride

- (e)  $\text{Li}^+[\text{:O:}]^{2-}$   $\text{Li}^+$   $\text{Li}_2\text{O}$ , lithium oxide (f)  $|\overline{\text{I}}-\text{Cl}|$   $\text{ICl}$ , iodine monochloride

27. (c) is the correct answer.

- (a)  $[\bar{\text{O}}-\text{C}=\bar{\text{N}}]^-$  does not have an octet of electrons around C.
- (b)  $[\text{C}=\text{C}:]^-$  does not have an octet around either C, it has only 6 valence electrons, and should have 10, and the sum of the formal charges on the two carbons doesn't equal the charge on the ion.
- (d) The total number of valence electrons in  $\ddot{\text{N}}=\ddot{\text{O}}$  is incorrect; this odd-electron species should have 11 valence electrons, not 12.

## Ionic bonding

29. (a)  $\text{Li}\cdot$  forms  $\text{Li}^+$  cations, and  $:\text{S}\cdot$  forms  $[\text{:S}:]^{2-}$  anions. Lithium sulfide:  $\text{Li}^+[\text{:S}:]^{2-}\text{Li}^+$
- (b)  $\text{Na}\cdot$  forms  $\text{Na}^+$  cations, and  $:\text{F}\cdot$  forms  $[\text{:F}:]^-$  anions. Sodium fluoride:  $\text{Na}^+[\text{:F}:]^-$
- (c)  $\text{Ca}\cdot$  forms  $\text{Ca}^{2+}$  cations, and  $:\text{I}\cdot$  forms  $[\text{:I}:]^-$  anions. Calcium iodide:  $[\text{:I}:]^- \text{Ca}^{2+}[\text{:I}:]^-$
- (d)  $\text{Sc}\cdot$  forms  $\text{Sc}^{3+}$  cations, and  $:\text{Cl}\cdot$  forms  $[\text{:Cl}:]^-$  anions. Scandium chloride is  

$$\begin{array}{c} [\text{Sc}]^{3+} \\ [:\text{Cl}:]^- \quad [:\text{Cl}:]^- \\ \quad [:\text{Cl}:]^- \end{array}$$

The formulas of the compounds are  $\text{Li}_2\text{S}$ ,  $\text{NaF}$ ,  $\text{CaI}_2$ , and  $\text{ScCl}_3$ .

## Formal Charge

31. There are three features common to formal charge and oxidation state. First, both indicate how electrons are distributed in the bonding of the compound. Second, negative formal charge (in the most plausible Lewis structure) and negative oxidation state are generally assigned to the more electronegative atoms. And third, both numbers are determined by a set of rules, rather than being determined experimentally. Bear in mind, however, that there are also significant differences. For instance, there are cases where atoms of the same type with the same oxidation state have different formal charges, such as oxygen in ozone,  $\text{O}_3$ . Another is that formal charges are used to decide between alternative Lewis structures, while oxidation state is used in balancing equations and naming compounds. Also, the oxidation state in a compound is invariant, while the formal charge can change. The most significant difference, though, is that whereas the oxidation state of an element in its compounds is usually not zero, its formal charge usually is.

- 33.** Formal charge = number of valence electrons  $- 2 \times$  number of lone pairs – number of bonding electron pairs. The formal charge of the central atom is calculated below the Lewis structure of each species.

	(a)	(b)	(c)	(d)	(e)
$\text{O} = \text{O} - \text{O} \mid$		$\left[ \begin{array}{c} \text{F} \\   \\ \text{F} - \text{B} - \text{F} \\   \\ \text{F} \end{array} \right]^-$	$\left[ \begin{array}{c} \text{O} \\   \\ \text{O} - \text{N} = \text{O} \\    \\ \text{O} \end{array} \right]^-$	$\begin{array}{c} \text{Cl} \\ \diagup \\ \text{Cl} - \text{P} - \text{Cl} \\ \diagdown \\ \text{Cl} \end{array}$	$\left[ \begin{array}{c} \text{Cl} \\   \\ \text{Cl} - \text{I} - \text{Cl} \\   \\ \text{Cl} \end{array} \right]^-$
valence e <sup>-</sup>	6	3	5	5	7
$-2(\text{lone pairs})$	-2	0	0	0	-4
$-\text{bonding pair}$	-3	-4	-4	-5	-4
formal charge	+1	-1	+1	0	-1

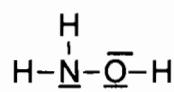
- 35.** We begin by counting the total number of valence electrons that must appear in the Lewis structure of the ion  $\text{CO}_2\text{H}^+$ : one from hydrogen, four from carbon, and six from each of the two oxygen (12 in all from the oxygen atoms). One electron is lost to establish the  $1^+$  charge on the ion. In all, sixteen electrons. If the usual rules for constructing valid Lewis structures are applied to  $\text{HCO}_2^+$ , we come up with the following structures:



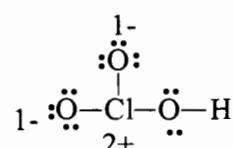
In structure (A), the internal oxygen atom carries the positive charge, while in structure (B), the positive charge is located on the terminal oxygen atom. Thus, in this case, we cannot use the concept of formal charge to pick one structure over the other because the positive formal charge in both structures is located on the same type of atom, namely, an oxygen atom. In other words, based on formal charge rules alone, we must conclude that structures (A) and (B) are equally plausible.

## Lewis structures

- 37. (a)** In  $\text{H}_2\text{NOH}$ , N and O atoms are the central atoms and the terminal atoms are the H atoms. The number of valence electrons in the molecule totals:  $(3 \times 1) + 5 + 6 = 14$  valence electrons, or seven electron pairs. A reasonable Lewis structure is:

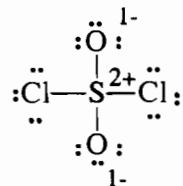


- (b)** In  $\text{HOClO}_2$ , two O atoms and one H atom are terminal atoms, and the Cl and O atoms are the central atoms. The total number of valence electrons in the structure is  $1 + 7 + (3 \times 6) = 26$  valence electrons, or 13 electron pairs. A reasonable Lewis structure is:

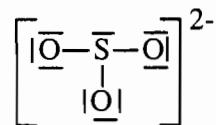


- (c) In  $\text{HONO}$ , the H atom and one O atom are the terminal atoms; the other O atom and the N atom are the central atoms. The total number of valence electrons in the structure is  $1+5+(2\times 6)=18$  valence electrons, or nine electron pairs. A plausible Lewis structure is  $\text{H}-\text{O}^-\text{—N}=\text{O}$

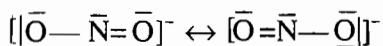
- (d) In  $\text{O}_2\text{SCl}_2$ , S is the central atom, with Cl and O as terminal atoms. The total number of valence electrons is  $(2\times 6)+6+(2\times 7)=32$  valence electrons, 16 electron pairs. A reasonable Lewis structure is:



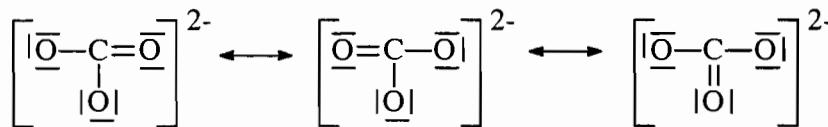
39. (a) The total number of valence electrons in  $\text{SO}_3^{2-}$  is  $6+(3\times 6)+2=26$ , or 13 electron pairs. A plausible Lewis structure is:



- (b) The total number of valence electrons in  $\text{NO}_2^-$  is  $5+(2\times 6)+1=18$ , or 9 electron pairs. There are two resonance forms for the nitrite ion:

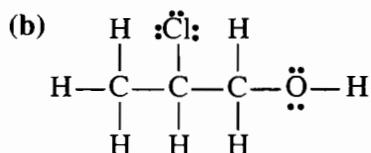
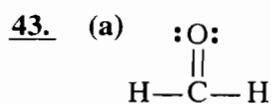
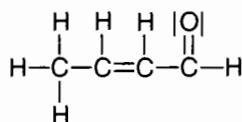


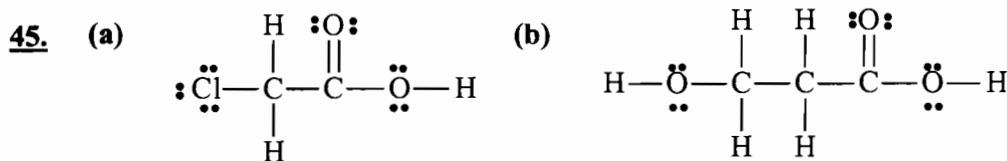
- (c) The total number of valence electrons in  $\text{CO}_3^{2-}$  is  $4+(3\times 6)+2=24$ , or 12 electron pairs. There are three resonance forms for the carbonate ion:



- (d) The total number of valence electrons in  $\text{HO}_2^-$  is  $1+(2\times 6)+1=14$ , or 7 electron pairs. A plausible Lewis structure is  $[\text{H}-\text{O}^-\text{—O}]^-$

41. In  $\text{CH}_3\text{CHCHCHO}$  there are  $(4\times 4)+(6\times 1)+6=28$  valence electrons, or 14 electron pairs. We expect that the carbon atoms bond to each other. A plausible Lewis structure is :





## Polar Covalent Bonds

47. The percent ionic character of a bond is based on the difference in electronegativity of its constituent atoms and Figure 11.7.

(a) S(2.5) — H(2.1)   (b) O(3.5) — Cl(3.0)   (c) Al(1.5) — O(3.5)   (d) As(2.0) — O(3.5)

$\Delta \text{EN}$  0.4  
 $\% \text{ionic} = 4\%$

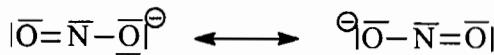
0.5  
 $= 5\%$

2.0  
 $= 60\%$

1.5  
 $= 33\%$

## Resonance

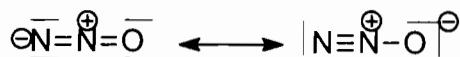
49. In  $\text{NO}_2^-$ , the total number of valence electrons is  $1+5+(2 \times 6)=18$  valence electrons, or 9 electron pairs. N is the central atom. There are two resonance forms.



51. Bond length data from Table 11.2 follow:

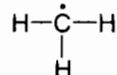
$\text{N} \equiv \text{N}$ 109.8 pm	$\text{N} = \text{N}$ 123 pm	$\text{N} - \text{N}$ 145 pm
$\text{N} = \text{O}$ 120 pm	$\text{N} - \text{O}$ 136 pm	

The experimental  $\text{N} - \text{N}$  bond length of 113 pm approximates that of the  $\text{N} \equiv \text{N}$  triple bond, which appears in structure (1). The experimental  $\text{N} - \text{O}$  bond length of 119 pm approximates that of the  $\text{N}=\text{O}$  double bond, which appears in structure (2). Structure (4) is highly unlikely because it contains no nitrogen-to-nitrogen bonds, and a  $\text{N}-\text{N}$  bond was found experimentally. Structure (3) also is unlikely, because it contains a very long (145 pm)  $\text{N} - \text{N}$  single bond, which does not agree at all well with the experimental N-to-N bond length. The molecule seems best represented as a resonance hybrid of (1) and (2).



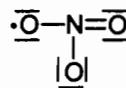
## Odd-electron species

53. (a)  $\text{CH}_3$  has a total of  $(3 \times 1) + 4 = 7$  valence electrons, or 3 electron pairs and a lone electron. C is the central atom. A plausible Lewis structure is



(b)  $\text{ClO}_2$  has a total of  $(2 \times 6) + 7 = 19$  valence electrons, or 9 electron pairs and a lone electron. Cl is the central atom. A plausible Lewis structure is:  $\text{:}\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}\cdot$

(c)  $\text{NO}_3$  has a total of  $(3 \times 6) + 5 = 23$  valence electrons, or 11 electron pairs, plus a lone electron. N is the central atom. A plausible Lewis structure is shown to the right. Resonance forms can also be drawn.



### Expanded octets

55. In  $\text{PO}_4^{3-}$ ;  $5 + (4 \times 6) + 3 = 32$  valence electrons or 16 electron pairs.  
Expanded octet is not needed.

In  $\text{PI}_3$ ;  $5 + (3 \times 7) = 26$  valence electrons or 13 electron pairs.  
An expanded octet is not needed.

In  $\text{ICl}_3$ ; are  $7 + (3 \times 7) = 28$  valence electrons or 14 electron pairs.  
An expanded octet is necessary.

In  $\text{OSCl}_2$ ;  $6 + 6 + (2 \times 7) = 26$  valence electrons or 13 electron pairs.  
Expanded octet is not needed.

In  $\text{SF}_4$ ;  $6 + (4 \times 7) = 34$  valence electrons or 17 electron pairs.  
An expanded octet is necessary.

In  $\text{ClO}_4^-$ ;  $7 + (4 \times 6) + 1 = 32$  valence electrons or 16 electron pairs.  
Expanded octet is not needed.

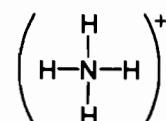
### Molecular shapes

57. The  $\text{AX}_n\text{E}_m$  designations that are cited below are to be found in Table 11.1 of the text, along with a sketch and a picture of a model of each type of structure.

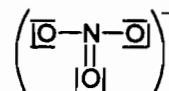
(a)  $|\text{N} \equiv \text{N}|$  is linear, two points define a line.

(b)  $\text{H} - \text{C} \equiv \text{N}|$  is linear. The molecule belongs to the  $\text{AX}_2\text{E}$  category, and these species are linear.

(c)  $\text{NH}_4^+$  is tetrahedral. The ion is of the  $\text{AX}_4$  type, which has a tetrahedral electron-group geometry and a tetrahedral shape.

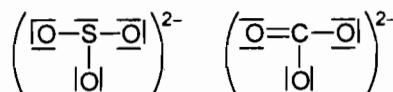


(d)  $\text{NO}_3^-$  is trigonal planar. The ion is of the  $\text{AX}_3$  type, which has a trigonal planar electron-group geometry and a trigonal planar shape. The other resonance forms are of the same type.



(e)  $\text{NSF}$  is bent. The molecule is of the  $\text{AX}_2\text{E}$  type, which has a trigonal planar electron-group geometry and a bent shape.  $\text{N}=\text{S}-\text{F}|$

- 59.** A trigonal planar shape requires that three ligands and no lone pairs be bonded to the central atom. Thus  $\text{PF}_6^-$  cannot have a trigonal planar shape, since six atoms are attached to the central atom. In addition,  $\text{PO}_4^{3-}$  cannot have a trigonal planar shape, since four O atoms are attached to the central P atom. We now draw the Lewis structure of each of the remaining ions, as a first step in predicting their shapes. The  $\text{SO}_3^{2-}$  ion is of the  $\text{AX}_3\text{E}$  type; it has a tetrahedral electron-group geometry and a trigonal pyramidal shape. The  $\text{CO}_3^{2-}$  ion is of the  $\text{AX}_3$  type, and has a trigonal planar electron-group geometry and a trigonal planar shape.



- 61. (a)** In  $\text{CO}_2$  there are a total of  $4 + (2 \times 6) = 16$  valence electrons, or 8 electron pairs. The following Lewis structure is plausible.  $\text{O} = \text{C} = \text{O}$  This is a molecule of type  $\text{AX}_2$ ;  $\text{CO}_2$  has a linear electron-shape geometry and a linear shape.

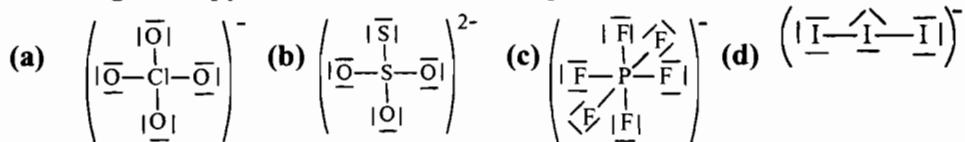
- (b)** In  $\text{Cl}_2\text{CO}$  there are a total of  $(2 \times 7) + 4 + 6 = 24$  valence electrons, or 12 electron pairs. The molecule can be represented by a Lewis structure with C as the central atom. This molecule is of the  $\text{AX}_3$  type; it has a trigonal planar electron-group geometry and molecular shape.
- (c)** In  $\text{ClNO}_2$  there are a total of  $7 + 5 + (2 \times 6) = 24$  valence electrons, or 12 electron pairs. N is the central atom. A plausible Lewis structure is shown:  

$$\begin{array}{c} \text{O} \\ || \\ \text{Cl}-\text{N}-\text{O} \end{array}$$
This molecule is of the  $\text{AX}_3$  type; it has a trigonal planar electron-group geometry and a trigonal planar shape.

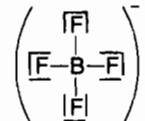
- 63.** First we draw the Lewis structure of each species, then use these Lewis structures to predict the molecular shape.

- (a)** In  $\text{ClO}_4^-$  there are  $7 + (4 \times 6) + 1 = 32$  valence electrons or 16 electron pairs. A plausible Lewis structure follows. Since there are four atoms and no lone pairs bonded to the central atom, the molecular shape and the electron-group geometry are the same: tetrahedral.
- (b)** In  $\text{S}_2\text{O}_3^{2-}$  there are  $(2 \times 6) + (3 \times 6) + 2 = 32$  valence electrons or 16 electron pairs. A plausible Lewis structure follows. Since there are four atoms and no lone pairs bonded to the central atom, both the electron-group geometry and molecular shape are tetrahedral.
- (c)** In  $\text{PF}_6^-$  there are  $5 + (6 \times 7) + 1 = 48$  valence electrons or 24 electron pairs. A plausible Lewis structure follows. Since there are six atoms and no lone pairs bonded to the central atom, the electron-group geometry and molecular shape are octahedral.

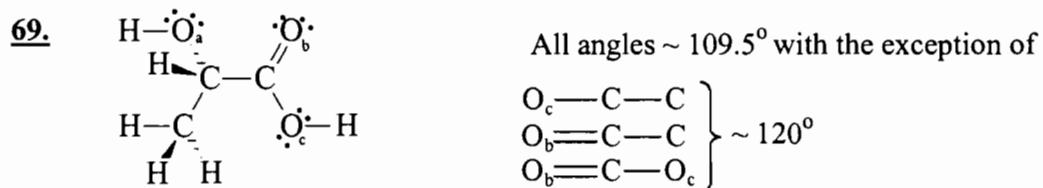
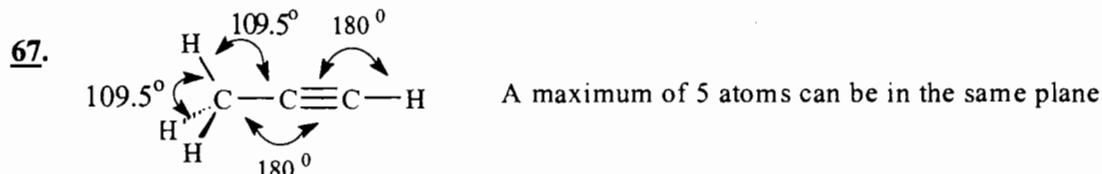
- (d) In  $I_3^-$  there are  $(3 \times 7) + 1 = 22$  valence electrons or 11 electron pairs. There are three lone pairs and two atoms bound to the central atom. The electron-group geometry is trigonal bipyramidal; the molecular shape is linear.



65. In  $BF_4^-$ , there are a total of  $1 + 3 + (4 \times 7) = 32$  valence electrons, or 16 electron pairs. A plausible Lewis structure has B as the central atom. This ion is of the type  $AX_4$ ; it has a tetrahedral electron-group geometry and a tetrahedral shape.



## Shapes of Molecules with More Than One Central Atom

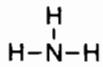


## Polar Molecules

71. For each molecule, we first draw the Lewis structure, which we use to predict the shape.

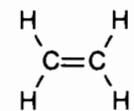
- (a)  $SO_2$  has a total of  $6 + (2 \times 6) = 18$  valence electrons, or 9 electron pairs. The molecule has two resonance forms.  $\overline{O}=\overline{S}-\overline{O} \longleftrightarrow \overline{O}-\overline{S}=\overline{O}$  Each of these resonance forms is of the type  $AX_2E$ ; it has a triangular planar electron-group geometry and a bent shape. Since each S—O bond is polar toward O, and since the bond dipoles do not point in opposite directions, the molecule has a resultant dipole moment, pointing from S through a point midway between the two O atoms;  $SO_2$  is polar.

- (b)  $NH_3$  has a total of  $5 + (3 \times 1) = 8$  valence electrons, or 4 electron pairs. N is the central atom. A plausible Lewis structure is shown. The molecule is of the  $AX_3E$  type; it has a tetrahedral electron-group geometry and a trigonal pyramidal shape. Each N-H bond is polar toward N. Since the bonds do not symmetrically oppose each other, there is a resultant molecular dipole moment, pointing from the triangular base (formed by the three H atoms) through N. The molecule is polar.

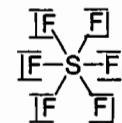


(c)  $\text{H}_2\text{S}$  has a total of  $6 + (2 \times 1) = 8$  valence electrons, or 4 electron pairs. S is the central atom and a plausible Lewis structure is  $\text{H}-\bar{\text{S}}-\text{H}$ . This molecule is of the  $\text{AX}_2\text{E}_2$  type; it has a tetrahedral electron-group geometry and a bent shape. Each H—S bond is polar toward S. Since the bonds do not symmetrically oppose each other, the molecule has a net dipole moment, pointing through S from a point midway between the two H atoms.  $\text{H}_2\text{S}$  is polar.

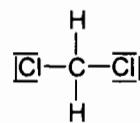
(d)  $\text{C}_2\text{H}_4$  consists of atoms that all have about the same electronegativities. Of course, the C—C bond is not polar, but neither are the C—H bonds. The molecule is planar. Thus, the entire molecule is nonpolar.



(e)  $\text{SF}_6$  has a total of  $6 + (6 \times 7) = 48$  valence electrons, or 24 electron pairs. S is the central atom. All atoms have zero formal charge in the Lewis structure. This molecule is of the  $\text{AX}_6$  type; it has an octahedral electron-group geometry and an octahedral shape. Even though each S—F bond is polar toward F, the bonds symmetrically oppose each other resulting in a molecule that is nonpolar.



(f)  $\text{CH}_2\text{Cl}_2$  has a total of  $4 + (2 \times 1) + (2 \times 7) = 20$  valence electrons, or 10 electron pairs. A plausible Lewis structure is shown. The molecule is tetrahedral and polar, since the two polar bonds (C—Cl) do not cancel the effect of each other.



73. In  $\text{H}_2\text{O}_2$ , there are a total of  $(2 \times 1) + (2 \times 6) = 14$  valence electrons, 7 electron pairs. The two O atoms are central atoms. A plausible Lewis structure has zero formal charge on each atom.  $\text{H}-\bar{\text{O}}-\bar{\text{O}}-\text{H}$ . In the hydrogen peroxide molecule, the O—O bond is non-polar, while the H—O bonds are polar, toward O. Since the molecule has a resultant dipole moment, it cannot be linear, for, if it were linear the two polar bonds would oppose each other and their polarities would cancel.

## Bond lengths

75. A heteronuclear bond length (one between two different atoms) is equal to the average of two homonuclear bond lengths (one between two like atoms) of the same order (both single, both double, or both triple).

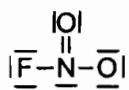
(a) I—Cl bond length  $= [(\text{I—I bond length}) + (\text{Cl—Cl bond length})] \div 2$   
 $= [266 \text{ pm} + 199 \text{ pm}] \div 2 = 233 \text{ pm}$

(b) O—Cl bond length  $= [(\text{O—O bond length}) + (\text{Cl—Cl bond length})] \div 2$   
 $= [145 \text{ pm} + 199 \text{ pm}] \div 2 = 172 \text{ pm}$

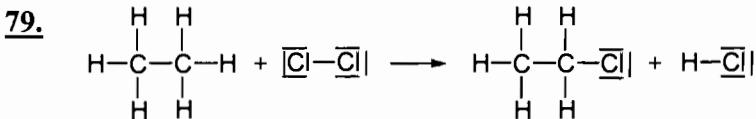
(c) C—F bond length  $= [(\text{C—C bond length}) + (\text{F—F bond length})] \div 2$   
 $= [154 \text{ pm} + 143 \text{ pm}] \div 2 = 149 \text{ pm}$

(d) C—Br bond length  $= [(\text{C—C bond length}) + (\text{Br—Br bond length})] \div 2$   
 $= [154 \text{ pm} + 228 \text{ pm}] \div 2 = 191 \text{ pm}$

77. The N—F bond is a single bond. Its bond length should be the average of the N—N single bond (145 pm) and the F—F single bond (143 pm). Thus, the average N—F bond length =  $(145 + 143) \div 2 = 144$  pm



## Bond Energies



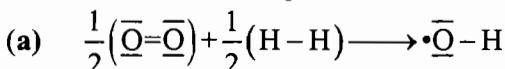
Analysis of the Lewis structures of products and reactants indicates that a C—H bond and a Cl—Cl bond are broken, and a C—Cl and a H—Cl bond are formed.

$$\text{Energy required to break bonds} = \text{C—H} + \text{Cl—Cl} = 414 \frac{\text{kJ}}{\text{mol}} + 243 \frac{\text{kJ}}{\text{mol}} = 657 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Energy realized by forming bonds} = \text{C—Cl} + \text{H—Cl} = 339 \frac{\text{kJ}}{\text{mol}} + 431 \frac{\text{kJ}}{\text{mol}} = 770 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H = 657 \text{ kJ/mol} - 770 \text{ kJ/mol} = -113 \text{ kJ/mol}$$

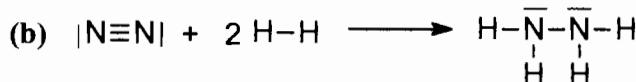
81. In each case we write the formation reaction, but specify reactants and products with their Lewis structures. All species are assumed to be gases.



$$\text{Bonds broken: } \frac{1}{2}(\text{O}=\text{O}) + \frac{1}{2}(\text{H}-\text{H}) = 0.5(498 \text{ kJ} + 436 \text{ kJ}) = 467 \text{ kJ}$$

$$\text{Bonds formed: } \text{O—H} = 464 \text{ kJ} \quad \Delta H^\circ = 467 \text{ kJ} - 464 \text{ kJ} = 3 \text{ kJ/mol}$$

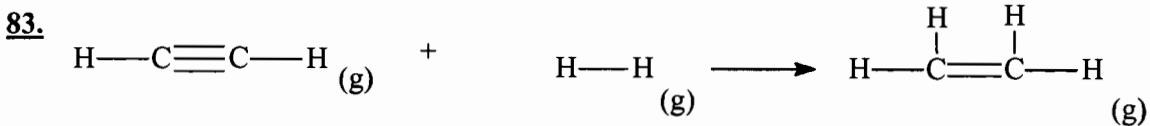
If the O—H bond dissociation energy of 428.0 kJ/mol from Figure 11-16 is used,  $\Delta H_f^\circ = 39 \text{ kJ/mol}$ .



$$\text{Bonds broken} = \text{N} \equiv \text{N} + 2 \text{H—H} = 946 \text{ kJ} + 2 \times 436 \text{ kJ} = 1818 \text{ kJ}$$

$$\text{Bonds formed} = \text{N—N} + 4 \text{N—H} = 163 \text{ kJ} + 4 \times 389 \text{ kJ} = 1719 \text{ kJ}$$

$$\Delta H_f^\circ = 1818 \text{ kJ} - 1719 \text{ kJ} = 99 \text{ kJ}$$



Bonds broken	Energy change	Bonds formed	Energy Change
1 mol C≡C	$1 \times 837 \text{ kJ}$	1 mol C=C	$1 \times -611 \text{ kJ}$
1 mol H—H	$1 \times 436 \text{ kJ}$	2 mol C-H	$2 \times -414 \text{ kJ}$

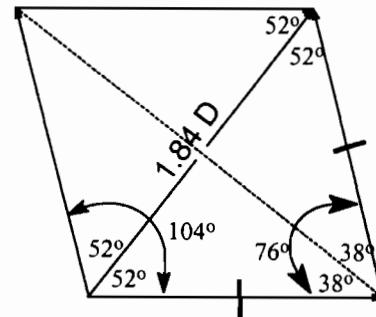
Energy required to break bonds	Energy obtained upon bond formation
+1273 kJ	-1439 kJ

$$\text{Overall energy change} = 1273 \text{ kJ} - 1439 \text{ kJ} = -166 \text{ kJ} = \Delta H^\circ_{\text{rxn}}$$

## FEATURE PROBLEMS

- 106. (a)** The average of the H—H and Cl—Cl bond energies is  $(436 + 243) \div 2 = 340$  kJ/mol. The ionic resonance energy is the difference between this calculated value and the measured value of the H—Cl bond energy:  $IRE = 431 - 340 = 91$  kJ/mol
- (b)**  $\Delta EN = \sqrt{IRE / 96} = \sqrt{91 / 96} = 0.97$
- (c)** An electronegativity difference of 0.97 gives about a 23% ionic character, read from Figure 11.7. The result of Example 11-4 is that the H—Cl bond is 20% ionic. These values are in good agreement with each other.

- 107. (a)** The two bond moments can be added geometrically, by placing the head of one at the tail of the other, as long as we do not change the direction or the length of the moved dipole. The resultant molecular dipole moment is represented by the arrow drawn from the tail of one bond dipole to the head of the other. This is shown in the figure at right. The  $52.0^\circ$  angle in the figure is one-half of the  $104^\circ$  bond angle in water. The length is given as 1.84 D. We can construct a right angle triangle by bisecting the  $76.0^\circ$  angle. The right angle triangle has a hypotenuse = O—H bond dipole and the two other angles are  $52^\circ$  and  $38^\circ$ . The side opposite the bisected  $76.0^\circ$  angles is  $\frac{1}{2}(1.84\text{ D}) = 0.92$  D. We can calculate the bond dipole using:  $\sin 38.0^\circ = \frac{0.92\text{ D}}{\text{O-H bond dipole}} = 0.61566$ , hence O—H bond dipole = 1.49 D.

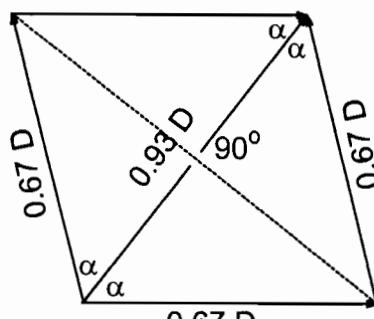


- (b)** For  $\text{H}_2\text{S}$ , we do not know the bond angle. We shall represent this bond angle as  $2\alpha$ . Using a similar procedure as above, a diagram can be constructed and the angle  $2\alpha$  calculated as follows:

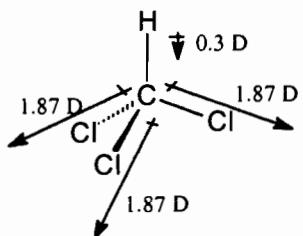
$$\cos \alpha = \frac{\frac{1}{2}(0.93\text{ D})}{0.67\text{ D}} = 0.694 \quad \alpha = 46.05^\circ$$

$$\text{or } 2\alpha = 92.1^\circ$$

The H—S—H angle is approximately  $92^\circ$ .



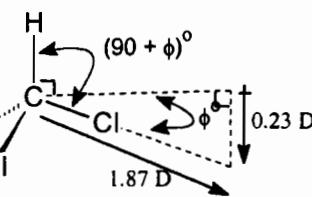
(c)



$$\mu_{C-H} + 3(\mu_{C-Cl}) = 1.04 D$$

$$0.30 D + 3(x) = 1.04 D$$

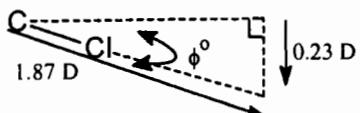
$$x = 0.25 D = \mu_{C-Cl}$$



Molecule and associated individual bond dipoles

Relationship between dipole moment(molecular) and bond dipoles(Vector addition)

Geometric Relationship



Mathematical solution:

$$\sin(\phi) = \frac{0.25 D}{1.87 D}$$

$$\phi = 7.6^\circ$$

The H-C-Cl bond angle is  $(90 + \phi)^\circ = 90^\circ + 7.6^\circ = 97.6^\circ$ 

108. Step 1 in the alternate approach is similar to the first step in the method used for drawing Lewis structures. The only significant difference is that "electron pairs" rather than the total number of valence electrons are counted in this alternate approach. The second step in the alternate strategy is also similar to the second step for writing Lewis structures. By counting the number of bonding electron pairs in the alternate method, one is effectively working out the number of bonds present in the skeletal structure of the Lewis diagram. In step 3, the number of electron pairs surrounding the central atom is calculated.

This is basically the same procedure as completing the octets for the terminal atoms and assigning the remaining electrons to the central atom in the Lewis structure. Finally, in step 4 of the alternate method, the number of lone pair electrons on the central atom is calculated. This number together with the result from step 3, allows one to establish the VSEPR class. Consequently, both the alternate strategy and the Lewis diagram provide the number of bonding electron pairs and lone pairs on the central atom in species whose shape is being predicted. Since the shape of the molecule or ion in the VSEPR approach is determined solely by the number and types of electron pairs on the central atom (i.e., the VSEPR class) both methods end up giving the same result.

Included in the "alternative strategy" is the assumption that the central atom does not form double bonds with any of the terminal atoms. This means that in many instances, the central atom does not possess a complete octet. The presence or absence of an octet is, however, of no consequence to the VSEPR method because, according to the tenets of this theory, the shape adopted by the molecule is determined solely by the number and types of electron pairs on the central atom. Examples follow on the next two pages.

(a)  $\text{PCl}_5$ 

$$1. \text{ Total e}^- \text{ pairs} = \frac{(1 \times 5\text{e}^- \text{ from P atom}) + (5 \times 7\text{e}^- \text{ from the 5 Cl atoms})}{2} = 20 \text{ pairs of e}^-$$

$$2. \text{ Number of bonding e}^- \text{ pairs} = 6 \text{ atoms} (5 \times \text{Cl} + 1 \times \text{P}) - 1 = 5 \text{ bonding e}^- \text{ pairs.}$$

$$3. \text{ Number of e}^- \text{ pairs around the central atom} = (20(\text{total}) \text{ e}^- \text{ pairs}) - 3 \times (5 \text{ terminal Cl}) \\ = 5 \text{ e}^- \text{ pairs around P atom.}$$

$$4. \text{ Number of lone pair e}^- = 5 \text{ e}^- \text{ pairs around P} - 5 \text{ bonding pairs of e}^- = 0$$

Thus, according to this alternate approach,  $\text{PCl}_5$  belongs to the VSEPR class  $\text{AX}_5$ . Molecules of this type adopt a trigonal bipyramidal structure.

(b)  $\text{NH}_3$ 

$$1. \text{ Total e}^- \text{ pairs} = \frac{(1 \times 5\text{e}^- \text{ from N atom}) + (3 \times 1\text{e}^- \text{ from the 3 H atoms})}{2} = 4 \text{ pairs of e}^-$$

$$2. \text{ Number of bonding e}^- \text{ pairs} = 4 \text{ atoms} (1 \times \text{N} + 3 \times \text{H}) - 1 = 3 \text{ bonding e}^- \text{ pairs.}$$

$$3. \text{ Number of e}^- \text{ pairs around the central atom} = 4(\text{total}) \text{ e}^- \text{ pairs} - 0 \\ = 4 \text{ e}^- \text{ pairs around N atom.}$$

$$4. \text{ Number of lone pair e}^- = 4 \text{ e}^- \text{ pairs around N} - 3 \text{ bonding pairs of e}^- = 1 \text{ lone pair e}^-$$

Thus, according to this alternate approach,  $\text{NH}_3$  belongs to the VSEPR class  $\text{AX}_3\text{E}$ . Molecules of this type adopt a trigonal pyramidal structure.

(c)  $\text{ClF}_3$ 

$$1. \text{ Total e}^- \text{ pairs} = \frac{(1 \times 7\text{e}^- \text{ from Cl atom}) + (3 \times 7\text{e}^- \text{ from the 3 F atoms})}{2} = 14 \text{ e}^- \text{ pairs}$$

$$2. \text{ Number of bonding e}^- \text{ pairs} = 4 \text{ atoms} (1 \times \text{Cl} + 3 \times \text{F}) - 1 = 3 \text{ bonding e}^- \text{ pairs.}$$

$$3. \text{ Number of e}^- \text{ pairs around the central atom} = 14(\text{total}) \text{ pairs} - 3 \times (3 \text{ terminal F atoms}) \\ = 5 \text{ e}^- \text{ pairs around Cl atom.}$$

$$4. \text{ Number of lone pair e}^- = 5 \text{ e}^- \text{ pairs around Cl} - 3 \text{ bonding pairs of e}^- = 2 \text{ lone pair e}^-$$

Thus, according to this alternate approach,  $\text{ClF}_3$  belongs to the VSEPR class  $\text{AX}_3\text{E}_2$ . Molecules of this type adopt a T-shaped structure.

(d)  $\text{SO}_2$ 

$$1. \text{ Total e}^- \text{ pairs} = \frac{(1 \times 6\text{e}^- \text{ from S atom}) + (2 \times 6\text{e}^- \text{ from the 2 O atoms})}{2} = 9 \text{ e}^- \text{ pairs}$$

$$2. \text{ Number of bonding e}^- \text{ pairs} = 3 \text{ atoms} (1 \times \text{S} + 2 \times \text{O}) - 1 = 2 \text{ bonding e}^- \text{ pairs.}$$

$$3. \text{ Number of e}^- \text{ pairs around the central atom} = 9(\text{total}) \text{ pairs} - 3 \times (2 \text{ terminal O atoms}) \\ = 3 \text{ e}^- \text{ pairs around S atom.}$$

$$4. \text{ Number of lone pair e}^- = 3 \text{ e}^- \text{ pairs around S} - 2 \text{ bonding pairs of e}^- = 12 \text{ lone pair e}^-$$

Thus, according to this alternate approach,  $\text{SO}_2$  belongs to the VSEPR class  $\text{AX}_2\text{E}$ . Molecules of this type adopt a bent structure.



$$1. \text{ Total } e^- \text{ pairs} = \frac{(1 \times 7e^- \text{ from Cl}) + (4 \times 7e^- \text{ from the 4 F}) + (1e^- \text{ for charge of } -1)}{2}$$

$$= 18 \text{ pairs of } e^-$$

2. Number of bonding  $e^-$  pairs = 5 atoms ( $1 \times \text{Cl} + 4 \times \text{F}$ ) - 1 = 4 bonding  $e^-$  pairs.
3. Number of  $e^-$  pairs around the central atom = 18(total) pairs -  $3 \times (4 \text{ terminal F atoms})$   
= 6  $e^-$  pairs around Cl atom.
4. Number of lone pair  $e^-$  = 6  $e^-$  pairs around Cl - 4 bonding pairs of  $e^-$  = 2 lone pair  $e^-$

Thus, according to this alternate approach,  $\text{ClF}_4^-$  belongs to the VSEPR class  $\text{AX}_4\text{E}_2$ . Molecules of this type adopt a square planar structure.



$$1. \text{ Total } e^- \text{ pairs} = \frac{(1 \times 5e^- \text{ from P}) + (4 \times 7e^- \text{ from the 4 Cl}) - (1e^- \text{ for } +1 \text{ charge})}{2}$$

$$= 16 \text{ pairs of } e^-$$

2. Number of bonding  $e^-$  pairs = 5 atoms ( $4 \times \text{Cl} + 1 \times \text{P}$ ) - 1 = 4 bonding  $e^-$  pairs.
3. Number of  $e^-$  pairs around the central atom = 16(total) pairs -  $3(4 \text{ terminal Cl atoms})$   
= 4  $e^-$  pairs around P atom.
4. Number of lone pair  $e^-$  = 4  $e^-$  pairs around P - 4 bonding pairs of  $e^-$  = 0

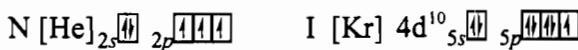
Thus, according to this alternate approach,  $\text{ClF}_4^+$  belongs to the VSEPR class  $\text{AX}_4$ . Molecules of this type adopt a tetrahedral structure.

# CHAPTER 12

## CHEMICAL BONDING II:ADDITIONAL ASPECTS

### PRACTICE EXAMPLES

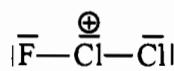
- 1A** The valence-shell orbital diagrams of N and I are as follows:



There are three half-filled  $2p$  orbitals on N, and one half-filled  $5p$  orbital on I. Each half-filled  $2p$  orbital from N will overlap with one half-filled  $5p$  orbital of a I. Thus, there will be three N—I bonds. The I atoms will be oriented in the same direction as the three  $2p$  orbitals of N: toward the  $x$ -,  $y$ -, and  $z$ -directions of a Cartesian coordinate system. Thus, the I—N—I angles will be approximately  $90^\circ$  (probably larger because the I atoms will repel each other). The three I atoms will lie in the same plane at the points of a triangle, with the N atom centered above them. The molecule is trigonal pyramidal. (The same molecular shape is predicted if N is assumed to be  $sp^3$  hybridized, but with  $109.5^\circ$  rather than  $90^\circ$  bond angles.)

- 1B** The valence-shell orbital diagrams of N and H are as follows. N: [He]  $2s\boxed{\text{I}} \quad 2p\boxed{\text{IIII}}$   
H:  $1s\boxed{\text{I}}$  There are three half-filled orbitals on N and one half-filled orbital on each H. There will be three N—H bonds, with bond angles of approximately  $90^\circ$ . The molecule is trigonal pyramid. (We obtain the same molecular shape if N is assumed to be  $sp^3$  hybridized, but bond angles are closer to  $109.5^\circ$ , the tetrahedral bond angle.) VSEPR theory begins with the Lewis structure and notes that there are three bond pairs and one lone pair attached to N. This produces a tetrahedral electron pair geometry and a trigonal pyramid molecular shape with bond angles a bit less than the tetrahedral angle of  $109.5^\circ$  because of the lone pair. Since VSEPR theory makes a prediction closer to the experimental bond angle of  $107^\circ$  it seems more appropriate in this case.

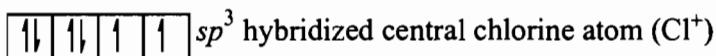
- 2A** Following the strategy outlined in the textbook, we begin by drawing a plausible Lewis structure for the cation in question. In this case, the Lewis structure must contain 20 valence electrons. The skeletal structure for the cation has a chlorine atom, the least electronegative element present, in the central position. Next we join the terminal chlorine and fluorine atoms to the central chlorine atom via single covalent bonds and then complete the octets for all three atoms.



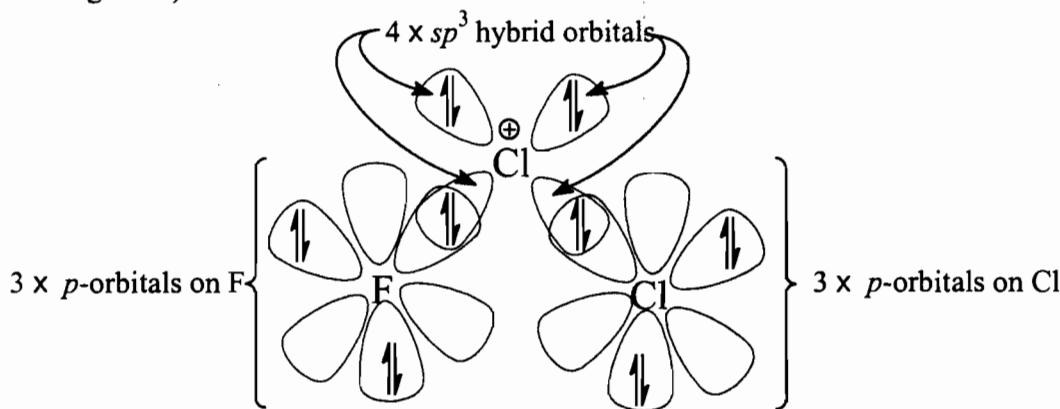
With this bonding arrangement, the central chlorine atom ends up with a  $1+$  formal charge.

Once the Lewis diagram is complete, we can then use the VSEPR method to establish the geometry for the electron pairs on the central atom. The Lewis structure has two bonding electron pairs and two lone pairs of electrons around the central chlorine atom. These four pairs of electrons assume a tetrahedral geometry to minimize electron-electron repulsions.

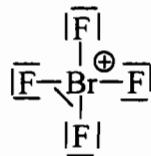
The VSEPR notation for the  $\text{Cl}_2\text{F}^+$  ion is  $\text{AX}_2\text{E}_3$ . According to Table 11.1, molecules of this type exhibit an angular molecular geometry. Our next task is to select a hybridization scheme that is consistent with the predicted shape. It turns out that the only way we can end up with a tetrahedral array of electron groups is if the central chlorine atom is  $sp^3$  hybridized. In this scheme, two of the  $sp^3$  hybrid orbitals are filled, while the remaining two are half occupied.



The  $\text{Cl}-\text{F}$  and  $\text{Cl}-\text{Cl}$  bonds in the cation are then formed by the overlap of the half-filled  $sp^3$  hybrid orbitals of the central chlorine atom with the half-filled p-orbitals of the terminal Cl and F atoms. Thus, by using  $sp^3$  hybridization, we end up with the same bent molecular geometry for the ion as that predicted by VSEPR theory (when the lone pairs on the central atom are ignored)

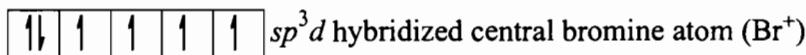


- 2B** As was the case in 2A, we begin by drawing a plausible Lewis structure for the cation in question. This time the Lewis structure must contain 34 valence electrons. The skeletal structure has bromine, the least electronegative element present, as the central atom. Next, we join the four terminal fluorine atoms to the central bromine atom via single covalent bonds and complete the octets for all of the fluorine atoms. Placing the last two electrons on the central bromine atom completes the diagram.

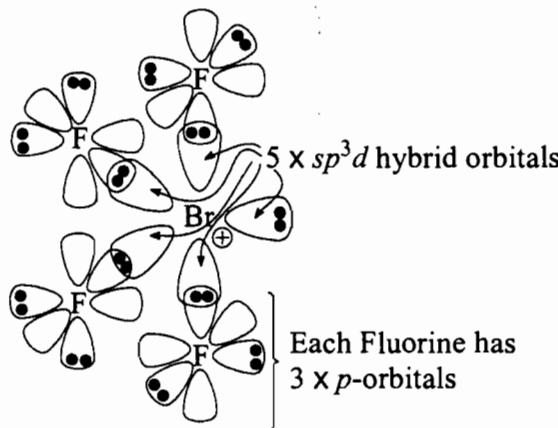


In order to accommodate ten electrons, the bromine atom is forced to expand its valence shell. Notice that the Br ends up with a  $1+$  formal charge in this structure. With the completed Lewis structure in hand, we can then use VSEPR theory to establish the geometry for the electron pairs around the central atom. The Lewis structure has four bonding pairs and one lone pair of electrons around the central bromine atom. These five pairs of electrons assume a trigonal bipyramidal geometry to minimize electron-electron repulsions. The VSEPR notation for the  $\text{BrF}_4^+$  cation is  $\text{AX}_4\text{E}$ . According to Table 11.1, molecules of this type exhibit a see-saw molecular geometry.

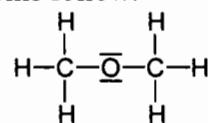
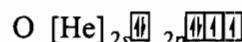
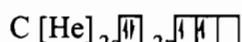
Next we must select a hybridization scheme for the Br atom that is compatible with the predicted shape. It turns out that only  $sp^3d$  hybridization will provide the necessary trigonal bipyramidal distribution of electron pairs around the bromine atom. In this scheme, one of the  $sp^3d$  hybrid orbitals is filled while the remaining four are half-occupied.



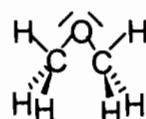
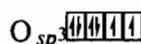
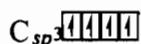
The four Br—F bonds in the cation are then formed by the overlap of the half-filled  $sp^3d$  hybrid orbitals of the bromine atom with the half-filled p-orbitals of the terminal fluorine atoms. Thus, by using  $sp^3d$  hybridization, we end up with the same see-saw molecular geometry for the cation as that predicted by VSEPR theory (when the lone pair on Br is ignored).



**3A** We begin by writing the Lewis structure. The H atoms are terminal atoms. There are three central atoms and  $(3 \times 1) + 4 + 6 + 4 + (3 \times 1) = 20$  valence electrons, or 10 pairs. A plausible Lewis structure is drawn at right. Each central atom is surrounded by four electron pairs, requiring  $sp^3$  hybridization. The valence-shell orbital diagrams for the atoms follow.

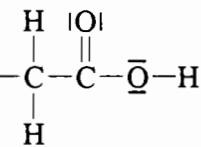


The valence-shell orbital diagrams for the hybridized central atoms then are:

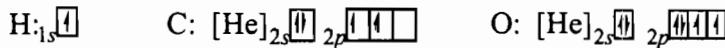


All bonds in the molecule are  $\sigma$  bonds. The H—C—H bond angles are  $109.5^\circ$ , as are the H—C—O bond angles. The C—O—C bond angle is possibly a bit smaller than  $109.5^\circ$  because of the repulsion of the two lone pairs of electrons on O. A wedge-and-dash sketch of the molecule is at right.

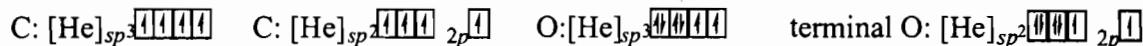
- 3B** The H atoms and one O are terminal atoms in the Lewis structure, which has  $3 \times 1 + 4 + 4 + 2 \times 6 + 1 = 24$  valence electrons, or 12 pairs. The left-most C and the right-most O are surrounded by four electron pairs, and thus require  $sp^3$  hybridization.



The central carbon is surrounded by three electron groups and is  $sp^2$  hybridized. The orbital diagrams for the un-hybridized atoms are:

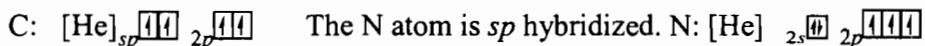
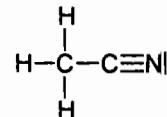


Hybridized orbital diagrams:



There is one  $\pi$  bond in the molecule: between the  $2p$  on the central C and the  $2p$  on the terminal O. The remaining bonds are  $\sigma$  bonds. The H—C—H and H—C—C bond angles are  $109.5^\circ$ . The H—O—C angle is somewhat less, perhaps  $105^\circ$ . The C—C—O bond angles and O—C—O bond angles are all  $120^\circ$ .

- 4A** There are four bond pairs around the left-hand C, requiring  $sp^3$  hybridization. Three of the bonds that form are C—H sigma bonds resulting from the overlap of a  $sp^3$  hybrid orbital on C with a  $1s$  orbital on H. The other C has two attached electron groups, utilizing  $sp$  hybridization.

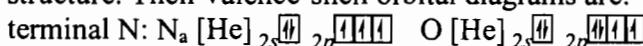


The two C atoms join with a sigma bond: overlap of  $sp^2$  on the left-hand C with  $sp$  on the right-hand C. The three bonds between C and N consist of a sigma bond ( $sp$  on C with  $sp$  on N), and two pi bonds ( $2p$  on C with  $2p$  on N).

- 4B** The bond lengths that are given indicate that N is the central atom. The molecule has  $(2 \times 5) + 6 = 16$  valence electrons, or 8 pairs. Average bond lengths are: N—N = 145 pm, N=N = 123 pm, N≡N = 110 pm, N—O = 136 pm, N=O = 120 pm. Plausible resonance structures are (with subscripts for identification):



In both structures, the central N is attached to two other atoms, and possesses no lone pairs. The geometry of the molecule thus is linear and the hybridization on this central N is  $sp$ .  $\text{N}_b$ :  $[\text{He}]_{sp}\boxed{111} 2p\boxed{111}$  We will assume that the terminal atoms are not hybridized in either structure. Their valence-shell orbital diagrams are:



In structure (1) the N≡N bond results from the overlap of three pairs of half-filled orbitals: (1)  $sp_x$  on  $\text{N}_b$  with  $2p_x$  on  $\text{N}_a$  forming a  $\sigma$  bond, (2)  $2p_y$  on  $\text{N}_b$  with  $2p_y$  on  $\text{N}_a$  forming a  $\pi$  bond, and (3)  $2p_z$  on  $\text{N}_b$  with  $2p_z$  on  $\text{N}_a$  also forming a  $\pi$  bond. The N—O bond is a coordinate covalent bond, and requires that the electron configuration of O

be written as  $O [He]_{2s} \boxed{\text{}} 2p \boxed{\text{}} \boxed{\text{}}$ . The N—O bond then forms by the overlap of the full  $sp_x$  orbital on  $N_b$  with the empty  $2p$  orbital on O.

In structure (2) the N = O bond results from the overlap of two pairs of half-filled orbitals: (1)  $sp_y$  on  $N_b$  with  $2p_y$  on O forming a  $\sigma$  bond and (2)  $2p_z$  on  $N_b$  with  $2p_z$  on O forming a  $\pi$  bond. The N = N  $\sigma$  bond is a coordinate covalent bond, and requires that the configuration of  $N_a$  be written  $N_a [He] \boxed{\text{}} 2p \boxed{\text{}} \boxed{\text{}}$ . The N = N bond is formed by two overlaps: (1) the overlap of the full  $sp_y$  orbital on  $N_b$  with the empty  $2p_y$  orbital on  $N_a$  to form a  $\sigma$  bond, and (2) the overlap of the half-filled  $2p_x$  orbital on  $N_b$  with the half-filled  $2p_x$  orbital on  $N_a$  to form a  $\pi$  bond. Based on formal charge arguments, structure (1) is preferred, because the negative formal charge is on the more electronegative atom, O.

**5A** Removing an electron from  $Li_2$  removes a bonding electron because the valence molecular orbital diagram for  $Li_2$  is the same as that for  $H_2$ , only it is just moved up a principal quantum level:  $\sigma_{1s} \boxed{\text{}} \sigma_{1s} \boxed{\text{}} \sigma_{2s} \boxed{\text{}} \sigma_{2s} \boxed{\text{}}$ . The molecular orbital diagram for  $Li_2^+$  is:  $\sigma_{1s} \boxed{\text{}} \sigma_{1s} \boxed{\text{}} \sigma_{2s} \boxed{\text{}} \sigma_{2s} \boxed{\text{}}$ . The bond order is  $Li_2^+$  in 1/2, while that in  $Li_2$  is one. Thus, the bond in  $Li_2^+$  should be one half as strong as the bond in  $Li_2$ :  $106 \text{ kJ/mol} \div 2 = 53 \text{ kJ/mol } Li_2^+$

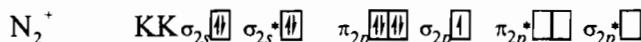
**5B** The  $H_2^-$  ion contains 1 electron from each H plus 1 electron (for the charge) for a total of three electrons. Its molecular orbital diagram is  $\sigma_{1s} \boxed{\text{}} \sigma_{1s} \boxed{\text{}}$ . There are 2 bonding and 1 anti-bonding electrons. The bond order in  $H_2^-$  is:

$$\text{Bond order} = \frac{(2 \text{ bonding } e^- - 1 \text{ antibonding } e^-)}{2} = \frac{1}{2}$$

Thus, we would expect the ion  $H_2^-$  to be stable, with a bond strength about half that of a hydrogen molecule.

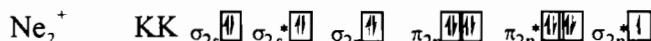
**6A** For each case, the empty molecular-orbital diagram has the following appearance. (KK indicates that the molecular orbitals formed from 1s atomic orbitals are full: KK =  $\sigma_{1s} \boxed{\text{}} \sigma_{1s} \boxed{\text{}}$ ) KK  $\sigma_{2s} \boxed{\text{}} \sigma_{2s} \boxed{\text{}} \sigma_{2p} \boxed{\text{}} \sigma_{2p} \boxed{\text{}} \pi_{2p} \boxed{\text{}} \boxed{\text{}} \pi_{2p} \boxed{\text{}} \boxed{\text{}} \sigma_{2p} \boxed{\text{}}$ . We need to simply count up the total number of electrons in each species, and place them in the valence-shell molecular-orbital diagram.

(a)  $N_2^+$  has  $(2 \times 5) - 1 = 9$  valence electrons. Its molecular orbital diagram is



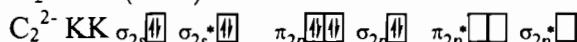
$$\text{bond order} = (7 \text{ bonding electrons} - 2 \text{ antibonding electrons}) \div 2 = 2.5$$

(b)  $Ne_2^+$  has  $(2 \times 8) - 1 = 15$  valence electrons. Its molecular orbital diagram is



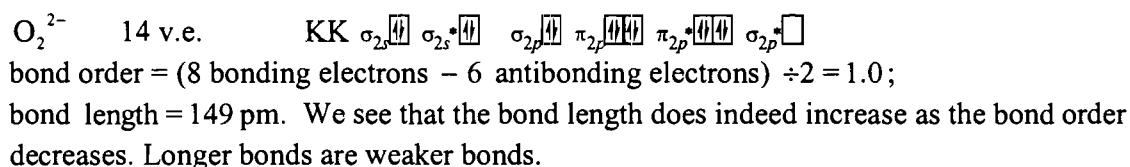
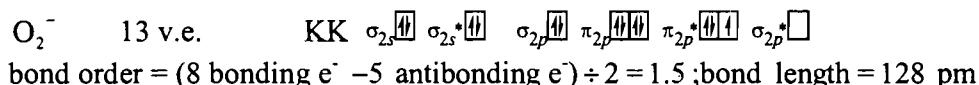
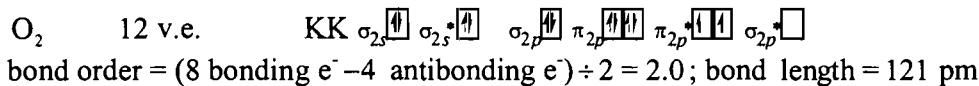
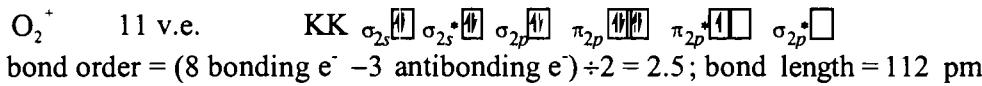
$$\text{bond order} = (8 \text{ bonding electrons} - 7 \text{ antibonding electrons}) \div 2 = 0.5$$

(c)  $C_2^{2-}$  has  $(2 \times 4) + 2 = 10$  valence electrons. Its molecular orbital diagram is

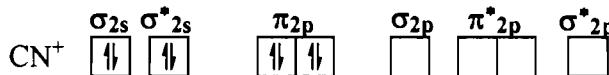


$$\text{bond order} = (8 \text{ bonding electrons} - 2 \text{ antibonding electrons}) \div 2 = 3.0$$

- 6B** For each case, the empty molecular-orbital diagram has the following appearance. (KK indicates that the molecular orbitals formed from 1s atomic orbitals are full: KK =  $\sigma_{1s} \uparrow\uparrow \sigma_{1s}^* \uparrow\uparrow$ ) KK  $\sigma_{2s} \square \sigma_{2s}^* \square \sigma_{2p} \square \pi_{2p} \square \square \pi_{2p}^* \square \square \sigma_{2p}^* \square$ . All of these species are based on  $O_2$ , which has  $2 \times 6 = 12$  valence electrons. We simply put the appropriate number of valence electrons in each diagram and determine the bond order.



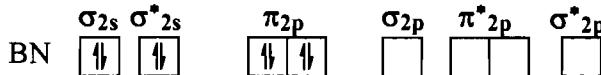
- 7A** There are 8 valence electrons that must be placed in the molecular orbital diagram for  $CN^+$  (5 electrons from nitrogen, four electrons from carbon and one electron is removed to produce the positive charge). Since both C and N precede oxygen and they are not far apart in atomic number, we must use the modified molecular-orbital energy-level diagram to get the correct configuration. By following the Aufbau orbital filling method, one obtains the ground state diagram asked for in the question.



The bond order for the C—N bond in  $CN^+$  is  $\frac{6 \text{ bonding e}^- - 2 \text{ antibonding e}^-}{2} = 2$

Thus the C and N atoms in  $CN^+$  are joined by a double bond.

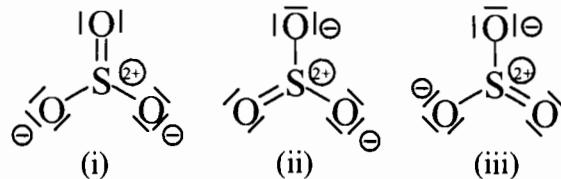
- 7B** There are 8 valence electrons that must be placed in the molecular orbital diagram for BN (3 electrons from boron and five electrons from nitrogen). Since both B and N precede oxygen and they are not far apart in atomic numbers, we must use the modified molecular-orbital energy-level diagram to get the correct configuration. By following the Aufbau orbital filling method, one obtains the ground-state diagram asked for in the question.



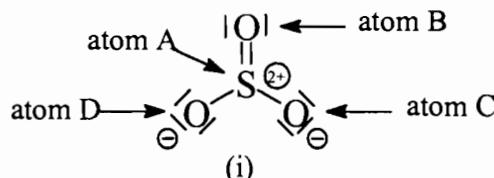
The bond order for the B—N bond in BN is  $\frac{6 \text{ bonding e}^- - 2 \text{ antibonding e}^-}{2} = 2$

Thus, the B and N atoms in BN are joined by a double bond.

- 8A** In this exercise we will combine valence-bond and molecular orbital methods to describe the bonding in the  $\text{SO}_3$  molecule. By invoking a  $\pi$ -bonding scheme, we can replace the three resonance structures for  $\text{SO}_3$  (shown below) with just one structure that exhibits both  $\sigma$ -bonding and delocalized  $\pi$ -bonding.

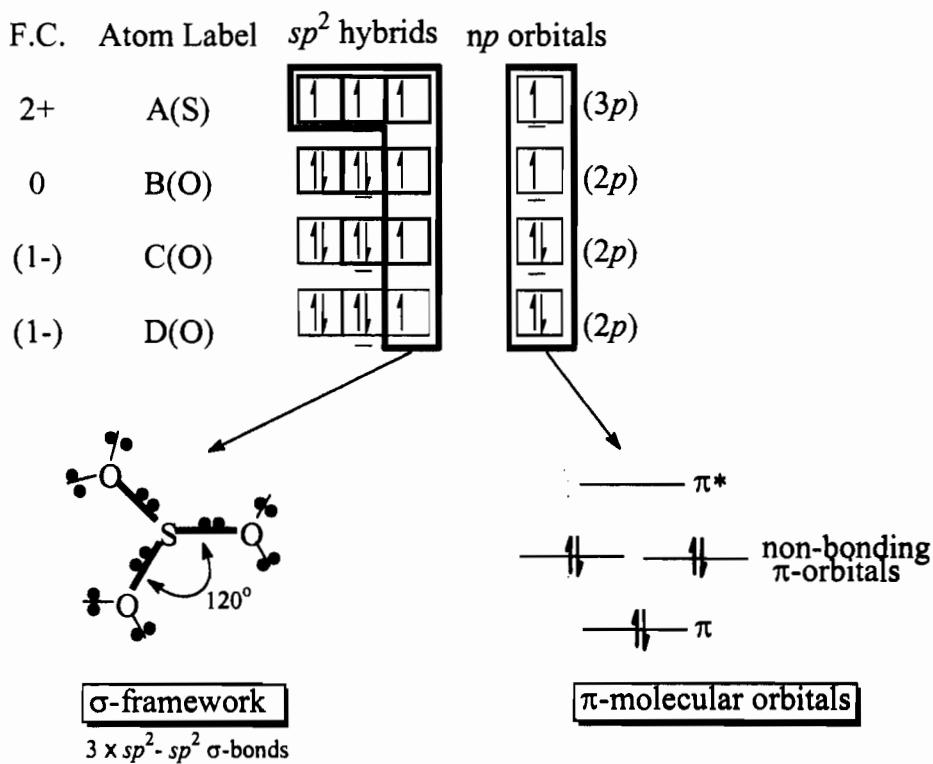


We will use structure (i) to develop a combined localized/delocalized bonding description for the molecule. (Note: Any one of the three resonance contributors can be used as the starting structure). We begin by assuming that every atom in the molecule is  $sp^2$  hybridized to produce the  $\sigma$ -framework for the molecule. The half-filled  $sp^2$  hybrid orbitals of the oxygen atoms will each be overlapped with a half-filled  $sp^2$  hybrid orbital on sulfur. By contrast, to generate a set of  $\pi$  molecular orbitals, we will combine one unhybridized  $2p$  orbital from each of three oxygen atoms with an unhybridized  $3p$  orbital on the sulfur atom. This will generate four  $\pi$  molecular orbitals: a bonding molecular orbital, two nonbonding molecular orbitals and an antibonding orbital. Remember that the number of valence electrons assigned to each atom must reflect the formal charge for that atom. Accordingly, sulfur, with a 2+ formal charge, can have only four valence electrons, the two oxygens with a 1- formal charge must each end up with 7 electrons and the oxygen with a zero formal charge must have its customary six electrons



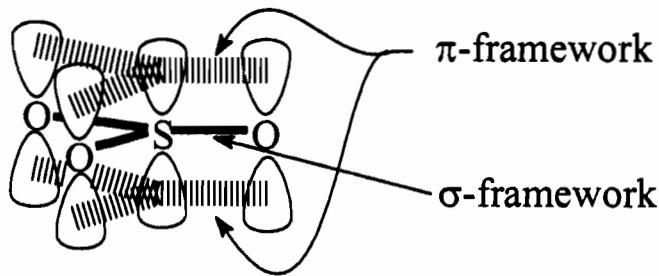
Let's begin assigning valence electrons by half-filling three  $sp^2$  hybrid orbitals on the sulfur atom (atom A) and one  $sp^2$  hybrid orbital on each of the oxygen atoms (atoms B, C and D).

Next, we half-fill the lone unhybridized  $3p$  orbital on sulfur and the lone  $2p$  orbital on the oxygen atom with a formal charge of zero (atom B). Following this, the  $2p$  orbital of the other two oxygen atoms (atoms C and D), are filled and then lone pairs are placed in the  $sp^2$  hybrid orbitals that are still empty. At this stage, then, all 24 valence electrons have been put into atomic and hybrid orbitals on the four atoms. Now we overlap the six half-filled  $sp^2$  hybrid orbitals to generate the  $\sigma$ -bond framework and combine the three  $2p$  orbitals (2 filled, one half-filled) and the  $3p$  orbital (half-filled) to form the four  $\pi$ -molecular orbitals, as shown below:



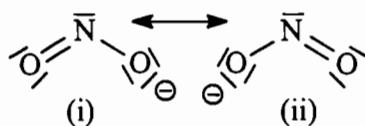
Overall bond order for this set of  $\pi$ -molecular orbitals  $\frac{2 \text{ bonding } e^- - 0 \text{ antibonding } e^-}{2} = 1$

The  $\pi$ -bond is spread out evenly over the three S—O linkages. This leads to an average bond order of 1.33 for the three S—O bonds in  $\text{SO}_3$ . By following this “combined approach”, we end up with a structure that has the  $\sigma$ -bond framework sandwiched between the delocalized  $\pi$ -molecular orbital framework:

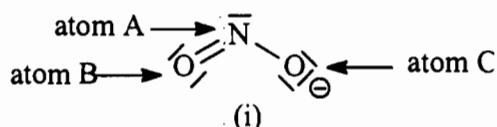


This is a much more accurate description of the bonding in  $\text{SO}_3$  than that provided by any one of the three Lewis diagrams given above.

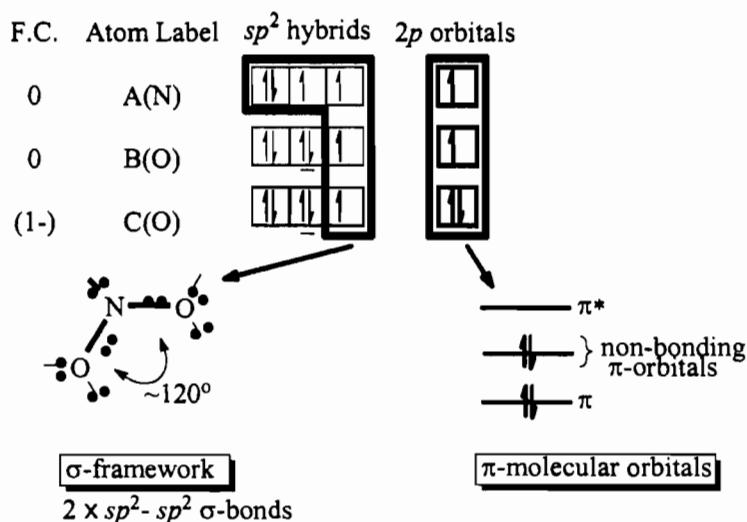
- 8B** We will use the same basic approach to answer this question as was used to solve practice example 12-8A. This time, the bonding in  $\text{NO}_2^-$  will be described by combining valence-bond and molecular orbital theory. With this approach we will be able to generate a structure that more accurately describes the bonding in  $\text{NO}_2^-$  than either of the two equivalent Lewis diagrams that can be drawn for the nitrate ion (below).



Structure (i) will be used to develop the combined localized/delocalized bonding description for the anion (either structure could have been used as the starting structure). We begin by assuming that every atom in the molecule is  $sp^2$  hybridized. To produce the  $\sigma$ -framework for the molecule, the half-filled  $sp^2$  orbitals of the oxygen atoms will be overlapped with a half-filled  $sp^2$  orbital of nitrogen. By contrast, to generate a set of  $\pi$ -molecular orbitals, we will combine one unhybridized  $2p$  orbital from each of the two oxygen atoms with an unhybridized  $2p$  orbital on nitrogen. This will generate three  $\pi$  molecular orbitals: a bonding molecular orbital, a non-bonding molecular orbital and an antibonding molecular orbital.

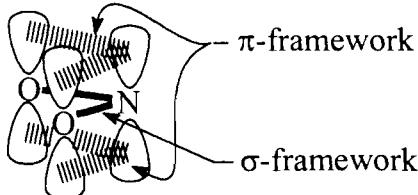


Remember that the number of valence electrons assigned to each atom must reflect the formal charge for that atom. Accordingly, the oxygen with a 1- formal charge (atom C) must end up with 7 electrons, whereas the nitrogen atom (atom A) and the other oxygen atom (atom B) must have their customary 5 and 6 valence electrons, respectively, because they both have a formal charge of zero. Let's begin assigning valence electrons by half-filling two  $sp^2$  hybrid orbitals on the nitrogen atom (atom A) and one  $sp^2$  hybrid orbital on each oxygen atoms (atoms B and C). Next, we half-fill the lone  $2p$  orbital on nitrogen (atom A) and the lone  $2p$  orbital on the oxygen atom with a formal charge of zero (atom B). Following this, the  $2p$  orbital for the remaining oxygen (atom C) is filled and then lone pairs are placed in the  $sp^2$  hybrid orbitals that are still empty. At this stage, then, all 18 valence electrons have been put into atomic and hybrid orbitals on the three atoms. Now, we overlap the four half-filled  $sp^2$  hybrid orbitals to generate the  $\sigma$ -bond framework and combine the three  $2p$  orbitals (two half-filled, one filled) to form three  $\pi$ -molecular orbitals as shown below.



$$\text{Overall bond order for this set of } \pi\text{-molecular orbitals} \frac{2 \text{ bonding } e^- - 0 \text{ antibonding } e^-}{2} = 1$$

The  $\pi$  bond is spread out evenly over the two N—O linkages. This leads to an average bond order of 1.5 for each of the two N—O bonds in  $\text{NO}_2$ . By following this combined approach, we end up with a structure that has the  $\sigma$ -bond framework sandwiched between the delocalized  $\pi$ -molecular orbitals:



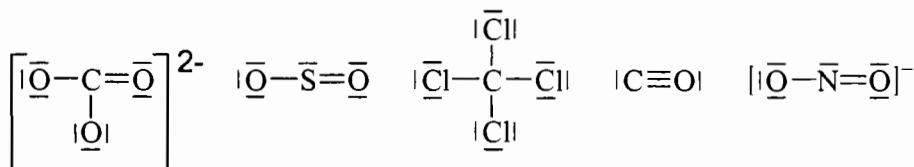
This is a much more accurate depiction of the bonding in  $\text{NO}_2$  than that provided by any one of the two Lewis diagrams given above.

## REVIEW QUESTIONS

**Note:** In VSEPR theory the term “bond pair” is used for a single bond, a double bond, or a triple bond, even though a single bond consists of one pair of electrons, a double bond two pairs of electrons, and a triple bond three pairs of electrons. To avoid any confusion between the number of electron pairs actually involved in the bonding to a central atom, and the number of atoms bonded to that central atom, we shall occasionally use the term “ligand” to indicate an atom or a group of atoms attached to the central atom.

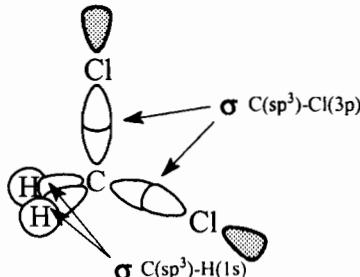
- An  $sp^2$  hybrid orbital is one of a set of three orbitals that are identical in shape and energy and are formed by the combination of an  $s$  orbital and two  $p$  orbitals. The three orbitals are trigonal planar in orientation.
  - $\sigma^*_{2p}$  is the symbol for the antibonding orbital that arises from the end on overlap of two atomic  $2p$  orbitals that are out of phase.
  - The bond order is an indication of bond strength. In valence bond theory, it indicates the number of electron pairs shared by two atoms. In molecular orbital theory it is one half of the difference between the number of bonding and the number of antibonding electrons.
  - A  $\pi$  bond is a bond that has regions of overlap above and below the internuclear axis.
- Hybridization of atomic orbitals is that process in which atomic orbitals are blended together to produce new hybrid.
  - The  $\sigma$ -bond framework consists of the atoms in the molecule and the single bonds that connect them, before the second (and third) bonds of multiple bonds are in place.
  - The Kekulé structures of benzene are the two resonance forms of benzene in which the alternating single and double carbon-to-carbon bonds exchange positions.
  - The band theory of metallic bonding describes the bonding between metal atoms in terms of molecular orbitals that extend throughout the crystal.

3. (a) A  $\sigma$  bond is located along the internuclear axis and is the first bond formed between two atoms. A  $\pi$  bond is located above and below the internuclear axis and only forms after a  $\sigma$  bond has formed.
- (b) Localized electrons are those confined either to the region around one atom or to the region between two atoms. Delocalized electrons are free to move among three or more atoms.
- (c) The constructive overlap of two atomic orbitals on two separate atoms produces a bonding molecular orbital. Electrons in bonding molecular orbitals tend to be localized in the region between the two nuclei. The mutual attraction between the positively charged nuclei and the negatively charged electrons hold the nuclei in close proximity. Because the electrons are attracted to two nuclei rather than just a single nucleus, electrons in bonding molecular orbitals are more stable (i.e., have lower energy) than electrons in the parent atomic orbitals. The destructive overlap of two atomic orbitals on two atoms produces an antibonding molecular orbital. In an antibonding molecular orbital, the charge density between the two nuclei decreases to zero. The vast majority of the electron density in an antibonding orbital is concentrated outside the internuclear region at opposite ends of the overlapping atoms. With very little electron density between them, the positively charged nuclei repel each other and consequently, a bond is not formed. Because an electron in an antibonding orbital is, on average, further away from its associated nucleus than an electron in one of the atoms parent atomic orbitals, it is less stable (higher in energy).
- (d) A metal is a material that readily conducts electricity (due to a small or non-existent band gap). A semiconductor conducts electricity only once it is heated or has a moderate voltage applied to it (due to a moderate band gap).
4. The Lewis structure of  $\text{H}_2\text{Se}$ ,  $\text{H}-\overline{\text{Se}}-\text{H}$ , indicates that there are two atoms and two lone pairs attached to the central atom. The bond angle of  $91^\circ$  indicates that the  $1s$  orbitals on  $\text{H}$  overlap the  $4p$  orbitals on  $\text{Se}$ . This would give an undistorted bond angle of  $90^\circ$ . But repulsions between the  $\text{H}$ 's open up the bond angle a slight bit.
5. Determining hybridization is made easier if we begin with Lewis structures. Only one resonance form is drawn for  $\text{CO}_3^{2-}$ ,  $\text{SO}_2$  and  $\text{NO}_2^-$ .



The C atom is attached to three ligands and no lone pairs and thus is  $sp^2$  hybridized in  $\text{CO}_3^{2-}$ . The S atom is attached to two ligands and one lone pair and thus is  $sp^2$  hybridized in  $\text{SO}_2$ . The C atom is attached to four ligands and no lone pairs and thus is  $sp^3$  hybridized in  $\text{CCl}_4$ .  $sp$  hybridization occurs in  $\text{CO}$ . The N atom is attached to two ligands and one lone pair in  $\text{NO}_2^-$  and thus is  $sp^2$  hybridized. The central atom is  $sp^2$  hybridized in  $\text{SO}_2$ ,  $\text{CO}_3^{2-}$ , and  $\text{NO}_2^-$ .

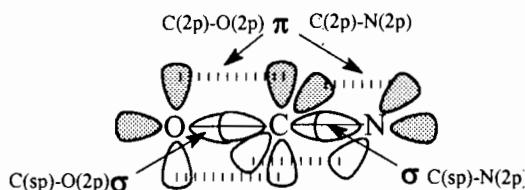
- 6.** Statement (b) is correct. The only consistently single bonds in C—H—O compounds are bonds to H atoms (a H atom can only form one bond), and single bonds must be  $\sigma$  bonds. Thus, both C—H and O—H bonds must be  $\sigma$  bonds, making (a) false and (b) true. Only C=C bonds (or C=O) bonds in these compounds, that is double bonds, consist of a  $\sigma$  bond and a  $\pi$  bond; (c) is false. A  $\sigma$  bond must form before a  $\pi$  bond forms to complete a double bond; (d) is false.
- 7.** (a) HI: H  $1s\boxed{1}$  I [Kr]  $4d^{10}$   $5s\boxed{1}$   $5p\boxed{\begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix}}$   
The  $1s$  orbital of H overlaps the half-filled  $5p$  orbital of I to produce a linear molecule.
- (b) BrCl: Br [Ar]  $3d^{10}$   $4s\boxed{1}$   $4p\boxed{\begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix}}$  Cl [Ne]  $3s\boxed{1}$   $3p\boxed{\begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix}}$   
The half-filled  $3p$  orbital of Cl overlaps the half-filled  $4p$  orbital of Br to produce a linear molecule.
- (c) H<sub>2</sub>Se: H  $1s\boxed{1}$  Se [Ar]  $3d^{10}$   $4s\boxed{1}$   $4p\boxed{\begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix}}$   
Each half-filled  $4p$  orbital of Se overlaps with a half-filled  $1s$  orbital of H to produce a bent molecule, with a bond angle of approximately  $90^\circ$ .
- (d) OCl<sub>2</sub>: O  $1s\boxed{1}$   $2s\boxed{1}$   $2p\boxed{\begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix}}$  Cl [Ne]  $3s\boxed{1}$   $3p\boxed{\begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix}}$   
Each half-filled  $2p$  orbital of O overlaps with a half-filled  $3p$  orbital of Cl to produce a bent molecule, with a bond angle of approximately  $90^\circ$ .
- 8.** The BF<sub>3</sub> molecule is planar with bond angles of  $120^\circ$ . The  $2p$  orbitals are perpendicular to each other, with angles between them of  $90^\circ$ . Thus, three atoms bound to three  $2p$  orbitals would not form a planar structure and would have the wrong bond angles. If two F atoms bonded to two  $2p$  orbitals on B and the third F bonded to the  $2s$  orbital, the resulting molecule could indeed be planar, but the bond angles would not equal  $120^\circ$ , and two of the bonds would be different from the other one. By hybridizing the  $2s$  and two  $2p$  orbitals of B, we create three equivalent orbitals that produce the observed bond angles.
- 9.** (a) The central C atom employs four  $sp^3$  hybrid orbitals; these have a tetrahedral geometry. Each of the two H atoms employs a  $1s$  orbital, and each of the two Cl atoms employs a half-filled  $3p$  orbital. A diagram of this follows:



- (b) The ground state C atom has the electron configuration  $[\text{He}] \ 2s^2 \ 2p^2$ . Based on this ground state electron configuration, we would expect a bent molecule. To produce the two half-filled orbitals required to form two linear bonds a hybridized electron configuration (which corresponds to an excited state for the individual atoms) is required:  $\text{C}^* \ 1s^1 \ 2s^1 \ 2p^4 \rightarrow \text{C}_{\text{hyb}}^* \ 1s^1 \ sp^2 \ 2p^2$

The overlap of the two half-filled  $sp$  orbitals of C, one with a half-filled  $2p$  orbital on O and the other with a half-filled  $2p$  orbital on  $\text{N}^-$ , produces the  $\sigma$  bond framework.  $\text{O} \ 1s^2 \ 2s^2 \ 2p^4$   $\text{N}^- \ 1s^2 \ 2s^2 \ 2p^4$

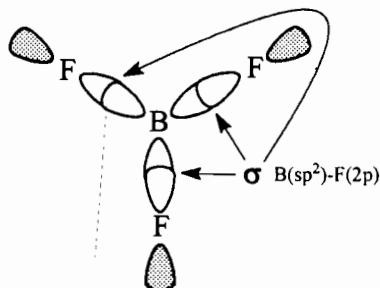
The  $\pi$  bonds are produced by the sidewise overlap of the two half-filled  $2p$  orbitals on C, one with a half-filled  $2p$  orbital on O, the other with a half-filled  $2p$  orbital on  $\text{N}^-$ . A diagram of this follows:



- (c) The ground-state electron configuration of B suggests an ability to form one B—F bond, rather than three.  $1s^2 \ 2s^2 \ 2p^1$  Again, excitation, or promotion of an electron to a higher energy orbital, followed by hybridization is required to form three equivalent half-filled B orbitals.

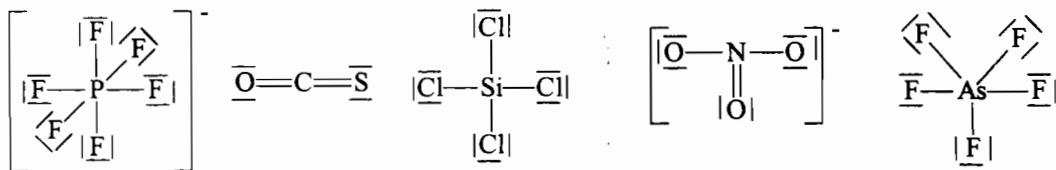


Recall that the ground-state electron configuration of F is  $[\text{He}] \ 2s^2 \ 2p^5$ . Bonds are produced through overlap of the half-filled  $sp^2$  orbitals on B with the half filled F  $2p$  orbitals. The  $\text{BF}_3$  molecule is trigonal planar, with F—B—F bond angles of  $120^\circ$ . A diagram of this follows:



- 10. (a)** In  $\text{PF}_6^-$  there are a total of  $5 + (6 \times 7) + 1 = 48$  valence electrons, or 24 pairs. A plausible Lewis structure follows. In order to form the six P—F bonds, the hybridization on P must be  $sp^3d^2$ .
- (b)** In COS there are a total of  $4 + 6 + 6 = 16$  valence electrons, or 8 pairs. A plausible Lewis structure follows. In order to bond two atoms to the central C, the hybridization on that C atom must be  $sp$ .

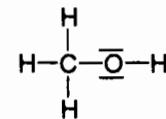
- (c) In  $\text{SiCl}_4$ , there are a total of  $4 + (4 \times 7) = 32$  valence electrons, or 16 pairs. A plausible Lewis structure follows. In order to form four Si—Cl bonds, the hybridization on Si must be  $sp^3$ .
- (d) In  $\text{NO}_3^-$ , there are a total of  $5 + (3 \times 6) + 1 = 24$  valence electrons, or 12 pairs. A plausible Lewis structure follows. In order to bond three O atoms to the central N atom, with no lone pairs on that N atom, its hybridization must be  $sp^2$ .
- (e) In  $\text{AsF}_5$ , there are a total of  $5 + (5 \times 7) = 40$  valence electrons, or 20 pairs. A plausible Lewis structure follows. This is a molecule of the type  $\text{AX}_5$ . To form five As—F bonds, the hybridization on As must be  $sp^3d$ .



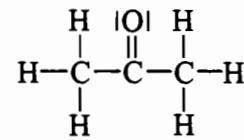
11. We base each hybridization scheme on the Lewis structure for the molecule.

- (a)  $\text{H}-\text{C}\equiv\text{N}$  There are two atoms bonded to C and no lone pairs on C. Thus, the hybridization for C must be  $sp$ .

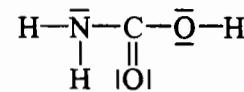
- (b) There are four atoms bonded to C and no lone pairs in this molecule. Thus, the hybridization for C must be  $sp^3$ . (O atom is also  $sp^3$  hybridized).



- (c) There are four atoms bonded to each terminal C and no lone pairs on these C atoms. Thus, the hybridization for each terminal C must be  $sp^3$ . There are three atoms and no lone pairs bonded to the central C. The hybridization for the central C must be  $sp^2$ .



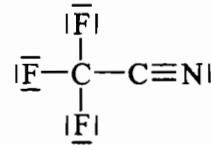
- (d) There are three atoms bonded to C and no lone pairs on C. This requires  $sp^2$  hybridization.



12. (a) This is a planar molecule. The hybridization on C is  $sp^2$  (one bond to each of the three attached atoms).

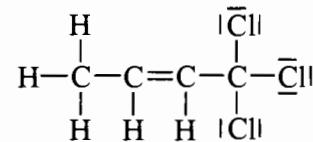
- (b)  $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$  is a linear molecule. The hybridization for each C is  $sp$  (one bond to each of the two ligands).

- (c) is neither linear nor planar. The shape around the left-hand C is tetrahedral and that C has  $sp^3$  hybridization. The shape around the right-hand carbon is linear and that C has  $sp$  hybridization. (N atom is  $sp$  hybridized).

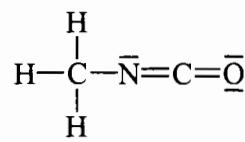


- (d)  $[\text{S}\equiv\text{N}]^-$  is a linear molecule. The hybridization for C is  $sp$ .

- 13.** (a) In HCN, there are a total of  $1+4+5=10$  valence electrons, or 5 pairs. A plausible Lewis structure follows:  $\text{H}-\text{C}\equiv\text{N}$ . The H—C bond is a  $\sigma$  bond, and the C≡N bond is composed of 1  $\sigma$  and 2  $\pi$  bonds.
- (b) In  $\text{C}_2\text{N}_2$ , there are a total of  $(2\times 4)+(2\times 5)=18$  valence electrons, or 9 pairs. A plausible Lewis structure follows:  $|\text{N}\equiv\text{C}-\text{C}\equiv\text{N}|$  The C—C bond is a  $\sigma$  bond, and each C≡N bond is composed of 1  $\sigma$  and 2  $\pi$  bonds.
- (c) In  $\text{CH}_3\text{CHCHCCl}_3$ , there are a total of 42 valence electrons, or 21 pairs. A plausible Lewis structure is shown to the right. All bonds are  $\sigma$  bonds except one of the bonds that comprise the C=C bond. The C=C bond is composed of one  $\sigma$  and one  $\pi$  bond.
- (d) In HONO, there is a total of  $1+5+(2\times 6)=18$  valence electrons, or 9 pairs. A plausible Lewis structure is  $\text{H}-\overline{\text{O}}-\overline{\text{N}}=\overline{\text{O}}$  All single bonds in this structure are  $\sigma$  bonds. The double bond is composed of one  $\sigma$  and one  $\pi$  bond.



- 14.** (a) In  $\text{CO}_2$ , there are  $4+(2\times 6)=16$  valence electrons, or 8 pairs. A plausible Lewis structure is  $|\text{O}=\text{C}=\text{O}|$
- (b) The molecule is linear and the hybridization on the C atom is  $sp$ . Each C=O bond is composed of a  $\sigma$  bond (end-to-end overlap of a half-filled  $sp$  orbital on C with a half-filled  $2p$  orbital on O) and a  $\pi$  bond (overlap of a half-filled  $2p$  orbital on O with a half-filled  $2p$  orbital on C).
- 15.** In  $\text{CH}_3\text{NCO}$ , there is a total of  $(3\times 1)+(2\times 4)+5+6=22$  valence electrons, or 11 pairs. A plausible Lewis structure is
- (a) Of course, all single bonds are  $\sigma$  bonds, and a double bond is composed of a  $\sigma$  bond and a  $\pi$  bond. Thus, each bond in the molecule consists of at least a  $\sigma$  bond. There are six (6)  $\sigma$  bonds in this molecule.
- (b) Since each double bond consists of a  $\sigma$  bond and a  $\pi$  bond, there are two (2)  $\pi$  bonds in this molecule.



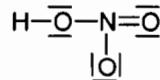
- 16.** (a) A  $\sigma_{1s}$  orbital must be lower in energy than a  $\sigma_{1s}^*$  orbital. The bonding orbital always is lower than the antibonding orbital if they are derived from the same atomic orbitals.
- (b) A  $\sigma_{2s}$  orbital should be lower in energy than a  $\sigma_{2p}$  orbital, since the  $2s$  atomic orbital is lower in energy than the  $2p$  atomic orbital, the orbitals from which the molecular orbitals, respectively, are derived.

- (c) A  $\sigma_{1s}^*$  orbital should be lower than a  $\sigma_{2s}$  orbital, since the  $1s$  atomic orbital is considerably lower in energy than is the  $2s$  orbital.
- (d) A  $\sigma_{2p}$  orbital should be lower in energy than a  $\sigma_{2p}^*$  orbital. Both orbitals are from atomic orbitals in the same subshell but we expect a bonding orbital to be more stable than an antibonding orbital.
17. Based on Lewis theory, one would expect  $C_2$  to have the greater bond energy due to the formation of quadruple bond,  $C \equiv C$  vs.  $Li-Li$ . The molecular orbital diagrams and bond orders are as follows.
- $C_2$  KK  $\sigma_{2s}[\overline{\text{II}}]$   $\sigma_{2s}^*[\text{II}]$   $\pi_{2p}[\overline{\text{II}}\overline{\text{II}}]$   $\sigma_{2p}[\text{II}]$  bond order =  $(6 \text{ bonding } e^- - 2 \text{ antibonding } e^-) \div 2 = 2$
- $Li_2$  KK  $\sigma_{2s}[\overline{\text{II}}]$   $\sigma_{2s}^*[\text{II}]$   $\pi_{2p}[\text{II}]$   $\sigma_{2p}[\text{II}]$  bond order =  $(2 \text{ bonding } e^- - 0 \text{ antibonding } e^-) \div 2 = 1$
- Thus, molecular orbital theory also predicts that  $C_2$  has a greater bond energy than does  $Li_2$ .
18. (a) In each case, the number of valence electrons in the species is determined first; this is followed by the molecular orbital diagram for each species.
- $C_2^+$  no. valence  $e^- = (2 \times 4) - 1 = 7$  KK  $\sigma_{2s}$   $\sigma_{2s}^*$   $\pi_{2p}$   $\sigma_{2p}$   $\pi_{2p}^*$   $\sigma_{2p}^*$
- $O_2^-$  no. valence  $e^- = (2 \times 6) + 1 = 13$  KK  $\sigma_{2s}$   $\sigma_{2s}^*$   $\sigma_{2p}$   $\pi_{2p}$   $\pi_{2p}^*$   $\sigma_{2p}^*$
- $F_2^+$  no. valence  $e^- = (2 \times 7) - 1 = 13$  KK  $\sigma_{2s}$   $\sigma_{2s}^*$   $\sigma_{2p}$   $\pi_{2p}$   $\pi_{2p}^*$   $\sigma_{2p}^*$
- $NO^+$  no. valence  $e^- = 5 + 6 - 1 = 10$  KK  $\sigma_{2s}$   $\sigma_{2s}^*$   $\sigma_{2p}$   $\pi_{2p}$   $\pi_{2p}^*$   $\sigma_{2p}^*$
- (b) Bond order =  $(\text{no. bonding electrons} - \text{no. antibonding electrons}) \div 2$
- $C_2^+$  bond order =  $(5 - 2) \div 2 = 1.5$  This species is stable.
- $O_2^-$  bond order =  $(8 - 5) \div 2 = 1.5$  This species is stable.
- $F_2^+$  bond order =  $(8 - 5) \div 2 = 1.5$  This species is stable.
- $NO^+$  bond order =  $(8 - 2) \div 2 = 3$  This species is stable.
- (c)  $C_2^+$  has an odd number of electrons and is paramagnetic, with one unpaired electron.
- $O_2^-$  has an odd number of electrons and is paramagnetic, with one unpaired electron.
- $F_2^+$  has an odd number of electrons and is paramagnetic, with one unpaired electron.
- $NO^+$  has an even number of electrons and is diamagnetic.
19. (a) stainless steel - electrical conductor (b) solid NaCl - insulator  
 (c) sulfur - insulator (d) germanium - semiconductor  
 (e) seawater - electrical conductor (f) solid iodine - insulator
20. The largest band gap between valence and conduction band is in an insulator. There is no energy gap between the valence and conduction bands in a metal. Metalloids are semiconductors; they have a small band gap between the valence and conduction bands.

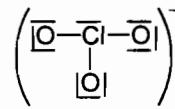
## EXERCISES

### Valence-Bond Theory

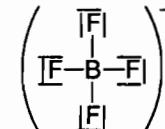
- 21.** There are several ways in which valence bond theory is superior to Lewis structures in describing covalent bonds. *First*, valence bond theory clearly distinguishes between sigma and pi bonds. In Lewis theory, a double bond appears to be just two bonds and it is not clear why a double bond is not simply twice as strong as a single bond. In valence bond theory, it is clear that a sigma bond must be stronger than a pi bond, for the orbitals overlap more effectively in a sigma bond (end-to-end) than they do in a pi bond (side-to-side). *Second*, molecular geometries are more directly obtained in valence bond theory than in Lewis theory. Although valence bond theory requires the introduction of hybridization to explain these geometries, Lewis theory does not predict geometries at all; it simply provides the basis from which VSEPR theory predicts geometries. *Third*, Lewis theory does not explain hindered rotation about double bonds. With valence bond theory, any rotation about a double results in poorer overlap of the *p* orbitals that produce the pi bond.
- 23.**
- (a) Lewis theory does not describe the shape of the water molecule. It does indicate that there is a single bond between each H atom and the O atom, and that there are two lone pairs attached to the O atom, but it says nothing about molecular shape.
  - (b) In valence-bond theory using simple atomic orbitals, each H—O bond results from the overlap of a *1s* orbital on H with a *2p* orbital on O. The angle between *2p* orbitals is  $90^\circ$  this method initially predicts a  $90^\circ$  bond angle. The observed  $104^\circ$  bond angle is explained as arising from repulsion between the two slightly positive H atoms.
  - (c) In VSEPR theory the  $\text{H}_2\text{O}$  molecule is categorized as being of the  $\text{AX}_2\text{E}_2$  type, with two atoms and two lone pairs attached to the central oxygen atom. The lone pairs repel each other more than do the bond pairs, explaining the smaller than  $109.5^\circ$  tetrahedral bond angle.
  - (d) In valence-bond theory using hybrid orbitals, each H—O bond results from the overlap of a *1s* orbital on H with a *sp*<sup>3</sup> orbital on O. The angle between *sp*<sup>3</sup> orbitals is  $109.5^\circ$ . The observed bond angle of  $104^\circ$  is rationalized based on the greater repulsion of lone pair electrons when compared to bonding pair electrons.
- 25.** For each species, we first draw the Lewis structure, as an aid to explaining the bonding.
- (a) In  $\text{CO}_2$ , there are a total of  $4 + (2 \times 6) = 16$  valence electrons, or 8 pairs. C is the central atom. The Lewis structure is  $\text{O}=\text{C}=\text{O}$ . The molecule is linear and C is *sp* hybridized.
  - (b) In  $\text{HONO}_2$ , there are a total of  $1 + 5 + (3 \times 6) = 24$  valence electrons, or 12 pairs. N is the central atom, and a plausible Lewis structure is shown on the right. The molecule is trigonal planar around N which is *sp*<sup>2</sup> hybridized. The O in the H—O—N portion of the molecule is *sp*<sup>3</sup> hybridized.



- (c) In  $\text{ClO}_3^-$ , there are a total of  $7 + (3 \times 6) + 1 = 26$  valence electrons, or 13 pairs. Cl is the central atom, and a plausible Lewis structure is shown on the right. The electron-group geometry around Cl is tetrahedral, indicating that Cl is  $sp^3$  hybridized.

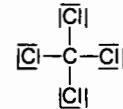


- (d) In  $\text{BF}_4^-$ , there are a total of  $3 + (4 \times 7) + 1 = 32$  valence electrons, or 16 pairs. B is the central atom, and a plausible Lewis structure is shown on the right. The electron-group geometry is tetrahedral, indicating that B is  $sp^3$  hybridized.

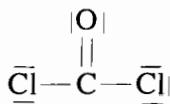


27. The Lewis structure of  $\text{ClF}_3$  is shown on the right. There are three atoms and two lone pairs attached to the central atom, its hybridization is  $sp^3d$ , which is achieved as follows.  $\text{Cl}_{\text{unhyb}}[\text{Ne}] 3s \boxed{\text{II}} \quad 3p \boxed{\text{IIII}} \quad 3d \boxed{\text{IIIIII}}$   $\longrightarrow \text{Cl}_{\text{hyb}}[\text{Ne}] \quad \begin{matrix} \text{IIIIII} \\ \text{dsp}^3 \end{matrix} \quad 3d \boxed{\text{IIIIII}}$  The orbital diagram of F is  $[\text{He}] 2s \boxed{\text{II}} \quad 2p \boxed{\text{IIII}}$  Each of the three sigma bonds are formed by the overlap of a  $2p$  orbital on F with one of the half-filled  $dsp^3$  orbitals on Cl. Since the  $sp^3$  hybridization has a trigonal bipyramidal shape, and the two lone pairs occupy the axial positions in the molecule,  $\text{ClF}_3$  is T-shaped.

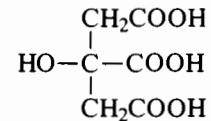
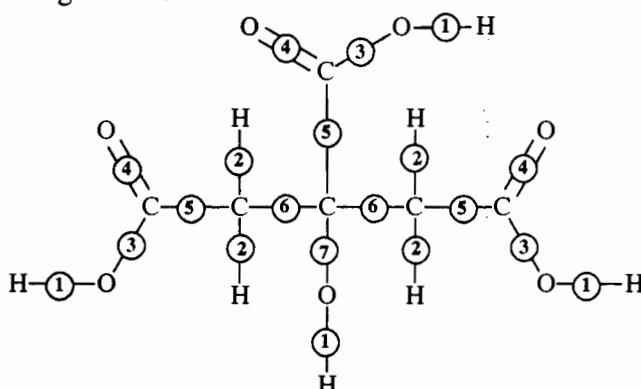
29. (a) In  $\text{CCl}_4$ , there is a total of  $4 + (4 \times 7) = 32$  valence electrons, or 8 pairs. C is the central atom. A plausible Lewis structure is shown. The geometry at C is tetrahedral; C is  $sp^3$  hybridized.  $\text{Cl}—\text{C}—\text{Cl}$  bond angles are  $109.5^\circ$ . Each C—Cl bond is represented by  $\sigma$ :  $\text{C}(sp^3)^1 — \text{Cl}(3p)^1$
- (b) In  $\text{ONCl}$ , there is a total of  $6 + 5 + 7 = 18$  valence electrons, or 9 pairs. N is the central atom. A plausible Lewis structure is  $\text{O}=\text{N}=\text{Cl}$ . The e<sup>-</sup> group geometry around N is triangular planar, and N is  $sp^2$  hybridized. The O—N—C bond angle is about  $120^\circ$ . The bonds are:  $\sigma$ :  $\text{O}(2p_y)^1 — \text{N}(sp^2)^1$   $\sigma$ :  $\text{N}(sp^2)^1 — \text{Cl}(3p_z)^1$   $\pi$ :  $\text{O}(2p_z)^1 — \text{N}(2p_z)^1$
- (c) In  $\text{HONO}$ , there are a total of  $1 + (2 \times 6) + 5 = 18$  valence electrons, or 9 pairs. A plausible Lewis structure is  $\text{H}—\overline{\text{O}_a}—\overline{\text{N}}=\overline{\text{O}_b}$ . The geometry of  $\text{O}_a$  is tetrahedral,  $\text{O}_a$  is  $sp^3$  hybridized, the  $\text{H}—\text{O}_a—\text{N}$  bond angle is (at least close to)  $109.5^\circ$ . The e<sup>-</sup> group geometry at N is trigonal, N is  $sp^2$  hybridized, the  $\text{O}_a—\text{N}—\text{O}_b$  bond angle is  $120^\circ$ . The four bonds are represented as follows.  $\sigma$ :  $\text{H}(1s)^1 — \text{O}_a(sp^3)^1$   $\sigma$ :  $\text{O}_a(sp^3)^1 — \text{N}(sp^2)^1$   $\sigma$ :  $\text{N}(sp^2)^1 — \text{O}_b(2p_y)^1$   $\pi$ :  $\text{N}(2p_z)^1 — \text{O}_b(2p_z)^1$ .



- (d) In  $\text{COCl}_2$ , there are a total of  $4 + 6 + (2 \times 7) = 24$  valence electrons, or 12 pairs. A plausible Lewis structure is shown to the right. The electron group geometry around C is trigonal planar; all bond angles around C are  $120^\circ$ , and the hybridization of C is  $sp^2$ . The four bonds in the molecule:  $2 \times \sigma : \text{Cl}(3p_x)^1 - \text{C}(sp^2)^1$   $\sigma : \text{O}(2p_y)^1 - \text{C}(sp^2)^1$   $\pi : \text{O}(2p_z)^1 - \text{C}(2p_z)^1$ .



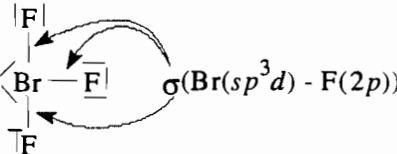
- 31.** Citric acid has the molecular structure (shown on right) Using Figure 12-16 as a guide, the following hybridization and bonding scheme is obtained for citric acid:



- ①  $\sigma(\text{O}(sp^3) - \text{H}(1s))$   
 ②  $\sigma(\text{C}(sp^3) - \text{H}(1s))$   
 ③  $\sigma(\text{C}(sp^2) - \text{O}(sp^3))$   
 ④  $\sigma(\text{C}(sp^2) - \text{O}(2p))$   
 +  
 $\pi(\text{C}(2p) - \text{O}(2p))$   
 ⑤  $\sigma(\text{C}(sp^3) - \text{C}(sp^2))$   
 ⑥  $\sigma(\text{C}(sp^3) - \text{C}(sp^3))$   
 ⑦  $\sigma(\text{C}(sp^3) - \text{O}(sp^3))$

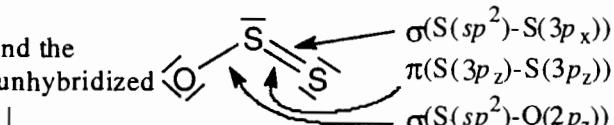
- 33. (a)**

Br atom is  $sp^3d$  hybridized  
F atoms are unhybridized



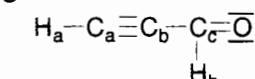
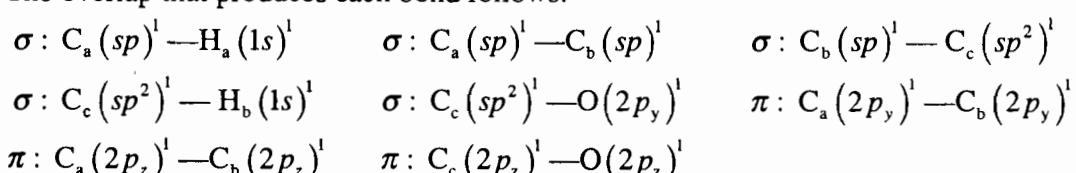
- (b)**

Central S is  $sp^2$  hybridized and the terminal O and S atoms are unhybridized



- 35.**

The bond lengths are consistent with the left-hand C—C bond being a triple bond (120 pm), the remaining C—C bond being a single bond (154 pm) rather than a double bond (134 pm), and the C—O bond being a double bond (123 pm). Of course, the two C—H bonds are single bonds (110 pm). All of this is depicted in the Lewis structure on the right. The overlap that produces each bond follows:



## Molecular-Orbital Theory

37. The valence-bond method describes a covalent bond as the result of the overlap of atomic orbitals. The more complete the overlap, the stronger the bond. Molecular orbital theory describes a bond as a region of space in a molecule where there is a good chance of finding the bonding electrons. The molecular orbital bond does not have to be created from atomic orbitals (although it often is) and the orientations of atomic orbitals do not have to be manipulated to obtain the correct geometric shape. There is little concept of the relative energies of bonding in valence bond theory. In molecular orbital theory, bonds are ordered energetically. These energy orderings, in fact, provide a means of checking the predictions of the theory through the spectroscopic analysis of the molecules.

39. The two molecular orbital diagrams follow:



$$N_2^- \text{ bond order} = (8 - 3) \div 2 = 2.5 \text{ (stable)} \quad N_2^{2-} \text{ bond order} = (8 - 4) \div 2 = 2 \text{ (stable)}$$

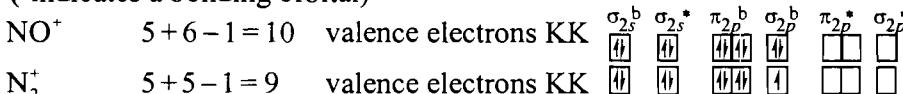
41. In order to have a bond order higher than three, there would have to be a region in a molecular orbital diagram where four bonding orbitals occur together in order of increasing energy, with no intervening antibonding orbitals. No such region exists in any of the molecular orbital diagrams in Figure 12-23. Alternatively, three bonding orbitals would have to occur together energetically, following an electron configuration which, when full, results in a bond order greater than zero. This arrangement does not occur either.

43. (b) indicates a bonding orbital)

			$\sigma_{2s}^b$	$\sigma_{2s}^*$	$\pi_{2p}^b$	$\sigma_{2p}^b$	$\pi_{2p}^*$	$\sigma_{2p}^*$
(a)	NO	$5 + 6 = 11$	valence electrons KK					
(b)	$NO^+$	$5 + 6 - 1 = 10$	valence electrons KK					
(c)	CO	$4 + 6 = 10$	valence electrons KK					
(d)	CN	$4 + 5 = 9$	valence electrons KK					
(e)	$CN^-$	$4 + 5 + 1 = 10$	valence electrons KK					
(f)	$CN^+$	$4 + 5 - 1 = 8$	valence electrons KK					
(g)	BN	$3 + 5 = 8$	valence electrons KK					

45. We first produce the molecular orbital diagram for each species.

(a) (b) indicates a bonding orbital)



$$\text{Bond order} = (\text{no. bonding electrons} - \text{no. antibonding electrons}) \div 2$$

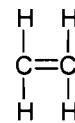
$$\text{For } NO^+ \text{ bond order} = (8 - 2) \div 2 = 3; \text{ for } N_2^+ \text{ bond order} = (7 - 2) \div 2 = 2.5$$

- (b)  $\text{NO}^+$  is diamagnetic; it has no unpaired electrons.  $\text{N}_2^+$  is paramagnetic; it has one unpaired electron.
- (c) The molecule with the lower bond order will also have the greater bond length. Thus,  $\text{N}_2^+$  should have the greater bond length.

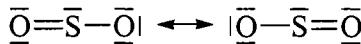
## Delocalized Molecular Orbitals

47. With either Lewis structures or the valence bond method, two structures must be drawn (and “averaged”) to explain the  $\pi$  bonding in  $\text{C}_6\text{H}_6$ . The  $\sigma$  bonding is well explained by assuming  $sp^2$  hybridization on each C atom. But the  $\pi$  bonding requires that all six C—C  $\pi$  bonds must be equivalent. This can be achieved by creating six  $\pi$  molecular orbitals—three bonding and three antibonding—into which the  $6\pi$  electrons are placed. This creates a single structure for the  $\text{C}_6\text{H}_6$  molecule.
49. We expect to find delocalized orbitals in those species for which bonding cannot be represented thoroughly by one Lewis structure, that is, for compounds that require several resonance forms.

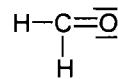
- (a) In  $\text{C}_2\text{H}_4$ , there is a total of  $(2 \times 4) + (4 \times 1) = 12$  valence electrons, or 6 pairs. C atoms are the central atoms. The bonding description of  $\text{C}_2\text{H}_4$  does not require the use of delocalized orbitals.



- (b) In  $\text{SO}_2$ , there is a total of  $6 + (2 \times 6) = 18$  valence electrons, or 9 pairs. S is the central atom. A plausible Lewis structure has two resonance forms. The bonding description of  $\text{SO}_2$  will require the use of delocalized molecular orbitals.



- (c) In  $\text{H}_2\text{CO}$ , there is a total of  $(2 \times 1) + 4 + 6 = 12$  valence electrons, or 6 pairs. C is the central atom. A plausible Lewis structure is shown on the right. Because one Lewis structure adequately represents the bonding in the molecule, the bonding description of  $\text{H}_2\text{CO}$  does not require the use of delocalized molecular orbitals.



## Metallic Bonding

51. (a) Atomic number, by itself, is not particularly important in determining whether a substance has metallic properties. However, atomic number determines where an element appears in the periodic table, and the location to the left and toward the bottom of the periodic table is a region where one finds atoms of high metallic character. Therefore atomic number—by locating an element in the periodic table—has some minimal predictive value in determining metallic character.
- (b) The answer for this part is much the same as the answer to part (a), since atomic mass generally parallels atomic number for the elements.

- (c) The number of valence electrons (electrons in the shell of highest principal quantum number) is important in predicting metallic character. Elements with few valence electrons—generally four or less—lose those electrons fairly readily to form cations, chemical behavior characteristic of metals. These elements also have a larger number of valence orbitals, which aids in metallic bond formation.
- (d) The more vacant atomic orbitals there are in the valence shell, the more readily metallic bonding occurs.
- (e) Because metals occur in every period of the periodic table—except the first—there is no particular relationship between the number of electron shells and the metallic behavior of an element. (Remember that one shell begins to be occupied at the start of each period.)

**53.** We first determine the number of Na atoms in the sample.

$$\text{no. Na atoms} = 26.8 \text{ mg Na} \times \frac{1 \text{ g Na}}{1000 \text{ mg Na}} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{6.022 \times 10^{23} \text{ Na atoms}}{1 \text{ mol Na}} \\ = 7.02 \times 10^{20} \text{ Na atoms}$$

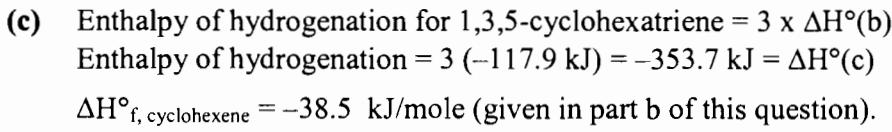
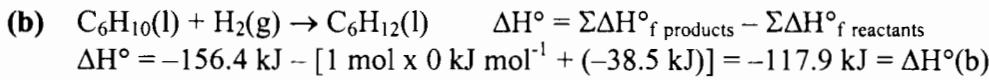
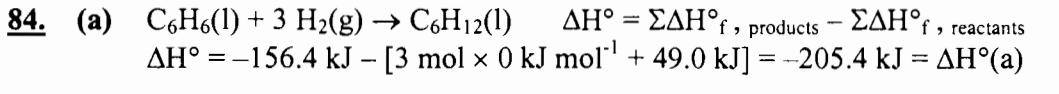
Because there is one  $3s$  orbital per Na atom, and since the number of energy levels (molecular orbitals) created is equal to the number of atomic orbitals initially present, there are  $7.02 \times 10^{20}$  energy levels present in the conduction band of this sample. Also, there is one  $3s$  electron contributed by each Na atom, for a total of  $7.02 \times 10^{20}$  electrons. Because each energy level can hold two electrons, the conduction band is half full.

**55.** A semiconducting element is one that displays poor conductivity when pure, but attains much higher levels of conductivity when doped with small quantities of selected elements or when heated. The best semiconducting materials are made from the Group 14 elements Si and Ge. *P*-type semiconductors result when Group 14 elements are doped with small quantities of an element that has fewer than four valence electrons. For instance, when Si is doped with B, each boron atom ends up forming one silicon bond that has just one electron in it. The transfer of valence electrons from adjacent atoms into these electron-deficient bonds creates a domino effect that results in the movement of an electron-deficient hole through the semiconductor in a direction opposite to the movement of the electrons. Thus, in order to produce a *p*-type semiconductor, the added dopant atom must each have at least one less valence electron than the individual atoms that make up the bulk of the material.

- (a) Sulfur has six valence electrons, which is three too many, so doping Si with sulfur will not produce a *p*-type semiconductor.
- (b) Arsenic has five valence electrons, which is two electrons too many, so doping Si with arsenic will not produce a *p*-type semiconductor.
- (c) Lead has four valence electrons which is one too many, so doping with lead will not produce a *p*-type semiconductor.
- (d) Boron, with one less valence electron than silicon, has the requisite number of electrons needed to form a *p*-type semiconductor.

- (e) Gallium arsenide is an *n*-type semiconductor with an excess of electrons, so doping Si with GaAs will not produce a *p*-type semiconductor.
- (f) Like boron, gallium has three valence electrons. Thus, doping Si with gallium will produce a *p*-type semiconductor.
- 57.** In ultra pure crystalline silicon, there are no extra electrons in the lattice that can conduct an electric current. If however, the silicon becomes contaminated with arsenic atoms, then there will be one additional electron added to the silicon crystal lattice for each arsenic atom that is introduced. Upon heating, some of those "extra" electrons will be promoted into the conduction band of the solid. The electrons that end up in the conduction band are able to move freely through the structure. In other words, the arsenic atoms increase the conductivity of the solid by providing additional electrons that can carry a current when they are promoted into the conduction band by thermal excitation. Thus, by virtue of having extra electrons in the lattice, silicon contaminated with arsenic will exhibit greater electrical conductance than pure silicon at elevated temperatures.
- 59.**  $\Delta E_{\text{Si}} = 110. \text{ kJ mol}^{-1}$ .  $\Delta E_{\text{Si atom}} = \frac{110. \text{ kJ mol}^{-1}}{6.022 \times 10^{23}} = 1.83 \times 10^{-19} \text{ J}$   $E = h\nu = \frac{hc}{\lambda}$  or  $\lambda = \frac{hc}{E}$   
 $\lambda = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{1.83 \times 10^{-19} \text{ J}} = 1.09 \times 10^{-6} \text{ m or } 1090 \text{ nm}$ . This is IR-radiation.

## FEATURE PROBLEMS



Resonance energy is the difference between  $\Delta H^\circ(\text{a})$  and  $\Delta H^\circ(\text{c})$ .  
Resonance energy =  $-353.7 \text{ kJ} - (-205.4 \text{ kJ}) = -148.3 \text{ kJ}$

**(d)** Using bond energies:

$$\Delta H^\circ_{\text{atomization}} = 6(\text{C-H}) + 3(\text{C-C}) + 3(\text{C=C})$$

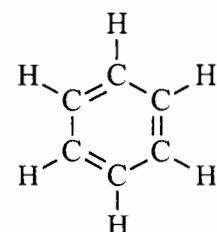
$$\Delta H^\circ_{\text{atomization}} = 6(414 \text{ kJ}) + 3(347 \text{ kJ}) + 3(611 \text{ kJ})$$

$$\Delta H^\circ_{\text{atomization}} = 5358 \text{ kJ} \text{ (per mole of C}_6\text{H}_6\text{)}$$

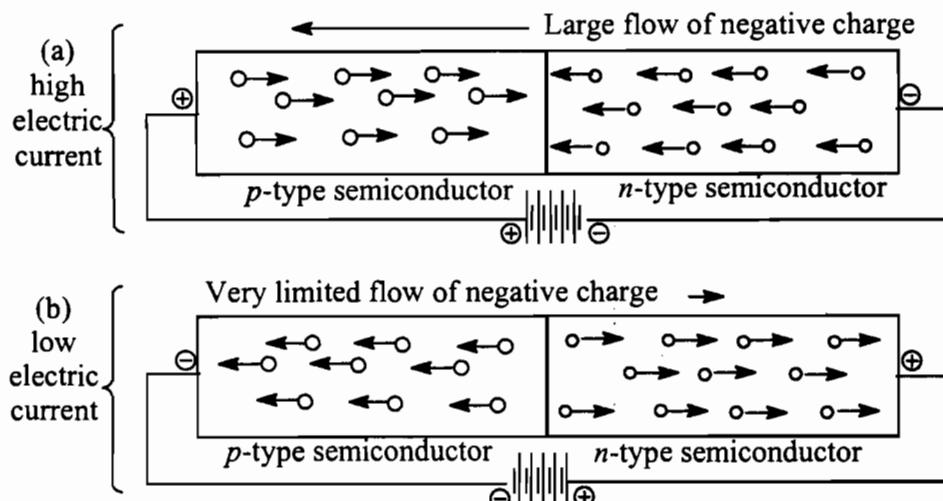


$$\Delta H^\circ = [6(716.7 \text{ kJ}) + 6(218 \text{ kJ})] - 82.6 \text{ kJ} = 5525.6 \text{ kJ}$$

$$\text{Resonance energy} = 5358 - 5525.6 \text{ kJ} = -168 \text{ kJ}$$



85. Consider the semiconductor device below which is hooked up to a battery (direct current). The *n*-type semiconductor (a) is connected to the negative terminal of a battery, the *p*-type to the positive terminal. This has the effect of pushing conduction electrons from right to left and positive holes from left to right.

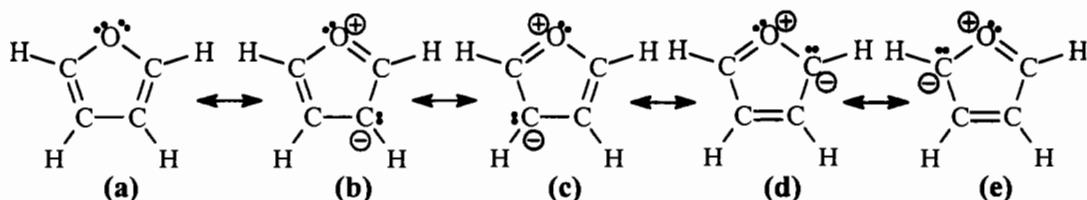


A large current flows across the *p*-*n* junction and through the electric circuit.

Note: the flow of positive holes in one direction is, in effect, a flow of electrons in the opposite direction. So, the *p*-*n* junction should still have the same orientation in (b) as in (a). Now the conduction electrons are pulled to the right and the positive holes to the left. Because there are very few conduction electrons in the *p*-type semiconductor and very few positive holes in the *n*-type semiconductor, there are very few carriers of electric charge across the *p*-*n* junction. Very little electric current flows.

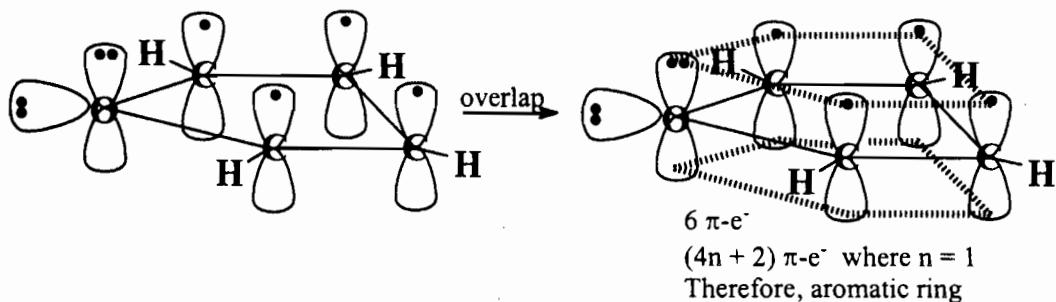
When the *p*-*n* junction rectifier is connected to 60-cycle alternating current, each terminal of the electric generator switches back and forth between being a positive and a negative terminal 120 times per second. If the electrical contact to the *p*-*n* junction rectifier is made through an electric generator rather than a battery, half of the time the situation is that depicted in (a) and half the time it is that depicted in (b). Thus, half the time there is a large current flow, always in the same direction, and half the time there is essentially no current. The alternating current is converted to direct current: it is rectified, and the *p*-*n* junction device shown above is called a rectifier.

86. (a) Five valid resonance forms can be drawn for furan:

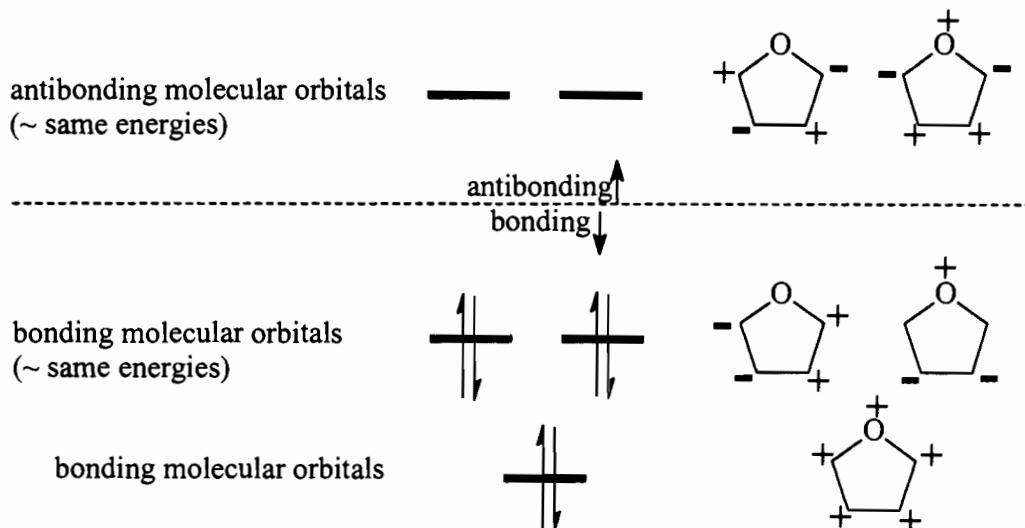


These individual resonance forms do not exist. The actual structure is a hybrid possessing characteristics of all five individual contributors.

- (b) Furan is an aromatic five-membered heterocycle. Its four carbon atoms and lone oxygen atom are  $sp^2$  hybridized in the classical bonding description. One of the lone pairs on oxygen occupies an unhybridized  $p$ -orbital, and this lone pair overlaps with the half-filled  $2p$  orbitals on the four carbon atoms to form an aromatic sextet:



The groundstate molecular orbital diagram for the  $\pi$ -system in furan is depicted below:



The diagram shows that the six  $\pi$ -electrons fill the three bonding molecular orbitals for the  $\pi$ -system. Keep in mind that the ensemble of  $\pi$ -molecular orbitals is superimposed on the  $sp^2$  framework for the molecule.

- (c) All five resonance structures for furan (structures a-e) have six electrons involved in  $\pi$ -bonding. In structure (a), a lone pair in a  $2p$  orbital on the oxygen atom along with the four  $\pi$ -electrons in unhybridized  $2p$  orbitals which form the two C=C bonds are combined to give a  $\pi$ -system. In structures (b) - (e) inclusive, a  $\pi$ -system is produced by the combination of a lone pair in a  $2p$  orbital on a carbon atom with the four  $\pi$ -electrons from the C=O and C=C bonds.

87. (a) In order to see the shape of the *sp* hybrid the simplest approach is to combine just the angular parts of the *s* and *p* orbitals. Including the radial part makes the plot more challenging (see below). The angular parts for the 2s and 2p<sub>z</sub> orbitals are

$$Y(s) = \left(\frac{1}{4\pi}\right)^{1/2} \quad \text{and} \quad Y(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

Combining the two angular parts:

$$\psi_1(sp) = \frac{1}{\sqrt{2}} [Y(2s) + Y(2p_z)]$$

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left[ \left(\frac{1}{4\pi}\right)^{1/2} + \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \right]$$

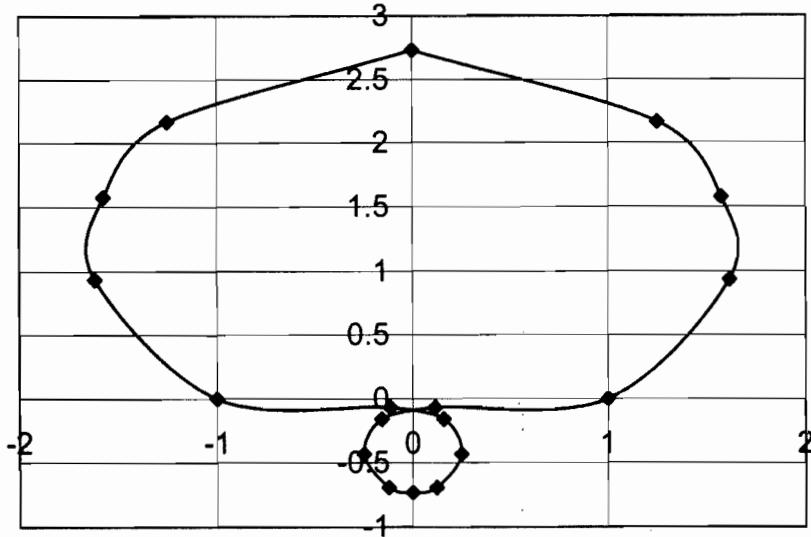
$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left(\frac{1}{4\pi}\right)^{1/2} [1 + \sqrt{3} \cos\theta]$$

We now evaluate this function (ignoring the constants in front of the square brackets) for various values of  $\theta$

Theta(deg)	Theta(rad)	<i>sp</i> <sub>1</sub>	<i>sp</i> <sub>2</sub>
0	0	2.732	-0.732
30	0.5236	2.500	-0.500
45	0.7854	2.225	-0.225
60	1.0472	1.866	0.134
90	1.5708	1.000	1.000
120	2.0944	0.134	1.866
135	2.3562	-0.225	2.225
150	2.6180	-0.500	2.500
170	2.9670	-0.706	2.706
180	3.1416	-0.732	2.732
190	3.3161	-0.706	2.706
210	3.6652	-0.500	2.500
225	3.9270	-0.225	2.225
240	4.1888	0.134	1.866
270	4.7124	1.000	1.000
300	5.2360	1.866	0.134
315	5.4978	2.225	-0.225
330	5.7596	2.500	-0.500
360	6.2832	2.732	-0.732

A plot of these values in the form of Figure 9.24 gives the general shape of the *sp* hybrid.

This is a plot in the xz-plane, for  $\Psi_1(sp)$ .

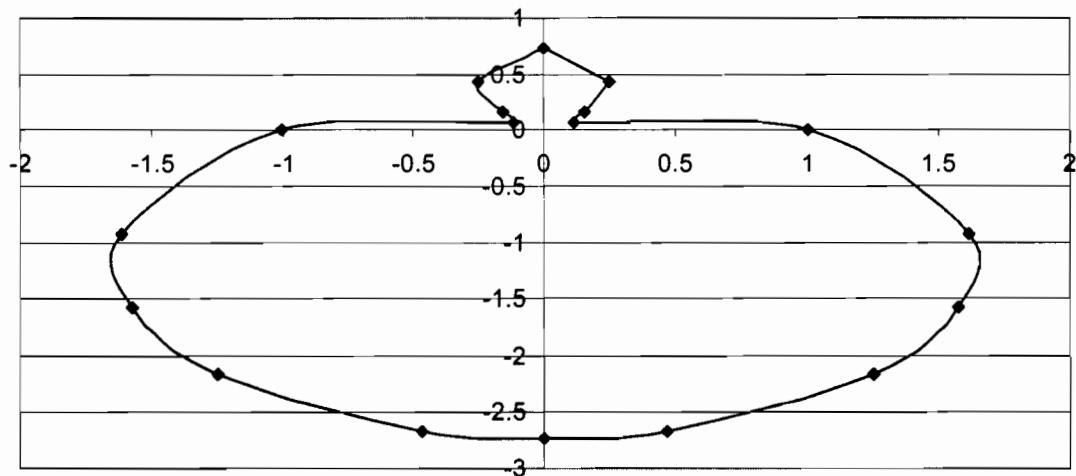


The other *sp* hybrid is

$$\psi_2(sp) = \frac{1}{\sqrt{2}} [Y(2s) - Y(2p)] \quad \psi_2(sp) = \frac{1}{\sqrt{2}} \left[ \left( \frac{1}{4\pi} \right)^{1/2} - \left( \frac{3}{4\pi} \right)^{1/2} \cos\theta \right]$$

$$\psi_2(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} [1 - \sqrt{3} \cos\theta]$$

Graphically,  $\Psi_2(sp)$  is generated as follows:



We now see that the second *sp* hybrid ( $\Psi_2(sp)$ ) points in a direction opposite to the first ( $\Psi_1(sp)$ )

- (b) Figure 12-10 pictorially shows the hybridization of a  $2s$  orbital and a  $2p$  (there is no mention of whether it is a  $2p_x$ ,  $2p_y$  or  $2p_z$  orbital). When one of the degenerate  $2p$ -orbitals and the  $2s$  orbital are hybridized, we expect that there should be no difference in shape or energy of the resulting  $sp$ -hybrid orbitals. The only difference between the  $2p_x$ ,  $2p_y$  and  $2p_z$  orbitals is the direction in which these atomic orbitals are oriented. Similarly, the only difference in the resulting hybrid orbitals should be their directional properties. Mathematically, we have shown (part (a)), that an  $sp_z$  hybrid orbital is proportional to  $1 - \sqrt{3}\cos\theta$ . Similar calculations for an  $sp_x$  hybrid orbital result in an analogous relationship, namely one proportional to  $1 - \sqrt{3}\sin\theta\cos\phi$ . (Note: in the  $xz$  plane,  $\phi = 90^\circ$ , therefore  $\cos\phi = 1$ ). In the  $xz$  plane, this expression simplifies to  $1 - \sqrt{3}\sin\theta$ . (Note:  $\sin\theta = \cos(90^\circ - \theta)$ ). These two relationships result in similar answers (i.e., same shape), the only difference being a shift by an expect  $90^\circ$ . Similar arguments can be made for an  $sp_y$  hybrid orbital expression.

- (c) The  $sp^2$  hybrids. To show the spatial distribution of the  $sp^2$  hybrids we will again use the angular functions only. Thus,

$$Y(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi \quad Y(s) = \left(\frac{1}{4\pi}\right)^{1/2}$$

Combining these functions

$$\psi_1(sp^2) = \frac{1}{\sqrt{3}}\psi(2s) + \frac{\sqrt{2}}{\sqrt{3}}\psi(2p_x) \quad \psi_1(sp^2) = \frac{1}{\sqrt{3}}\left(\frac{1}{4\pi}\right)^{1/2} + \frac{\sqrt{2}}{\sqrt{3}}\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$$

$$\psi_1(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} + \sqrt{2}\sin\theta\cos\phi \right]$$

In the  $xy$  plane  $\theta = 90^\circ$  so that the function becomes ( $\sin(90^\circ) = 1$ )

$$\psi_1(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} + \sqrt{2}\cos\phi \right]$$

We now evaluate the functional form of one of the other  $sp^2$  hybrids

$$Y(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi \quad \psi_2(sp^2) = \frac{1}{\sqrt{3}}\psi(2s) - \frac{1}{\sqrt{6}}\psi(2p_x) + \frac{1}{\sqrt{2}}\psi(2p_y)$$

$$\psi_2(sp^2) = \frac{1}{\sqrt{3}}\left(\frac{1}{4\pi}\right)^{1/2} - \frac{1}{\sqrt{6}}\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi + \frac{1}{\sqrt{2}}\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$$

$$\psi_2(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} \sqrt{3} \sin \theta \cos \phi + \frac{1}{\sqrt{2}} \sqrt{3} \sin \theta \sin \phi \right]$$

$$\psi_2(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \sin \theta \cos \phi + \frac{\sqrt{3}}{\sqrt{2}} \sin \theta \sin \phi \right]$$

Again in the xy plane we have

$$\psi_2(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cos \phi + \frac{\sqrt{3}}{\sqrt{2}} \sin \phi \right]$$

The third  $sp^2$  hybrid is

$$\psi_3(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \sin \theta \cos \phi - \frac{\sqrt{3}}{\sqrt{2}} \sin \theta \sin \phi \right]$$

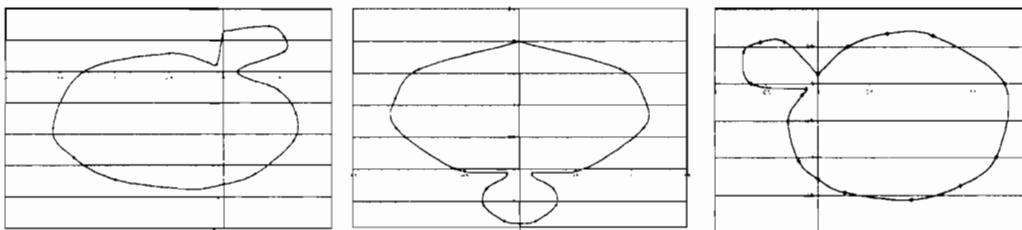
and in the xy plane

$$\psi_3(sp^2) = \left(\frac{1}{4\pi}\right)^{1/2} \left[ \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cos \phi - \frac{\sqrt{3}}{\sqrt{2}} \sin \phi \right]$$

We can evaluate these functions and obtain  $sp^2$  angular values:

Phi(deg)	Phi(rad)	$sp^2(1)$	$sp^2(2)$	$sp^2(3)$
0	0	1.992	-0.130	-0.647
30	0.5236	1.802	0.577	-0.837
45	0.7854	1.577	0.943	-0.789
60	1.0472	1.284	1.284	-0.647
90	1.5708	0.577	1.802	-0.130
120	2.0944	-0.123	1.992	0.577
135	2.3562	-0.423	1.943	0.943
150	2.6180	-0.647	1.802	1.284
170	2.9671	-0.815	1.486	1.661
180	3.1416	-0.837	1.284	1.802
190	3.3161	-0.815	1.061	1.906
210	3.6652	-0.647	0.577	1.992
225	3.9270	-0.423	0.211	1.943
240	4.1888	-0.130	-0.130	1.802
270	4.7124	0.577	-0.647	1.284
300	5.2360	1.284	-0.837	0.577
315	5.4978	1.577	-0.789	0.211
330	5.7596	1.802	-0.647	-0.130
360	6.2832	1.992	-0.130	-0.647

The graphs are as follows:



### Part (a) INCLUDING THE RADIAL PART

If we combine the angular and radial parts of the  $2s$  and  $2p$  orbitals the situation becomes more complicated as we have two variables to deal with. The angular and radial parts of the  $2s$  and  $2p$  orbitals are:

$$Y(s) = \left(\frac{1}{4\pi}\right)^{1/2} \quad R(2s) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2}$$

$$Y(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \quad R(2p) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}$$

Combining these

$$\psi(2s) = \left(\frac{1}{4\pi}\right)^{1/2} \times \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2}$$

$$\psi(2p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \times \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}$$

We now combine these to form the  $sp$ -hybrids

$$\psi_1(sp) = \frac{1}{\sqrt{2}} [\psi(2s) + \psi(2p)]$$

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left[ \left(\frac{1}{4\pi}\right)^{1/2} \times \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2} + \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \times \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \right]$$

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left[ \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2} + \sqrt{3} \times \cos\theta \times \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \right]$$

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \frac{1}{2\sqrt{2}} \left[ (2 - \sigma) e^{-\sigma/2} + \sqrt{3} \times \cos \theta \times \frac{1}{\sqrt{3}} \sigma e^{-\sigma/2} \right]$$

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \frac{e^{-\sigma/2}}{2\sqrt{2}} [(2 - \sigma) + \cos \theta \times \sigma]$$

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \frac{e^{-\sigma/2}}{2\sqrt{2}} [2 + \sigma(\cos \theta - 1)]$$

Similarly

$$\psi_2(sp) = \frac{1}{\sqrt{2}} [\psi(2s) - \psi(2p)]$$

$$\psi_2(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \frac{e^{-\sigma/2}}{2\sqrt{2}} [2 - \sigma(\cos \theta + 1)]$$

We are dealing with orbitals with  $n=2$ , so that

$$\sigma = \frac{2Zr}{na_0} = \frac{Zr}{a_0}$$

In order to proceed further we have to choose values of  $r$  and  $\theta$ , but how do we plot this? The way to do this is to evaluate the function for various values of  $(r/a_0)$  and  $\theta$  and plot points in the  $xz$  plane calculating the values of  $x$  and  $z$  from the polar coordinates

$$z = r \cos \theta \quad \text{and} \quad x = r \sin \theta \cos \phi$$

choosing  $\phi=0$  in the  $xz$  plane so that  $x = r \sin \theta$

Thus, we evaluate the probability as the square of the functions

$$\psi_1(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \frac{e^{-Zr/2a_0}}{2\sqrt{2}} \left[ 2 + \frac{Zr}{a_0} (\cos \theta - 1) \right]$$

$$\psi_2(sp) = \frac{1}{\sqrt{2}} \left( \frac{1}{4\pi} \right)^{1/2} \left( \frac{Z}{a_0} \right)^{3/2} \frac{e^{-Zr/2a_0}}{2\sqrt{2}} \left[ 2 - \frac{Zr}{a_0} (\cos \theta + 1) \right]$$

and plot the value of the function at the  $x,z$  coordinate and join points of equal value of the probability in the manner of a contour plot. The shape of the  $sp$  hybrid will then be revealed. Choose a value of  $Z$  (or  $Z_{\text{eff}}$ ) that is convenient.

This is suitable for a class team project using *Microsoft Excel*. A primitive spreadsheet is available upon request.

# CHAPTER 13

## LIQUIDS, SOLIDS, AND INTERMOLECULAR FORCES

### PRACTICE EXAMPLES

**1A**  $d = 0.701 \text{ g/L}$  at  $25^\circ\text{C}$  for  $\text{C}_6\text{H}_{14}$  (Molar Mass =  $86.177 \text{ g mol}^{-1}$ )

Consider a  $1.00 \text{ L}$  sample. This contains  $0.701 \text{ g C}_6\text{H}_{14}$

$$\text{Moles C}_6\text{H}_{14} \text{ in } 1.00 \text{ L sample} = 0.701 \text{ g C}_6\text{H}_{14} \times \frac{1 \text{ mol C}_6\text{H}_{14}}{86.177 \text{ g C}_6\text{H}_{14}} = 8.13 \times 10^{-3} \text{ mol C}_6\text{H}_{14}$$

$$\text{Find pressure using the ideal gas law: } P = \frac{nRT}{V} = \frac{(8.31 \times 10^{-3} \text{ mol})(\frac{0.08206 \text{ Latm}}{\text{Kmol}})(298\text{K})}{1.00 \text{ L}}$$

$$P = 0.199 \text{ atm}$$

$$P(\text{torr}) = 0.199 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 151 \text{ torr}$$

**1B** From Figure 13-9, the vapor pressure is  $\approx 420 \text{ mmHg}$  or  $420 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.55_3 \text{ atm}$

$$\text{Molar mass} = 74.123 \text{ g mol}^{-1}. P = \frac{nRT}{V} = \frac{\left(\frac{\text{mass}}{\text{molar mass}}\right)RT}{V} = \frac{(\text{density})RT}{\text{molar mass}}$$

$$\text{or } d = \frac{(\text{molar mass})P}{RT} = \frac{\left(\frac{74.123 \text{ g}}{\text{mol}}\right)(0.55_3 \text{ atm})}{\left(\frac{0.08206 \text{ Latm}}{\text{Kmol}}\right)(293\text{K})} = 1.70 \text{ g L}^{-1} \approx 1.7 \text{ g/L}$$

**2A** We first calculate pressure created by the water at  $80.0^\circ\text{C}$ , assuming all  $0.132 \text{ g H}_2\text{O}$  vaporizes.

$$P_2 = \frac{nRT}{V} = \frac{\left(0.132 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}\right) \times 0.08206 \frac{\text{Latm}}{\text{molK}} \times 353.2 \text{ K}}{0.525 \text{ L}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}}$$

$$P_2 = 307 \text{ mmHg}$$

At  $80.0^\circ\text{C}$ , the vapor pressure of water is  $355.1 \text{ mmHg}$ . Thus, all the water can exist as vapor at  $80.0^\circ\text{C}$ .

- 2B** The result of Example 13-2 is that 0.132 g H<sub>2</sub>O would exert a pressure of 281 mmHg if it all existed as a vapor. Since that 281 mmHg is greater than the vapor pressure of water at this temperature, some of the water must exist as liquid. The calculation of the example is based on the equation  $P = nRT/V$ , which means that the pressure of water is proportional to its mass. Thus, the mass of water needed to produce a pressure of 92.5 mmHg under this situation is

$$\text{mass of water vapor} = 92.5 \text{ mmHg} \times \frac{0.132 \text{ g H}_2\text{O}}{281 \text{ mmHg}} = 0.0435 \text{ g H}_2\text{O}$$

$$\text{mass of liquid water} = 0.132 \text{ g H}_2\text{O total} - 0.0435 \text{ g H}_2\text{O vapor} = 0.089 \text{ g liquid water}$$

- 3A** From Table 13-1 we know that  $\Delta H_{vap} = 38.0 \text{ kJ/mol}$  for methyl alcohol. We now can use the Clausius-Clapeyron equation to determine the vapor pressure at 25.0°C = 298.2 K.

$$\ln \frac{P}{100 \text{ mmHg}} = \frac{38.0 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{(273.2 + 21.2) \text{ K}} - \frac{1}{298.2 \text{ K}} \right) = +0.198$$

$$\frac{P}{100 \text{ mmHg}} = e^{+0.198} = 1.22 \quad P = 1.22 \times 100 \text{ mmHg} = 121 \text{ mmHg}$$

- 3B** The vapor pressure at the normal boiling point (99.2°C = 372.4 K) is 760 mmHg precisely. We can use the Clausius-Clapeyron equation to determine the vapor pressure at 25°C = 298 K.

$$\ln \frac{P}{760 \text{ mmHg}} = \frac{35.76 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{372.4 \text{ K}} - \frac{1}{298.2 \text{ K}} \right) = -2.874$$

$$\frac{P}{760 \text{ mmHg}} = e^{-2.874} = 0.0565 \quad P = 0.0565 \times 760 \text{ mmHg} = 42.9 \text{ mmHg}$$

- 4A** Moving from point R to P we begin with H<sub>2</sub>O(g) at high temperature (>100°C). When the temperature reaches the point on the vaporization curve, OC, water condenses at constant temperature (100°C). Once all of the water is in the liquid state, the temperature drops. When the temperature reaches the point on the fusion curve, OD, ice begins to form at constant temperature (0°C). Once all of the water has been converted to H<sub>2</sub>O(s), the temperature of the sample decreases slightly until point P is reached.

Since solids are not very compressible, very little change occurs until the pressure reaches the point on the fusion curve OD. Here, melting begins. A significant decrease in the volume occurs ( $\approx 10\%$ ) as ice is converted to liquid water. After melting, additional pressure produces very little change in volume because liquids are not very compressible.

**4B**

1.00 mol H<sub>2</sub>O. At Point R, T = 374.1 °C or 647.3 K

$$V_{\text{point R}} = \frac{nRT}{P} = \frac{(1.00 \text{ mol}) \left( 0.08206 \frac{\text{L atm}}{\text{K mol}} \right) (647.3 \text{ K})}{1.00 \text{ atm}} = 53.1 \text{ L}$$

51.3 L  
At  
Point  
R

1.00 mol H<sub>2</sub>O on P-R line, if 1/2 of water is vaporized, T = 100 °C (273.015 K)

$$V_{1/2 \text{ vap(P-R)}} = \frac{nRT}{P} = \frac{(0.500 \text{ mol}) \left( 0.08206 \frac{\text{L atm}}{\text{K mol}} \right) (273.015 \text{ K})}{1.00 \text{ atm}} = 15.3 \text{ L}$$

15.3 L  
at 100°C  
1/2 vap

A much smaller volume results when just 1/2 of the sample is vaporized (moles of gas smaller as well, temperature is smaller). 53.1 L vs 15.3 L (about 28.8 % of the volume as that seen at point R).

**5A**

The substance with the highest boiling point will have the strongest intermolecular forces. The weakest of van der Waals forces are London forces, which depend on molar mass (and surface area): C<sub>3</sub>H<sub>8</sub> is 44 g/mol, CO<sub>2</sub> is 44 g/mol, and CH<sub>3</sub>CN is 41 g/mol. Thus, the London forces are approximately equal for these three compounds. Next to consider are dipole-dipole forces. C<sub>3</sub>H<sub>8</sub> is nonpolar; its bonds are not polar bonds. CO<sub>2</sub> is nonpolar; its two bond moments cancel each other. CH<sub>3</sub>CN is polar and thus has the strongest intermolecular forces and should have the highest boiling point. Boiling points are -78.44°C for CO<sub>2</sub>, -42.1°C for C<sub>3</sub>H<sub>8</sub>, and 81.6°C for CH<sub>3</sub>CN.

**5B**

Dispersion forces, which depend on molar mass and structure, are one of the determinants of boiling point. The molar masses are: C<sub>8</sub>H<sub>18</sub> (114.2 g/mol), CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (58.1 g/mol), (CH<sub>3</sub>)<sub>3</sub>CH (58.1 g/mol), C<sub>6</sub>H<sub>5</sub>CHO (106.1 g/mol), and SO<sub>3</sub> (80.1 g/mol). We would expect (CH<sub>3</sub>)<sub>3</sub>CH to have the lowest boiling point because it has the lowest molar mass and the most compact (ball-like) shape, whereas CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, which has the same mass, but is longer (and so has more chances for intermolecular interactions), should have the second highest boiling point. Then should follow polar SO<sub>3</sub>. C<sub>6</sub>H<sub>5</sub>CHO should have a boiling point higher than the more massive C<sub>8</sub>H<sub>18</sub> because benzaldehyde is polar while octane is not. Actual boiling points are given in parentheses in the following ranking. (CH<sub>3</sub>)<sub>3</sub>CH (-11.6°C) < CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (-0.5°C) < SO<sub>3</sub> (44.8°C) < C<sub>8</sub>H<sub>18</sub> (125.7°C) < C<sub>6</sub>H<sub>5</sub>CHO (178°C)

**6A**

We first look to molar masses: Ne (20.2 g/mol), He (4.0 g/mol), Cl<sub>2</sub> (70.9 g/mol), (CH<sub>3</sub>)<sub>2</sub>CO (58.1 g/mol), O<sub>2</sub> (32.0 g/mol), and O<sub>3</sub> (48.0 g/mol). Both (CH<sub>3</sub>)<sub>2</sub>CO and O<sub>3</sub> are polar, O<sub>3</sub> weakly so (because of its uneven distribution of electrons). We expect (CH<sub>3</sub>)<sub>2</sub>CO to be the highest boiling, followed by Cl<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub>, Ne, and He. In the following ranking, actual boiling points are given in parentheses. He (-268.9 °C), Ne (-245.9 °C), O<sub>2</sub> (-183.0 °C), O<sub>3</sub> (-111.9 °C), Cl<sub>2</sub> (-34.6 °C), and (CH<sub>3</sub>)<sub>2</sub>CO (56.2°C)

- 6B** The magnitude of the enthalpy of vaporization is strongly related to the strength of intermolecular forces: the stronger those forces are, the more endothermic the vaporization process. The first three substances all are nonpolar and, therefore, their only intermolecular forces are London forces, whose strength primarily depends on molar mass. The substances are arranged in order of increasing molar mass:  $\text{H}_2 = 2.0 \text{ g/mol}$ ,  $\text{CH}_4 = 16.0 \text{ g/mol}$ ,  $\text{C}_6\text{H}_6 = 78.1 \text{ g/mol}$ , and also in order of increasing heat of vaporization. The last substance has a molar mass of 61.0 g/mol, which would produce intermolecular forces smaller than those of  $\text{C}_6\text{H}_6$  if  $\text{CH}_3\text{NO}_2$  were nonpolar. But the molecule is definitely polar. Dipole-dipole forces are strong enough that the intermolecular forces are stronger and the enthalpy of vaporization is larger for  $\text{CH}_3\text{NO}_2$  than for  $\text{C}_6\text{H}_6$ .
- 7A** Strong interionic forces lead to high melting points. Strong interionic forces are created by ions with high charge and of small size. Thus, a compound with a lower melting point than KI would have ions of larger size, such as RbI or CsI. A compound with a melting point higher than CaO would have either smaller ions, such as MgO, or more highly charged ions, such as  $\text{Ga}_2\text{O}_3$  or  $\text{Ca}_3\text{N}_2$ , or both, such as AlN or  $\text{Mg}_3\text{N}_2$ .
- 7B**  $\text{Mg}^{2+}$  has a higher charge and a smaller size than does  $\text{Na}^+$ . In addition,  $\text{Cl}^-$  has a smaller size than  $\text{I}^-$ . Thus, interionic forces should be stronger in  $\text{MgCl}_2$  than in NaI. We expect  $\text{MgCl}_2$  to have lower solubility and, in fact, 12.3 mol (1840 g) of NaI dissolves in a liter of water, compared to just 5.7 mol (543 g) of  $\text{MgCl}_2$ , confirming our prediction.
- 8A** The length ( $l$ ) of a bcc unit cell and the radius ( $r$ ) of the atom involved are related as  $4r = l\sqrt{3}$ . For potassium,  $r = 227 \text{ pm}$ . Then  $l = 4 \times 227 \text{ pm} / \sqrt{3} = 524 \text{ pm}$
- 8B** Consider just the face of Figure 13.42c. Note that it is composed of one atom at each of four corners and one in the center. The four corner atoms touch the atom in the center, but not each other. Thus, the atoms are in contact across the diagonal of the face. If each atomic radius is designated  $r$ , then the length of the diagonal is  $4r$  ( $= r$  for one corner atom +  $2r$  for the center atom +  $r$  for the other corner atom). The diagonal also is related to the length of a side,  $l$ , by the Pythagorean theorem:  $d^2 = l^2 + l^2 = 2l^2$  or  $d = \sqrt{2}l$ . We have two quantities equal to the diagonal, and thus to each other.

$$\sqrt{2}l = \text{diagonal} = 4r = 4 \times 143.1 \text{ pm} = 572.4 \text{ pm}$$

$$l = \frac{572.4}{\sqrt{2}} = 404.7 \text{ pm}$$

The cubic unit cell volume,  $V$ , is equal to the cube of one side.

$$V = l^3 = (404.7 \text{ pm})^3 = 6.628 \times 10^7 \text{ pm}^3$$

- 9A** In a bcc unit cell, there are eight corner atoms, of which  $\frac{1}{8}$  of each is apportioned to the unit cell. There is also one atom in the center. The total number of atoms per unit cell is:

$$= 1 \text{ center} + 8 \text{ corners} \times \frac{1}{8} = 2 \text{ atoms. The density, in g/cm}^3, \text{ for this cubic cell:}$$

$$\text{density} = \frac{2 \text{ atoms}}{(524 \text{ pm})^3} \times \left( \frac{10^{12} \text{ pm}}{10^2 \text{ cm}} \right)^3 \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{39.10 \text{ g K}}{1 \text{ mol K}} = 0.903 \text{ g/cm}^3$$

The tabulated density of potassium at 20°C is 0.86 g/cm<sup>3</sup>.

- 9B** In a fcc unit cell the number of atoms is computed as 1/8 atom for each of the eight corner atoms (since each is shared among eight unit cells) plus 1/2 atom for each of the six face atoms (since each is shared between two unit cells). This gives the total number of atoms per unit cell as: atoms/unit cell = (1/8 corner atom × 8 corner atoms/unit cell) + (1/2 face atom × 6 face atoms/unit cell) = 4 atoms/unit cell

Now we can determine the mass per Al atom, and a value for the Avogadro constant.

$$\frac{\text{mass}}{\text{Al atom}} = \frac{2.6984 \text{ g Al}}{1 \text{ cm}^3} \times \left( \frac{100 \text{ cm}}{1 \text{ m}} \times \frac{1 \text{ m}}{10^{12} \text{ pm}} \right)^3 \times \frac{6.628 \times 10^7 \text{ pm}^3}{1 \text{ unit cell}} \times \frac{1 \text{ unit cell}}{4 \text{ Al atoms}}$$

$$= 4.471 \times 10^{-23} \text{ g/Al atom}$$

$$N_A = \frac{26.9815 \text{ g Al}}{1 \text{ mol Al}} \times \frac{1 \text{ Al atom}}{4.471 \times 10^{-23} \text{ g Al}} = 6.035 \times 10^{23} \frac{\text{atoms}}{\text{mol}}$$

- 10A** Across the diagonal of a CsCl unit cell are Cs<sup>+</sup> and Cl<sup>-</sup> ions, so that the body diagonal equals  $2r(\text{Cs}^+) + 2r(\text{Cl}^-)$ . This body diagonal equals  $\sqrt{3}l$ , where  $l$  is the length of the unit cell.

$$l = \frac{2r(\text{Cs}^+) + 2r(\text{Cl}^-)}{\sqrt{3}} = \frac{2(167 + 181) \text{ pm}}{\sqrt{3}} = 402 \text{ pm}$$

- 10B** Since NaCl is fcc, the Na<sup>+</sup> ions are in the same locations as were the Al atoms in Practice Example 13-9B, and there are 4 Na<sup>+</sup> ions per unit cell. For stoichiometric reasons, there must also be 4 Cl<sup>-</sup> ions per unit cell. These are accounted for as follows: There is one Cl<sup>-</sup> along each edge, and each of these edge Cl<sup>-</sup> ions are shared among four unit cells and there is one Cl<sup>-</sup> precisely in the body center of the unit cell, not shared with any other unit cells. Thus, the number of Cl<sup>-</sup> ions is given by: Cl<sup>-</sup> ions/unit cell = (1/4 Cl<sup>-</sup> on edge × 12 edges per unit cell) + 1 Cl<sup>-</sup> in body center = 4 Cl<sup>-</sup>/unit cell.

The volume of this cubic unit cell is the cube of its length. The density is:

$$\text{NaCl density} = \frac{4 \text{ formula units}}{1 \text{ unit cell}} \times \frac{1 \text{ unit cell}}{(560 \text{ pm})^3} \times \left( \frac{10^{12} \text{ pm}}{1 \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \times \frac{1 \text{ mol NaCl}}{6.022 \times 10^{23} \text{ f.u.}}$$

$$\times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} = 2.21 \text{ g/cm}^3$$

<b>11A</b>	Sublimation of Cs(g):	$\text{Cs(s)} \rightarrow \text{Cs(g)}$	$\Delta H_{sub} = +78.2 \text{ kJ/mol}$
	Ionization of Cs(g):	$\text{Cs(g)} \rightarrow \text{Cs}^+(g) + e^-$	$\Delta I_1 = +375.7 \text{ kJ/mol}$ (Table 10.3)
	$\frac{1}{2}$ Dissociation of Cl <sub>2</sub> (g):	$\frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Cl(g)}$	$\text{DE} = \frac{1}{2} \times 243 = 121.5 \text{ kJ/mol}$ (Table 11.3)
	Cl(g) electron affinity:	$\text{Cl(g)} + e^- \rightarrow \text{Cl}^-(g)$	$\text{EA}_1 = -349.0 \text{ kJ/mol}$ (Figure 10-10)
	Lattice energy:	$\text{Cs}^+(g) + \text{Cl}^-(g) \rightarrow \text{CsCl(s)}$	L.E.
<hr/>			
	Enthalpy of formation:	$\text{Cs(s)} + \frac{1}{2} \text{Cl}_2(s) \rightarrow \text{CsCl(s)}$	$\Delta H_f^\circ = -442.8 \text{ kJ/mol}$
		$-442.8 \text{ kJ/mol} = +78.2 \text{ kJ/mol} + 375.7 \text{ kJ/mol} + 121.5 \text{ kJ/mol} - 349.0 \text{ kJ/mol} + \text{L.E.}$	
		$= +226.4 \text{ kJ/mol} + \text{L.E.}$	
		$\text{L.E.} = -442.8 \text{ kJ} - 226.4 \text{ kJ} = -669.2 \text{ kJ/mol}$	
<b>11B</b>	Sublimation:	$\text{Ca(s)} \rightarrow \text{Ca(g)}$	$\Delta H_{sub} = +178.2 \text{ kJ/mol}$
	First ionization energy:	$\text{Ca(g)} \rightarrow \text{Ca}^+(g) + e^-$	$I_1 = +590 \text{ kJ/mol}$
	Second ionization energy:	$\text{Ca}^+(g) \rightarrow \text{Ca}^{2+}(g) + e^-$	$I_2 = +1145 \text{ kJ/mol}$
	Dissociation energy:	$\text{Cl}_2(g) \rightarrow 2\text{Cl(g)}$	$\text{D.E.} = (2 \times 122) \text{ kJ/mol}$
	Electron Affinity:	$2\text{Cl(g)} + 2e^- \rightarrow 2\text{Cl}^-(g)$	$2 \times \text{E.A.} = 2(-349) \text{ kJ/mol}$
	Lattice energy:	$\text{Ca}^{2+}(g) + 2\text{Cl}^-(g) \rightarrow \text{CaCl}_2(s)$	$\text{L.E.} = -2223 \text{ kJ/mol}$
<hr/>			
	Enthalpy of formation:	$\text{Ca(s)} + \text{Cl}_2(s) \rightarrow \text{CaCl}_2(s)$	$\Delta H_f^\circ = ?$
		$\Delta H_f^\circ = \Delta H_{sub} + I_1 + I_2 + \text{D.E.} + (2 \times \text{E.A.}) + \text{L.E.}$	
		$= 178.2 \text{ kJ/mol} + 590 \text{ kJ/mol} + 1145 \text{ kJ/mol} + 244 \text{ kJ/mol} - 698 \text{ kJ/mol} - 2223 \text{ kJ/mol}$	
		$= -764 \text{ kJ/mol}$	

## REVIEW QUESTIONS

- $\Delta H_{vap}$  symbolizes the molar enthalpy of vaporization, the quantity of heat needed to convert one mole of a substance from liquid to vapor.
  - $T_c$  symbolizes the critical temperature, that temperature above which a gas cannot be condensed to a liquid, no matter how high the applied pressure.
  - An instantaneous dipole is a momentary imbalance of the positive and negative charges in an atom or a molecule, caused when the electron cloud moves off center in a random manner.
  - Coordination number refers to the number of atoms of one type surrounding another atom at the same distance, often those touching the central atom.
  - A unit cell is the smallest portion of a crystal that will replicate the crystal through simple translations.

2. (a) Capillary Action: A liquid with strong adhesive forces with the glass in tubes of small diameter rises noticeably higher inside the capillary tube than the liquid level outside of the tube. Inversely proportional to the diameter of the tube and proportional to the surface tension (simplest test for  $\gamma$ ).
- (b) Polymorphism: Existence of a solid substance in more than one form (i.e., ice I, ice II, ice III, ...)
- (c) Sublimation is the physical change in which a substance is converted directly from a solid to a vapor.
- (d) Supercooling refers to the cooling of a liquid below its freezing point without the formation of any solid. The supercooled liquid is in a metastable state.
- (e) The freezing point of a liquid is the point on the cooling curve of a liquid where the temperature remains constant while heat is withdrawn from the sample. During that period, solid forms as liquid freezes.
3. (a) Adhesive forces are those between different types of substances, usually forces between two condensed phases. Cohesive forces are those within a substance, again usually referring to liquids or solids.
- (b) Vaporization is the physical process of transforming a liquid into a vapor. Condensation is the reverse process, namely, converting a vapor to liquid.
- (c) A triple point of a substance is the point where three phases coexist, often solid, liquid, and vapor. The critical point is that temperature and pressure above which liquid and vapor cannot be distinguished; just a fluid exists, called a supercritical fluid.
- (d) Face-centered and body-centered cubic unit cells both have atoms at the vertices of a cube. In a face-centered unit cell there also is an atom on the center of each of the six faces of the cube. In contrast, in a body-centered cubic unit cell there is an atom exactly in the center of the three-dimensional cubic cell.
- (e) A tetrahedral hole is one surrounded by four atoms at the vertices of a tetrahedron. An octahedral hole is surrounded by six atoms: above and below, in front and behind, and to the right and the left.
4. *Instantaneous dipole-induced dipole* forces occur after a chance distortion of the electron cloud of an atom or molecule creates an instantaneous imbalance of charge in that particle: an instantaneous dipole. This imbalance creates a similar imbalance in an adjacent particle: an induced dipole. The two dipoles reinforce each other and can induce dipoles in other nearby particles. The dipoles thus created attract each other and hold the particles together. *Dipole-dipole forces* exist between molecules that have permanent resultant dipole moments, which attract each other and hold these molecules together. *Hydrogen bonds* result from the attraction between a highly electronegative atom, usually N, O, or F, and a hydrogen atom bonded to another highly electronegative atom. *Relative strengths* of these forces are hydrogen bonds > dipole-dipole forces > instantaneous dipole-induced dipole forces. Each force in the preceding ordering is approximately ten times stronger than the one that follows it.

5. (a/ b) It is possible for a substance not to have a normal melting point or a normal boiling point. Since normal is defined as the boiling point at 760 mmHg, if the solid-liquid-vapor triple point occurs at a pressure higher than 1 atm, for instance, then melting and vaporization must occur at pressures greater than 1 atm. In such a case, however, there will be a normal sublimation point.
- (c) Every substance should have a critical point. There should always be a temperature above which molecules are moving so rapidly that forces of attraction between them are ineffective in producing a condensed phase.
6. One would expect the enthalpy of sublimation (d) to be the largest of the four quantities cited. Molar heat capacities are quite small, on the order of fractions of a kilojoule per mole-degree. (Remember that specific heats have values of joules per gram-degree.) All of the heats of transition (or latent heats) are positive numbers and on the order of kilojoules per mole. Since the heat of sublimation is the sum of the heat of fusion and the heat of vaporization,  $\Delta H_{subl}$  must be the largest of the three.
7. (a) Intermolecular forces in a liquid *do* affect its vapor pressure. The stronger these forces are, the more difficult it is for molecules to vaporize and the lower the vapor pressure is at a given temperature.
- (b) The volume of liquid present *does not* affect its vapor pressure. Vaporization occurs at the surface of the liquid and thus volume of liquid is of no consequence.
- (c) The volume of vapor present also *does not* affect the vapor pressure of a liquid, for similar reasons to those given in part (b).
- (d) The size of the container also *does not* affect a liquid's vapor pressure, again following the reasoning in part (b). Of course, both liquid and vapor must be present at the point of equilibrium.
- (e) The temperature of the liquid *does* affect that liquid's vapor pressure. Higher temperature means that more energy is present per molecule, each molecule has a larger fraction of the energy needed to overcome cohesive forces, and thus it is more likely that it will be able to overcome those cohesive forces and vaporize.
8. (a) mass CHCl<sub>3</sub> vaporized =  $6.62 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ g CHCl}_3}{247 \text{ J}} = 26.8 \text{ g CHCl}_3$
- (b)  $\Delta H_{vap} = \frac{247 \text{ J}}{1 \text{ g CHCl}_3} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{119.38 \text{ g CHCl}_3}{1 \text{ mol CHCl}_3} = 29.5 \text{ kJ/mol chloroform}$
- (c) heat evolved =  $19.6 \text{ g CHCl}_3 \times \frac{247 \text{ J}}{1 \text{ g CHCl}_3} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 4.84 \text{ kJ}$  or  $\Delta H = -4.84 \text{ kJ}$ .
9. (a) We read up the 100°C line until we arrive at C<sub>6</sub>H<sub>7</sub>N curve (e). This occurs at about 45 mmHg.
- (b) We read across the 760 mmHg line until we arrive at the C<sub>7</sub>H<sub>8</sub> curve (d). This occurs at about 110°C.

10. (a) The normal boiling point occurs where the vapor pressure is 760 mmHg, and thus  $\ln P = 6.63$ . For aniline, this occurs at about the uppermost data point (open circle) on the aniline line. This corresponds to  $1/T = 2.18 \times 10^{-3} \text{ K}^{-1}$ . Thus,

$$T_{nbp} = \frac{1}{2.18 \times 10^{-3} \text{ K}^{-1}} = 459 \text{ K}.$$

- (b)  $25^\circ \text{ C} = 298 \text{ K} = T$  and thus  $1/T = 3.36 \times 10^{-3} \text{ K}^{-1}$ . This occurs at about  $\ln P = 6.25$ . Thus,  $P = e^{6.25} = 518 \text{ mmHg}$ .

11. Use the ideal gas equation,  $n = \text{moles Br}_2 = 0.486 \text{ g Br}_2 \times \frac{1 \text{ mol Br}_2}{159.8 \text{ g Br}_2} = 3.04 \times 10^{-3} \text{ mol Br}_2$ .

$$P = \frac{nRT}{V} = \frac{3.04 \times 10^{-3} \text{ mol Br}_2 \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}}{0.2500 \text{ L}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} \\ = 226 \text{ mmHg}$$

12. We use the Clausius-Clapeyron equation (13.2).

$$T_1 = (56.0 + 273.2) \text{ K} = 329.2 \text{ K} \quad T_2 = (103.7 + 273.2) \text{ K} = 376.9 \text{ K}$$

$$\ln \frac{10.0 \text{ mmHg}}{100.0 \text{ mmHg}} = \frac{\Delta H_{vap}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{376.9 \text{ K}} - \frac{1}{329.2 \text{ K}} \right) = -2.30 = -4.624 \times 10^{-5} \Delta H_{vap}$$

$$\Delta H_{vap} = 4.97 \times 10^4 \text{ J/mol} = 49.7 \text{ kJ/mol}$$

13. We use the Clausius-Clapeyron equation (13.2).  $T_1 = (5.0 + 273.2) \text{ K} = 278.2 \text{ K}$

$$\ln \frac{760.0 \text{ mmHg}}{40.0 \text{ mmHg}} = 2.944 = \frac{38.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{278.2 \text{ K}} - \frac{1}{T_{nbp}} \right)$$

$$\left( \frac{1}{278.2 \text{ K}} - \frac{1}{T_{nbp}} \right) = 2.944 \times \frac{8.3145 \text{ K}^{-1}}{38.0 \times 10^3} = 6.44 \times 10^{-4} \text{ K}^{-1}$$

$$\frac{1}{T_{nbp}} = \frac{1}{278.2 \text{ K}} - 6.44 \times 10^{-4} \text{ K}^{-1} = 2.95 \times 10^{-3} \text{ K}^{-1} \quad T_{nbp} = 339 \text{ K}$$

14. heat needed =  $(5.08 \text{ cm})^3 \times \frac{0.92 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol}}{18.0 \text{ g}} \times \frac{6.01 \text{ kJ}}{1 \text{ mol}} = 40 \text{ kJ}$

15. (a) heat evolved =  $3.78 \text{ kg Cu} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{13.05 \text{ kJ}}{1 \text{ mol Cu}} = 776 \text{ kJ}$  evolved or  
 $\Delta H = -776 \text{ kJ}$

- (b) heat absorbed =  $(75 \text{ cm} \times 15 \text{ cm} \times 12 \text{ cm}) \times \frac{8.92 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{13.05 \text{ kJ}}{1 \text{ mol Cu}} = 2.5 \times 10^4 \text{ kJ}$

16. Let us use the ideal gas law to determine the final pressure in the container, assuming that all of the dry ice vaporizes. We then locate this pressure, at a temperature of  $25^\circ\text{ C}$ , on the phase diagram of Figure 13-19.

$$P = \frac{nRT}{V} = \frac{\left(80.0\text{ g CO}_2 \times \frac{1\text{ mol CO}_2}{44.0\text{ g CO}_2}\right) \times 0.08206 \frac{\text{Latm}}{\text{mol K}} \times 298\text{ K}}{0.500\text{ L}} = 88.9\text{ atm}$$

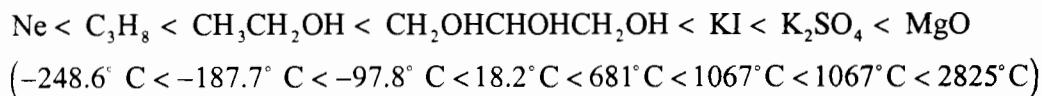
Although this point ( $25^\circ\text{ C}$  and  $88.9\text{ atm}$ ) is most likely in the region labeled “liquid” in Figure 13-19, we computed its pressure assuming the  $\text{CO}_2$  is a gas. Some of this gas should condense to a liquid. Thus, both liquid and gas are present in the container.

17. (After each formula is that substance’s boiling point)

- (a)  $\text{C}_{10}\text{H}_{22}$  ( $174.1^\circ\text{ C}$ ) has a higher boiling point than  $\text{C}_7\text{H}_{16}$  ( $98.4^\circ\text{ C}$ ). All else being equal, the substance with the higher molar mass has the higher boiling point.
- (b)  $\text{CH}_3\text{OCH}_3$  ( $M = 46.0\text{ g/mol}$ ) ( $-25^\circ\text{ C}$ ) has a higher boiling point than  $\text{C}_3\text{H}_8$  ( $M = 44.0\text{ g/mol}$ ) ( $-42.1^\circ\text{ C}$ ). For two substances with nearly the same molar masses, the polar substance has a higher boiling point than the nonpolar substance.
- (c)  $\text{CH}_3\text{CH}_2\text{OH}$  ( $M = 46.0\text{ g/mol}$ ) has a higher boiling point than  $\text{CH}_3\text{CH}_2\text{SH}$  ( $M = 62.1\text{ g/mol}$ ). Even though  $\text{CH}_3\text{CH}_2\text{SH}$  ( $35^\circ\text{ C}$ ) is the heavier molecule, hydrogen bonds form between  $\text{CH}_3\text{CH}_2\text{OH}$  ( $78.5^\circ\text{ C}$ ) molecules, requiring more energy to vaporize them.

18. All of these substances are homonuclear molecules, composed of the same type of atoms. Thus, boiling point should increase with increasing molar mass:  $\text{N}_2$  ( $M = 28.0\text{ g/mol}$ ),  $\text{O}_3$  ( $M = 48.0\text{ g/mol}$ ),  $\text{F}_2$  ( $M = 38.0\text{ g/mol}$ ),  $\text{Ar}$  ( $M = 39.9\text{ g/mol}$ ), and  $\text{Cl}_2$  ( $M = 70.9\text{ g/mol}$ ). Thus,  $\text{O}_3$  is seen to be out of order. The correct order is:
- $$\text{N}_2(-195.8^\circ\text{ C}) < \text{F}_2(-188.1^\circ\text{ C}) < \text{Ar}(-185.7^\circ\text{ C}) < \text{O}_3(-111.9^\circ\text{ C}) < \text{Cl}_2(-34.6^\circ\text{ C})$$

19. Both  $\text{Ne}$  and  $\text{C}_3\text{H}_8$  are nonpolar; their solids are held together by relatively weak London forces, which are stronger for substances with higher molecular masses (or larger surface areas).  $\text{Ne}$  has a lower melting point than  $\text{C}_3\text{H}_8$ . Next in melting are  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ , which are held together with hydrogen bonds in addition to London forces. There are more hydrogen bonds possible for a molecule of  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$  than for one of  $\text{CH}_3\text{CH}_2\text{OH}$ , and  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$  molecules are heavier;  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$  has the higher melting point.  $\text{KI}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MgO}$  are ionic solids and have the highest melting points. For ionic solids the melting point is high for small, highly charged ions. Thus,  $\text{MgO}$  has the highest melting point of these three,  $\text{KI}$  the lowest. Arranged in order of increasing melting point, the seven substances are as follows:



20. The polarity of hydrazine (34.0 g/mol) might explain its high boiling point. But HCl (36.5 g/mol) also is polar, and it is a gas at room temperature. The distinction between the two substances is that hydrazine can form strong hydrogen bonds, while HCl cannot. This raises the boiling point of hydrazine significantly above that of HCl ( $-114.18^\circ \text{ C}$ ).
21. (a) Si(s) is a network covalent solid. Its structure is similar to that of diamond; both elements are in the same family of the periodic table.
- (b)  $\text{SiCl}_4(s)$  is a molecular solid.  $\text{SiCl}_4$  exists as discrete nonpolar molecules. The molecules are attracted to each other by London forces.
- (c)  $\text{CaCl}_2(s)$  is an ionic solid. Calcium chloride consists of  $\text{Ca}^{2+}$  cations and  $\text{Cl}^-$  anions.
- (d) Ag(s) is a metallic solid. Silver is one of the metals in the periodic table.
- (e)  $\text{SO}_2(s)$  will form a molecular solid.  $\text{SO}_2$  exists as discrete polar molecules. The molecules are attracted to each other by London forces and dipole-dipole attractions.
22. Answer (c) is correct; atoms at the corners, along the edges, and on the faces of a unit cell are shared with adjacent unit cells. (a) is incorrect; often there are several formula units within a unit cell, as in the case for NaCl. (b) is incorrect; the unit cell need not be cubic; that of hexagonal close packing is not. (d) is incorrect; a unit cell will not contain the same number of cations as anions if their numbers are not equal in the formula of the compound.
23. In the unit cell of Figure 13-49, there is one  $\text{Cs}^+$  ion completely contained within the unit cell. There are eight “corner”  $\text{Cl}^-$  ions, each shared by eight other unit cells. Thus, the number of  $\text{Cl}^-$  ions =  $(8 \times 1/8) = 1$   $\text{Cl}^-$  ions. Thus, the “formula of cesium chloride” is  $\text{CsCl}$ .
24. (a) The atoms touch along the face diagonal,  $d$ . The length of that diagonal thus is  $4r$  ( $r$  from one corner atom,  $+2r$  from the center atom,  $+r$  from the other corner atom). The Pythagorean theorem relates the length of the unit cell,  $l$ , to the face diagonal:  $d^2 = l^2 + l^2$  (the cell is square; both sides are equal) or  $d = \sqrt{2}l$ . Two quantities equal to the face diagonal are equal to each other:  $d = \sqrt{2}l = 4r = 4 \times 128 \text{ pm}$
- $$l = \frac{4 \times 128 \text{ pm}}{1.414} = 362 \text{ pm}$$
- (b) The volume of the unit cell is that of a cube:  $V = l^3 = (362 \text{ pm})^3 = 4.74 \times 10^7 \text{ pm}^3$ .
- (c) In a face-centered unit cell, there are eight “corner” Cu atoms, each shared by eight unit cells; there are six “face” Cu atoms, each shared by two unit cells.

$$\text{No. Cu atoms} = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4 \text{ Cu atoms.}$$

$$(d) \text{ Volume of 4 Cu atoms} = 4 \left( \frac{4}{3} \pi r^3 \right) = 4 \left( \frac{4}{3} \pi (128 \text{ pm})^3 \right) = 3.51 \times 10^7 \text{ pm}^3$$

$$\text{Percentage of unit cell occupied by Cu} = \frac{3.51 \times 10^7 \text{ pm}^3}{4.74 \times 10^7 \text{ pm}^3} \times 100\% = 74.1\%$$

- (e) The mass of 4 Cu atoms is determined from the atomic mass.

$$\frac{\text{mass}}{\text{unit cell}} = \frac{4 \text{ Cu atoms}}{\text{unit cell}} \times \frac{1 \text{ mol Cu atoms}}{6.022 \times 10^{23} \text{ Cu atoms}} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu atoms}} = \frac{4.221 \times 10^{-22} \text{ g Cu}}{1 \text{ unit cell}}$$

$$(f) \text{ density} = \frac{\text{mass}}{\text{volume}} = \frac{4.221 \times 10^{-21} \text{ g}}{4.74 \times 10^7 \text{ pm}^3} \times \left( \frac{10^{12} \text{ pm}}{1 \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} \right)^3 = 8.91 \text{ g/cm}^3$$

## EXERCISES

### Surface Tension; Viscosity

- 25.** Since both the silicone oil and the cloth or leather are composed of relatively nonpolar molecules, they attract each other. The oil thus adheres well to the material. Water, on the other hand is polar and adheres very poorly to the silicone oil (actually, the water is repelled by the oil), much more poorly, in fact, than it adheres to the cloth or leather. This is because the oil is more nonpolar than is the cloth or the leather. Thus, water is repelled from the silicone-treated cloth or leather.
- 27.** (a) Molasses, like honey, is a very viscous liquid (high resistance to flow)  
 (b) Temperatures in January (Northern Hemisphere) are generally at their lowest point during the year  
 (c) Viscosity generally increases as the temperature decreases. Hence, molasses at low temperature is a very slow flowing liquid - there is indeed a scientific basis for "slower than molasses" in January.

### Vaporization

- 29.** The process of evaporation is an endothermic one; it requires energy. If evaporation occurs from an uninsulated container, this energy is obtained from the surroundings, through the walls of the container. However, if the evaporation occurs from an insulated container, the only source of the needed energy is the liquid that is evaporating. Therefore, the temperature of the liquid decreases.

31. We use the quantity of heat to determine the number of moles of benzene that vaporize.

$$V = \frac{nRT}{P} = \frac{\left(1.54 \text{ kJ} \times \frac{1 \text{ mol}}{33.9 \text{ kJ}}\right) \times 0.08206 \frac{\text{Latm}}{\text{mol K}} \times 298 \text{ K}}{95.1 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 8.88 \text{ L C}_6\text{H}_6(\text{l})$$

33. 25.00 mL of  $\text{N}_2\text{H}_4$  ( $25^\circ\text{C}$ ) density( $25^\circ\text{C}$ ) =  $1.0036 \text{ g mL}^{-1}$  (Molar mass =  $32.0452 \text{ g mol}^{-1}$ )  
Mass of  $\text{N}_2\text{H}_4$  = (volume)(density) =  $(25.00 \text{ mL})(1.0036 \text{ g mL}^{-1}) = 25.09 \text{ g N}_2\text{H}_4$

$$n_{\text{N}_2\text{H}_4} = 25.09 \text{ g N}_2\text{H}_4 \times \frac{1 \text{ mol N}_2\text{H}_4}{32.0452 \text{ g N}_2\text{H}_4} = 0.7830 \text{ mol}$$

Energy required to increase temperature from  $25.0^\circ\text{C}$  to  $113.5^\circ\text{C}$  ( $\Delta t = 88.5^\circ\text{C}$ )

$$q_{\text{heating}} = (n)(C)(\Delta t) = (0.78295 \text{ mol N}_2\text{H}_4) \left( \frac{98.84 \text{ J}}{1 \text{ mol N}_2\text{H}_4 \text{ }^\circ\text{C}} \right) (88.5^\circ\text{C}) = 6848.7 \text{ J or } 6.85 \text{ kJ}$$

$$q_{\text{vap}} = (n_{\text{N}_2\text{H}_4})(\Delta H_{\text{vap}}) = (0.78295 \text{ mol N}_2\text{H}_4) \left( \frac{43.0 \text{ kJ}}{1 \text{ mol N}_2\text{H}_4} \right) = 33.7 \text{ kJ}$$

$$q_{\text{overall}} = q_{\text{heating}} + q_{\text{vap}} = 6.85 \text{ kJ} + 33.7 \text{ kJ} = 40.5 \text{ kJ}$$

35. heat needed =  $3.78 \text{ L H}_2\text{O} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times \frac{0.958 \text{ g H}_2\text{O}}{1 \text{ cm}^3} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = 8.18 \times 10^3 \text{ kJ}$

$$\text{amount CH}_4 \text{ needed} = 8.18 \times 10^3 \text{ kJ} \times \frac{1 \text{ mol CH}_4}{890 \text{ kJ}} = 9.19 \text{ mol CH}_4$$

$$V = \frac{nRT}{P} = \frac{9.19 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1}\text{K}^{-1} \times 296.6 \text{ K}}{768 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 221 \text{ L methane}$$

## Vapor Pressure and Boiling Point

37. (a) When the water vaporizes in the outer container, heat is required; vaporization is an endothermic process. When this vapor (steam) condenses on the outside walls of the inner container, that same heat is liberated; condensation is an exothermic process.
- (b) Liquid water, condensed on the outside wall, is in equilibrium with the water vapor that fills the space between the two containers. This equilibrium exists at the boiling point of water. We assume that the pressure is 1.000 atm, and thus, the temperature of the equilibrium must be  $373.15 \text{ K}$  or  $100.00^\circ\text{C}$ . This is the maximum temperature that can be realized without pressurizing the apparatus.

- 39.** With the Clausius-Clapeyron equation, we use the vapor pressure of water at  $100.0^{\circ}\text{C} = 373.2\text{ K}$  and  $120.0^{\circ}\text{C} = 393.2\text{ K}$  to determine  $\Delta H_{\text{vap}}$  of water near its boiling point. We then use the equation again, to determine the temperature where water's vapor pressure is 2.00 atm.

$$\ln \frac{1489.1 \text{ mmHg}}{760.0 \text{ mmHg}} = \frac{\Delta H_{\text{vap}}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{373.2 \text{ K}} - \frac{1}{393.2 \text{ K}} \right) = 0.6726 = 1.639 \times 10^{-5} \Delta H_{\text{vap}}$$

$$\Delta H_{\text{vap}} = 4.104 \times 10^4 \text{ J / mol} = 41.04 \text{ kJ / mol}$$

$$\ln \frac{1520.0 \text{ mmHg}}{760.0 \text{ mmHg}} = 0.6931 = \frac{41.04 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{373.2 \text{ K}} - \frac{1}{T} \right)$$

$$\left( \frac{1}{373.2 \text{ K}} - \frac{1}{T_{\text{bp}}} \right) = 0.6931 \times \frac{8.1345 \text{ K}^{-1}}{41.03 \times 10^3} = 1.404 \times 10^{-4} \text{ K}^{-1}$$

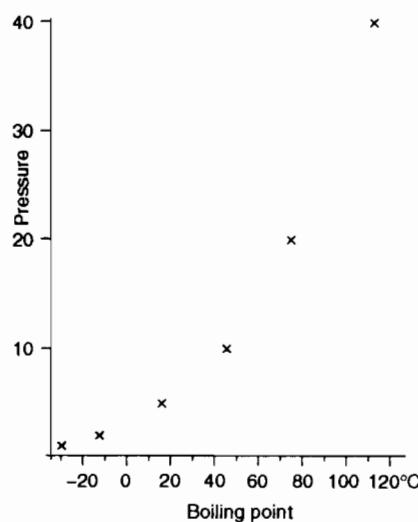
$$\frac{1}{T_{\text{bp}}} = \frac{1}{373.2 \text{ K}} - 1.404 \times 10^{-4} \text{ K}^{-1} = 2.539 \times 10^{-3} \text{ K}^{-1} \quad T_{\text{bp}} = 393.9 \text{ K} = 120.7^{\circ}\text{C}$$

- 41.** The 25.0 L of He becomes saturated with aniline vapor, at a pressure equal to the vapor pressure of aniline.

$$n_{\text{aniline}} = (6.220 \text{ g} - 6.108 \text{ g}) \times \frac{1 \text{ mol aniline}}{93.13 \text{ g aniline}} = 0.00120 \text{ mol aniline}$$

$$P = \frac{nRT}{V} = \frac{0.00120 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 303.2 \text{ K}}{25.0 \text{ L}} = 0.00119 \text{ atm} = 0.907 \text{ mmHg}$$

- 43.**



The graph of pressure vs. boiling point for Freon-12 is shown.

At a temperature of  $25^{\circ}\text{C}$  the vapor pressure is approximately 6.5 atm for Freon-12. Thus the compressor must be capable of producing a pressure greater than 6.5 atm.

## The Clausius-Clapeyron Equation

**45.**  $T = 56.2^\circ \text{ C}$  is  $T = 329.4 \text{ K}$

$$\ln \frac{760 \text{ mmHg}}{375 \text{ mmHg}} = \frac{25.5 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{T} - \frac{1}{329.4 \text{ K}} \right) = 0.706$$

$$\left( \frac{1}{T} - \frac{1}{329.4 \text{ K}} \right) = \frac{0.706 \times 8.3145}{25.5 \times 10^3} \text{ K}^{-1} = 2.30 \times 10^{-4} \text{ K}^{-1} = 1/T - 3.03 \times 10^{-3} \text{ K}^{-1}$$

$$1/T = (3.03 \times 10^{-3} + 0.230) \times 10^{-3} \text{ K}^{-1} = 3.266 \times 10^{-3} \text{ K}^{-1} \quad T = 306 \text{ K} = 33^\circ \text{ C}$$

**47.** normal boiling point =  $179^\circ \text{ C}$  and critical point =  $422^\circ \text{ C}$  and  $45.9 \text{ atm}$

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ln \left( \frac{45.9}{1} \right) = \frac{\Delta H_{\text{vap}}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{452.2 \text{ K}} - \frac{1}{695.2 \text{ K}} \right)$$

$$\Delta H_{\text{vap}} = 41.2 \text{ kJ mol}^{-1}$$

$$\ln \left( \frac{1}{P} \right) = \frac{41,200 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{373.2} - \frac{1}{452.2 \text{ K}} \right) \quad P = 0.0981 \text{ atm} \text{ or } 74.6 \text{ torr}$$

## Critical Point

**49.** A substance that can exist as a liquid at room temperature (about  $20^\circ \text{ C}$ ) is one whose critical temperature is above  $20^\circ \text{ C}$ ,  $293 \text{ K}$ . Of the substances listed in Table 13.3, this includes  $\text{CO}_2$  ( $T_c = 304.2 \text{ K}$ ),  $\text{HCl}$  ( $T_c = 324.6 \text{ K}$ ),  $\text{NH}_3$  ( $T_c = 405.7 \text{ K}$ ),  $\text{SO}_2$  ( $T_c = 431.0 \text{ K}$ ), and  $\text{H}_2\text{O}$  ( $T_c = 647.3 \text{ K}$ ). In fact,  $\text{CO}_2$  exists as a liquid in  $\text{CO}_2$  fire extinguishers.

## States of Matter and Phase Diagrams

**51. (a)** As heat is added initially, the temperature of the ice rises from  $-20^\circ \text{ C}$  to  $0^\circ \text{ C}$ . At (or just slightly below)  $0^\circ \text{ C}$ , ice begins to melt to liquid water. The temperature remains at  $0^\circ \text{ C}$  until all of the ice has melted. Adding heat then warms the liquid until a temperature of about  $93.5^\circ \text{ C}$  is reached, where the liquid begins to vaporize to steam. The temperature remains fixed until all the water is converted to steam. Adding heat then warms the steam to  $200^\circ \text{ C}$ . (Data for this part are taken from Figure 13-21 and Table 13.2.)

**(b)** As the pressure is raised, initially gaseous iodine is compressed. At about  $91 \text{ mmHg}$ , liquid iodine appears; the system remains at a fixed pressure with further compression until all vapor is converted to liquid. Increasing the pressure further simply compresses the liquid until a high pressure is reached, perhaps  $50 \text{ atm}$ , where solid iodine appears. Again the pressure remains fixed with further compression until

all iodine is converted to solid. After this has occurred further compression raises the pressure of the system until 100 atm is reached. (Data for this part are from Figure 13-18 and the surrounding text.)

- (c) Cooling of gaseous  $\text{CO}_2$  simply lowers the temperature until a temperature of perhaps  $20^\circ \text{ C}$  is reached. At this point, liquid  $\text{CO}_2$  appears. The temperature remains constant as more heat is removed until all the gas is converted to liquid. Further cooling then lowers the temperature of the liquid until a temperature of slightly higher than  $-56.7^\circ \text{ C}$  is reached, where solid  $\text{CO}_2$  appears. At this point, further cooling simply converts liquid to solid at constant temperature, until all liquid has been converted to solid. From this point, further cooling lowers the temperature of the solid. (Data for this part are taken from Figure 13-19 and Table 13.3.)
- 53.** 0.240 g  $\text{H}_2\text{O}$  corresponds to 0.0133 mol  $\text{H}_2\text{O}$ . If the water does not vaporize completely, the pressure of the vapor in the flask equals the vapor pressure of water at the indicated temperature. However, if the water vaporizes completely, the pressure of the vapor is determined by the ideal gas law.

- (a)  $30.0^\circ \text{ C}$ , vapor pressure of  $\text{H}_2\text{O} = 31.8 \text{ mmHg} = 0.0418 \text{ atm}$

$$n = \frac{PV}{RT} = \frac{0.0418 \text{ atm} \times 3.20 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 303.2 \text{ K}}$$

$n = 0.00538 \text{ mol H}_2\text{O vapor}$ , this is less than 0.0133 mol  $\text{H}_2\text{O}$ ;

This represents a non-equilibrium condition, as not all the  $\text{H}_2\text{O}$  vaporizes.

The pressure in the flask is 0.0418 atm. (from tables)

- (b)  $50.0^\circ \text{ C}$ , vapor pressure of  $\text{H}_2\text{O} = 92.5 \text{ mmHg} = 0.122 \text{ atm}$

$$n = \frac{PV}{RT} = \frac{0.122 \text{ atm} \times 3.20 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 323.2 \text{ K}} \\ = 0.0147 \text{ mol H}_2\text{O vapor} > 0.0133 \text{ mol H}_2\text{O}; \text{ all the H}_2\text{O vaporizes. Thus,}$$

$$P = \frac{nRT}{V} = \frac{0.0133 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 323.2 \text{ K}}{3.20 \text{ L}} = 0.110 \text{ atm} = 83.8 \text{ mmHg}$$

- (c)  $70.0^\circ \text{ C}$  All the  $\text{H}_2\text{O}$  must vaporize, as this temperature is higher than that of part (b). Thus,

$$P = \frac{nRT}{V} = \frac{0.0133 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 343.2 \text{ K}}{3.20 \text{ L}} = 0.117 \text{ atm} = 89.0 \text{ mmHg}$$

- 55. (a)** According to Figure 13-19,  $\text{CO}_2(\text{s})$  exists at temperatures below  $-78.5^\circ \text{ C}$  when the pressure is 1 atm or less. We do not expect to find temperatures this low and partial pressures of  $\text{CO}_2(\text{g})$  of 1 atm on the surface of the Earth.

- (b) According to Table 13.3, the critical temperature of  $\text{CH}_4$ , the maximum temperature at which  $\text{CH}_4(\text{l})$  can exist, is  $191.1 \text{ K} = -82.1^\circ \text{ C}$ . We do not expect to find temperatures this low on the surface of the earth.
- (c) Since, according to Table 13.3, the critical temperature of  $\text{SO}_2$  is  $431.0 \text{ K} = 157.8^\circ \text{ C}$ ,  $\text{SO}_2(\text{g})$  can be found on the surface of the earth.
- (d) According to Figure 13-18,  $\text{I}_2(\text{l})$  can exist at pressures less than 1.00 atm between the temperatures of  $114^\circ \text{ C}$  and  $184^\circ \text{ C}$ . There are very few places on the Earth that reach temperatures this far above the boiling point of water at pressures below 1 atm, places such as the mouths of volcanoes high above sea level. Essentially,  $\text{I}_2(\text{l})$  is not found on the surface of the earth.
- (e) According to Table 13.3, the critical temperature—the maximum temperature at which  $\text{O}_2(\text{l})$  exists, is  $154.8 \text{ K} = -118.4^\circ \text{ C}$ . Temperatures this low do not exist on the surface of the Earth.

57. (a) Heat lost by water =  $q_{\text{water}} = (m)(C)(\Delta t)$

$$q_{\text{water}} = (100.0 \text{ g}) \left( 4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (0.00^\circ\text{C} - 20.00^\circ\text{C}) \left( \frac{1\text{kJ}}{1000\text{J}} \right) = -8.37 \text{ kJ}$$

Using  $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$  and heat lost by system = heat loss of condensation + cooling

$$q_{\text{steam}} = (175 \text{ g H}_2\text{O}) \left( 4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (0.0^\circ\text{C} - 100.0^\circ\text{C}) \left( \frac{1\text{kJ}}{1000\text{J}} \right) \\ + (175 \text{ g H}_2\text{O}) \left( \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \right) \left( \frac{-40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \right)$$

$$q_{\text{steam}} = -395.4 \text{ kJ} + -73.2 \text{ kJ} = -468.6 \text{ kJ} \text{ or } \sim -469 \text{ kJ}$$

$$\text{Total energy to melt the ice} = q_{\text{water}} + q_{\text{steam}} = -8.37 \text{ kJ} + -469 \text{ kJ} = -477 \text{ kJ}$$

$$\text{Moles of ice melted} = (477 \text{ kJ}) \left( \frac{1 \text{ mol ice}}{6.01 \text{ kJ}} \right) = 79.4 \text{ mol ice melted}$$

$$\text{Mass of ice melted} = (79.4 \text{ mol H}_2\text{O}) \left( \frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) \left( \frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}} \right) = 1.43 \text{ kg}$$

$$\text{Mass of unmelted ice} = 1.65 \text{ kg} - 1.43 \text{ kg} = 0.22 \text{ kg}$$

(b) Mass of unmelted ice = 0.22 kg (above)

$$\text{Heat required to melt ice} = n \Delta H_{\text{fusion}}$$

$$\text{Heat required} = (0.22 \text{ kg ice}) \left( \frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) \left( \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \right) \left( \frac{6.01 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \right) = 73.4 \text{ kJ}$$

Need to determine heat produced when 1 mole of steam (18.015 g) condenses and cools

from 100. °C to 0.0 °C. Heat evolved,

$$\begin{aligned}
 &= (1 \text{ mol H}_2\text{O}) \left( \frac{-40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \right) + (18.015 \text{ g}) \left( 4.184 \frac{\text{J}}{\text{g} \text{ }^\circ\text{C}} \right) (0.0 \text{ }^\circ\text{C} - 100. \text{ }^\circ\text{C}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\
 &= -40.7 \text{ kJ} + -7.54 \text{ kJ} = -48.2 \text{ kJ} \text{ per mole of H}_2\text{O(g) or per 18.015 g H}_2\text{O(g)}
 \end{aligned}$$

$$\text{Mass of steam required} = (73.4 \text{ kJ}) \left( \frac{1 \text{ mol H}_2\text{O(g)}}{48.2 \text{ kJ}} \right) \left( \frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 27 \text{ g steam}$$

- 59.** The liquid in the can is supercooled. When the can is opened, gas bubbles released from the carbonated beverage serve as nuclei for the formation of ice crystals. The condition of supercooling is destroyed and the liquid reverts to the solid phase instantly.

An alternative explanation follows. The process of the gas coming out of solution is endothermic (heat is required). (We know this to be true because the reaction solution of gas in water → gas + liquid water proceeds to the right as the temperature is raised, a characteristic direction of an endothermic reaction.) The required heat is taken from the cooled liquid, causing it to freeze.

## Intermolecular Forces

- 61.** (a) HCl is not a very heavy diatomic molecule; London forces are expected to be relatively weak. Hydrogen bonding is weak in the case of H — Cl bonds; Cl is not one of the three atoms (F, O, N) that form strong hydrogen bonds. Finally, because Cl is an electronegative atom, and H is only moderately electronegative, dipole-dipole interactions should be relatively strong.
- (b) In Br<sub>2</sub>, neither hydrogen bonds nor dipole-dipole attractions are important; there are no H atoms in the molecule, and homonuclear molecules are nonpolar. London forces are more important than in HCl since Br<sub>2</sub> is heavier.
- (c) In ICl there are no hydrogen bonds since there are no H atoms in the molecule. The London forces are as strong as in Br<sub>2</sub> since the two molecules have the same number of electrons. However, dipole-dipole interactions are important in ICl; the molecule is polar toward Cl.
- (d) In HF London forces are not very important; the molecule has only 10 electrons. Hydrogen bonding is quite important and definitely overshadows even the strong dipole-dipole interactions.
- (e) In CH<sub>4</sub>, H bonds are not important; the H atoms are not bonded to F, O, or N. In addition the molecule is not polar, so there are no dipole-dipole interactions. Finally, London forces are quite weak since the molecule contains only 10 electrons, and this is why CH<sub>4</sub> is a gas with a low critical temperature.

63. (c) < (b) < (d) < (a)  
 (ethane thiol) (ethanol) (butanol) (acetic acid)

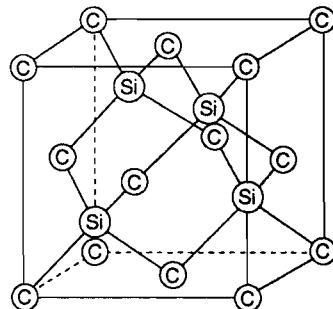
Viscosity will depend on the intermolecular forces, e.g. varying H-bonding forces.

65. We expect  $\text{CH}_3\text{OH}$  to be a liquid from among the four substances listed. Of these four molecules,  $\text{C}_3\text{H}_8$  has the most electrons and should have the strongest London forces. However, only  $\text{CH}_3\text{OH}$  satisfies the conditions for hydrogen bonding (H bonded to and attracted to N, O, or F) and thus its intermolecular attractions should be much stronger than those of the other substances.

## Network Covalent Solids

67. One would expect diamond to have a greater density than graphite. Although the bond distance in graphite, “one-and-a-half” bonds, would be expected to be shorter than the single bonds in diamond, the large spacing between the layers of C atoms in graphite makes its crystals much less dense than those of diamond.

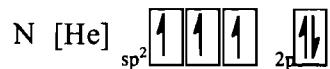
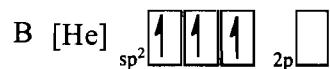
69. (a) We expect Si and C atoms to alternate in the structure, as shown at right. The C atoms are on the corners ( $8 \times 1/8 = 1$  C atom) and on the faces ( $6 \times 1/2 = 3$  C atoms), a total of four C atoms/unit cell. The Si atoms are each totally within the cell, a total of four Si atoms/unit cell.



- (b) To have a graphite structure, we expect  $sp^2$  hybridization for each atom. The hybridization schemes for B and N atoms are shown to the right. The half-filled  $sp^2$  hybrid orbitals overlap to form the  $\sigma$  bonding structure, and a hexagonal array of atoms. The  $2p_z$  orbitals then overlap to form the  $\pi$  bonding orbitals. There are as many  $\pi$  electrons in a sample of BN as there are in a sample of graphite, assuming both samples have the same number of atoms.

## Ionic Bonding and Properties

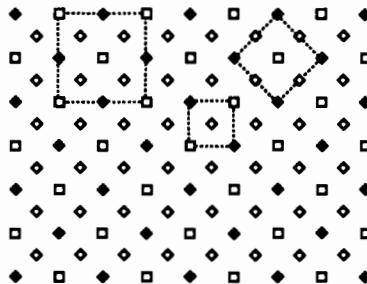
71. We expect forces in ionic compounds to increase as sizes of ions become smaller and as ionic charges become greater. As the forces between ions become stronger, a higher temperature is required to melt the crystal. In the series of compounds  $\text{NaF}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ , and  $\text{NaI}$ , the anions are progressively larger, and thus the ionic forces become weaker. We



expect the melting points to decrease in this series from NaF to NaI. This is precisely what we see.

## Crystal Structures

- 73.** In each layer of a closest packing arrangement of spheres, there are six spheres surrounding and touching any given sphere. A second similar layer then is placed on top of this first layer so that its spheres fit into the indentations in the layer below. The two different closest packing arrangements arise from two different ways of placing the third layer on top of these two, with its spheres fitting into the indentations of the layer below. In one case, one can look down into these indentations and see a sphere of the bottom (first) layer. If these indentations are used, the closest packing arrangement *abab* results (hexagonal closest packing). In the other case, no first layer sphere is visible through the indentation; the closest packing arrangement *abcabc* results (cubic closest packing).
- 75. (a)** We naturally tend to look at crystal structures in right-left, up-down terms. If we do that here, we might assign a unit cell as a square, with its corners at the centers of the light-colored squares. But the crystal does not “know” right and left or top and bottom. If we look at this crystal from the lower right corner, we see a unit cell that has its corners at the centers of dark-colored diamonds. These two types of unit cells are outlined at the top of the diagram below.



- (b)** The unit cell has one light-colored square fully inside it. It has four light-colored “circles” (which the computer doesn’t draw as very round) on the edges, each shared with one other unit cell. So a total of  $4 \times 1/2 = 2$  circles per unit cell. And the unit cell has four dark-colored diamonds, one at each corner, and each shared with four other unit cells, for a total of  $4 \times 1/4 = 1$  diamond per unit cell.
- (c)** One example of an erroneous unit cell is the small square outlined near the center of the figure drawn in part (a). But notice that simply repeatedly translating this unit cell toward the right, so that its left edge sits where its right edge is now, will not generate the lattice.

77. In Figure 13-45 we see that the body diagonal of a cube has a length of  $\sqrt{3}l$ , where  $l$  is the length of one edge of the cube. The length of this body diagonal also equals  $4r$ , where  $r$  is the radius of the atom in the structure. Hence  $4r = \sqrt{3}l$  or  $l = 4r \div \sqrt{3}$ . Recall that the volume of a cube is  $l^3$ , and  $\sqrt{3} = 1.732$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{\frac{2 \text{ W atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol W}}{6.022 \times 10^{23} \text{ W atoms}} \times \frac{183.85 \text{ g W}}{1 \text{ mol W}}}{\left( \frac{4 \times 139 \text{ pm}}{1.732} \times \frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3} = 18.5 \text{ g/cm}^3$$

This compares well with a tabulated density of  $19.25 \text{ g/cm}^3$ .

79. (a)  $335 \text{ pm} = 2 \text{ radii or 1 diameter}$ . Hence Po diameter =  $335 \text{ pm}$   
 (b)  $1 \text{ Po unit cell} = (335 \text{ pm})^3 = 3.76 \times 10^7 \text{ pm}^3 (3.76 \times 10^{-23} \text{ cm}^3)$  per unit cell.

$$\text{density} = \frac{m}{V} = \frac{3.47 \times 10^{-22} \text{ g}}{3.76 \times 10^{-23} \text{ cm}^3} = 9.23 \text{ g cm}^{-3}$$

- (c)  $n = 1$ ,  $d = 335 \text{ pm}$  and  $\lambda = 1.785 \times 10^{-10}$  or  $178.5 \text{ pm}$   
 solve for  $\sin \theta$  then determine  $\theta$

$$\sin \theta = \frac{n\lambda}{2d} = \frac{(1)(1.785 \times 10^{-10})}{2(335 \times 10^{-12})} = 0.2664 \text{ or } \theta = 15.45^\circ$$

## Ionic Crystal Structures

81.  $\text{CaF}_2$ . There are eight  $\text{Ca}^{2+}$  ions on the corners, each shared among eight unit cells, for a total of  $(8 \times 1/8)$  one corner ion per unit cell. There are six  $\text{Ca}^{2+}$  ions on the faces, each shared between two unit cells, for a total of  $(6 \times 1/2)$  three face ions per unit cell. This gives a total of four  $\text{Ca}^{2+}$  ions per unit cell. There are eight  $\text{F}^-$  ions, each wholly contained within the unit cell. The ratio of  $\text{Ca}^{2+}$  ions to  $\text{F}^-$  ions is 4  $\text{Ca}^{2+}$  ions per 8  $\text{F}^-$  ions:  $\text{Ca}_4\text{F}_8$  or  $\text{CaF}_2$ .

$\text{TiO}_2$ . There are eight  $\text{Ti}^{4+}$  ions on the corners, each shared among eight unit cells, for a total of  $(8 \times 1/8)$  one  $\text{Ti}^{4+}$  corner ion per unit cell. There is one  $\text{Ti}^{4+}$  ion in the center, wholly contained within the unit cell. Thus, there are a total of two  $\text{Ti}^{4+}$  ions per unit cell. There are four  $\text{O}^{2-}$  ions on the faces of the unit cell, each shared between two unit cells, for a total of  $(4 \times 1/2)$  two face atoms per unit cells. There are two  $\text{O}^{2-}$  ions totally contained within the unit cell. This gives a total of four  $\text{O}^{2-}$  ions per unit cell. The ratio of  $\text{Ti}^{4+}$  ions to  $\text{O}^{2-}$  ions is 2  $\text{Ti}^{4+}$  ions per 4  $\text{O}^{2-}$  ion:  $\text{Ti}_2\text{O}_4$  or  $\text{TiO}_2$ .

- 83.** (a) In a sodium chloride type of lattice, there are six cations around each anion and six anions around each cation. These oppositely charged ions are arranged as follows: one above, one below, one in front, one in back, one to the right, and one to the left. Thus the coordination number of  $Mg^{2+}$  is 6 and that of  $O^{2-}$  is 6 also.
- (b) In the unit cell, there is an oxide ion at each of the eight corners; each of these is shared between eight unit cells. There also is an oxide ion at the center of each of the six faces; each of these oxide ions is shared between two unit cells. Thus, the total number of oxide ions is computed as follows.

$$\text{total # of oxide ions} = 8 \text{ corners} \times \frac{1 \text{ oxide ion}}{8 \text{ unit cells}} + 6 \text{ faces} \times \frac{1 \text{ oxide ion}}{2 \text{ unit cells}} = 4 O^{2-} \text{ ions}$$

There is a magnesium ion on each of the twelve edges; each of these is shared between four unit cells. There also is a magnesium ion in the center which is not shared with another unit cell.

$$\begin{aligned} \text{total # of } Mg^{2+} \text{ ions} &= 12 \text{ adjoining cells} \times \frac{1 \text{ magnesium ion}}{4 \text{ unit cells}} + 1 \text{ central } Mg^{2+} \text{ ion} \\ &= 4 Mg^{2+} \text{ ions} \end{aligned}$$

Thus, there are four formula units per unit cell of  $MgO$ .

- (c) Along the edge of the unit cell,  $Mg^{2+}$  and  $O^{2-}$  ions are in contact. The length of the edge is equal to the radius of one  $O^{2-}$ , plus the diameter of  $Mg^{2+}$ , plus the radius of another  $O^{2-}$ .

$$\text{edge length} = 2 \times O^{2-} \text{ radius} + 2 \times Mg^{2+} \text{ radius} = 2 \times 140 \text{ pm} + 2 \times 72 \text{ pm} = 424 \text{ pm}$$

The unit cell is a cube; its volume is the cube of its length.

$$\text{volume} = (424 \text{ pm})^3 = 7.62 \times 10^7 \text{ pm} \left( \frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 7.62 \times 10^{-23} \text{ cm}^3$$

$$(d) \text{ density} = \frac{\text{mass}}{\text{volume}} = \frac{4 \text{ MgO f.u.}}{7.62 \times 10^{-23} \text{ cm}^3} \times \frac{1 \text{ mol MgO}}{6.022 \times 10^{23} \text{ f.u.}} \times \frac{40.30 \text{ g MgO}}{1 \text{ mol MgO}} = 3.51 \text{ g/cm}^3$$

**85.**  $CaO \rightarrow \text{radius ratio} = \frac{r_{Ca^{2+}}}{r_{O^{2-}}} = \frac{100 \text{ pm}}{140 \text{ pm}} = 0.714$

Cations occupies octahedral holes of a face centered cubic array of anions

$$CuCl \rightarrow \text{radius ratio} = \frac{r_{Cu^{+}}}{r_{Cl^{-}}} = \frac{96 \text{ pm}}{181 \text{ pm}} = 0.530$$

Cations occupy octahedral holes of a face centered cubic array of anions

$$LiO_2 \rightarrow \text{radius ratio} = \frac{r_{Li^{+}}}{r_{O_2^{-}}} = \frac{59 \text{ pm}}{128 \text{ pm}} = 0.461$$

Cations occupy octahedral holes of a face centered cubic array of anions

## Lattice Energy

- 87.** Whether or not enthalpies of sublimation of the alkali metals are approximately the same, lattice energies of a series such as LiCl(s), NaCl(s), KCl(s), RbCl(s), and CsCl(s) will vary approximately with the size of the cation. A smaller cation will produce a more exothermic lattice energy. Thus, the lattice energy for LiCl(s) should be the most exothermic and CsCl(s) the least in this series, with NaCl(s) falling in the middle of the series.

- 89.** Second ionization energy:  $Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \quad I_2 = 1451 \text{ kJ/mol}$   
 Lattice energy:  $Mg^{2+}(g) + 2 Cl^-(g) \rightarrow MgCl_2(s) \quad L.E. = -2526 \text{ kJ/mol}$   
 Sublimation:  $Mg(s) \rightarrow Mg(g) \quad \Delta H_{sub} = 146 \text{ kJ/mol}$   
 First ionization energy  $Mg(g) \rightarrow Mg^+(g) + e^- \quad I_1 = 738 \text{ kJ/mol}$   
 Dissociation energy:  $Cl_2(g) \rightarrow 2 Cl(g) \quad D.E. = (2 \times 122) \text{ kJ/mol}$   
 Electron Affinity:  $2 Cl(g) + 2 e^- \rightarrow 2 Cl^-(g) \quad 2 \times E.A. = 2(-349) \text{ kJ/mol}$

$$\Delta H_f^\circ = \Delta H_{sub} + I_1 + I_2 + D.E. + (2 \times E.A.) + L.E.$$

$$= 146 \frac{\text{kJ}}{\text{mol}} + 738 \frac{\text{kJ}}{\text{mol}} + 1451 \frac{\text{kJ}}{\text{mol}} + 244 \frac{\text{kJ}}{\text{mol}} - 698 \frac{\text{kJ}}{\text{mol}} - 2526 \frac{\text{kJ}}{\text{mol}} = -645 \frac{\text{kJ}}{\text{mol}}$$

In Example 13-11, the value of  $\Delta H_f^\circ$  for MgCl is calculated as  $-19 \text{ kJ/mol}$ . Therefore, MgCl<sub>2</sub> is much more stable than MgCl, since considerably more energy is released when it forms. We expect MgCl<sub>2</sub>(s) to be more stable than MgCl(s) because a 2+ cation more strongly attracts anions than does a 1+ cation.

## FEATURE PROBLEMS

- 120.** We obtain the surface tension by substituting the experimental values into the equation for surface tension.

$$h = \frac{2\gamma}{dgr} \quad \gamma = \frac{hdgr}{2} = \frac{1.1 \text{ cm} \times 0.789 \text{ g cm}^{-3} \times 981 \text{ cm s}^{-2} \times 0.050 \text{ cm}}{2} = 21 \text{ g/s}^2 = 0.021 \text{ J/m}^2$$

- 121. (a)**  $\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)} = \frac{\Delta H_{vap}}{T(V_g)} \quad \text{Note: } V_l \approx 0 \quad \text{Rearrange expression, Use } V_g = \frac{nRT}{P}$

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T\left(\frac{nRT}{P}\right)} = \frac{\Delta H_{vap}}{\frac{nRT^2}{P}} = \frac{P\Delta H_{vap}}{nRT^2} \quad \text{or} \quad \frac{dP}{P} = \frac{\Delta H_{vap} \times dT}{nRT^2}$$

Consider 1 mole ( $n = 1$ ) and substitute in  $\Delta H_{vap} = 15,971 + 14.55 T - 0.160 T^2$

$$\frac{dP}{P} = \frac{(15,971 + 14.55 T - 0.160 T^2)dT}{RT^2} = \frac{(15,971)dT}{RT^2} + \frac{(14.55 T)dT}{RT^2} - \frac{(0.160 T^2)dT}{RT^2}$$

Simplify and collect constants

$$\frac{dP}{P} = \frac{(15,971)}{R} \frac{dT}{T^2} + \frac{(14.55)}{R} \frac{dT}{T} - \frac{(0.160)}{R} dT$$

Integrate from  $P_1 \rightarrow P_2$  and  $T_1 \rightarrow T_2$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{(15,971)}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{(14.55)}{R} \ln\left(\frac{T_2}{T_1}\right) - \frac{(0.160)}{R} (T_2 - T_1)$$

- (b) Consider 1 mole ( $n = 1$ )  $P_1 = 10.16$  torr (0.01337 atm) and  $T_1 = 120$  K  
Find the boiling point ( $T_2$ ) when the pressure ( $P_2$ ) is 1 atm.

$$\ln\left(\frac{1}{0.01337}\right) = \frac{(15,971)}{0.08206} \left( \frac{1}{120} - \frac{1}{T_2} \right) + \frac{(14.55)}{0.08206} \ln\left(\frac{T_2}{120}\right) - \frac{(0.160)}{0.08206} (T_2 - 120)$$

Solve for  $T_2$  using the method of successive approximations:  $T_2 = 169$  K

122. (a) 1 NaCl unit missing from the NaCl unit cell  $\rightarrow$  overall stoichiometry is the same. The unit cell usually has 4  $\text{Na}^+$  and 4  $\text{Cl}^-$  in the unit cell. Now the unit cell will have 3  $\text{Na}^+$  and 3  $\text{Cl}^-$ . Accordingly, the density will decrease by a factor of 25% (1/4) if 1  $\text{Na}^+$  and 1  $\text{Cl}^-$  are consistently absent throughout the structure. Thus, the density will be 0.75( $d_{\text{NaCl, normal}}$ ).

- (b) No change in stoichiometry or density, as this is just a simple displacement of an ion within the unit cell.
- (c) Unit cell should contain 4  $\text{Ti}^{2+}$  and 4  $\text{O}^{2-}$  ions (same as in the NaCl unit cell). 4 TiO ions have a mass of :

$$4 \text{ formula units} \times \left( \frac{1 \text{ mol TiO}}{6.022 \times 10^{23} \text{ formula units}} \right) \left( \frac{63.88 \text{ g TiO}}{1 \text{ mol TiO}} \right) = 4.243 \times 10^{-22} \text{ g TiO}$$

$$V = (418 \text{ pm})^3 \times \left( \frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \right)^3 \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 7.30 \times 10^{-23} \text{ cm}^3$$

$$\text{Calculated density} = \frac{\text{mass}}{V} = \frac{4.243 \times 10^{-22} \text{ g}}{7.30 \times 10^{-23} \text{ cm}^3} = 5.81 \text{ g cm}^{-3} \text{ (actual density} = 4.92 \text{ g cm}^{-3}\text{)}$$

This indicates the presence of vacancies, possibly an example of the Schottky defect.

# CHAPTER 14

## SOLUTIONS AND THEIR PHYSICAL PROPERTIES

### PRACTICE EXAMPLES

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- 1A** To determine mass percent, we need both the mass of ethanol and the mass of solution. From volume percent, we know that 100.0 mL of solution contains 20.0 mL pure ethanol. The density of pure ethanol is 0.789 g/mL. We now can determine the mass of solute (ethanol) and solution. We perform the calculation in one set-up.

$$\text{mass percent ethanol} = \frac{20.0 \text{ mL ethanol} \times \frac{0.789 \text{ g}}{1 \text{ mL ethanol}}}{100.0 \text{ mL soln} \times \frac{0.977 \text{ g}}{1 \text{ mL soln}}} \times 100\% = 16.2\% \text{ ethanol by mass}$$

- 1B** In each case, we use the definition of the concentration unit, making sure that numerator and denominator are converted to the correct units.

- (a) We first determine the mass in grams of the solute and of the solution.

$$\text{mass CH}_3\text{OH} = 11.3 \text{ mL CH}_3\text{OH} \times \frac{0.793 \text{ g}}{1 \text{ mL}} = 8.96 \text{ g CH}_3\text{OH}$$

$$\text{mass soln} = 75.0 \text{ mL soln} \times \frac{0.980 \text{ g}}{1 \text{ mL}} = 73.5 \text{ g soln}$$

$$\text{amount of H}_2\text{O} = (73.5 \text{ g soln} - 8.96 \text{ g CH}_3\text{OH}) \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}$$

$$\text{amount of H}_2\text{O} = 3.58 \text{ mol H}_2\text{O} (= 64.5 \text{ g H}_2\text{O})$$

$$\text{amount of CH}_3\text{OH} = 8.96 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} = 0.280 \text{ mol CH}_3\text{OH}$$

$$\text{H}_2\text{O mole fraction} = \frac{\text{amount of H}_2\text{O in moles}}{\text{amount of soln in moles}} = \frac{3.58 \text{ mol H}_2\text{O}}{3.58 \text{ mol H}_2\text{O} + 0.280 \text{ mol CH}_3\text{OH}} = 0.927$$

$$(b) [\text{CH}_3\text{OH}] = \frac{\text{amount of CH}_3\text{OH in moles}}{\text{volume of soln in L}} = \frac{0.280 \text{ mol CH}_3\text{OH}}{75.0 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 3.73 \text{ M}$$

$$(c) \text{molality of CH}_3\text{OH} = \frac{\text{amount of CH}_3\text{OH in moles}}{\text{mass of H}_2\text{O in kg}} = \frac{0.280 \text{ mol CH}_3\text{OH}}{64.5 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 4.34 \text{ m}$$

- 2A** First we need the amount of each component in solution. We use a 100.00-g sample of solution, in which there are 16.00 g glycerol and 84.00 g water.

$$\text{amount of glycerol} = 16.00 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3 \times \frac{1 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3}{92.10 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3} = 0.1737 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3$$

$$\text{amount of water} = 84.00 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} = 4.661 \text{ mol } \text{H}_2\text{O}$$

$$\begin{aligned}\text{mole fraction of } \text{C}_3\text{H}_5(\text{OH})_3 &= \frac{\text{amount } \text{C}_3\text{H}_5(\text{OH})_3}{\text{amount } [\text{C}_3\text{H}_5(\text{OH})_3 + \text{H}_2\text{O}]} \\ &= \frac{0.1737 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3}{0.1737 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3 + 4.661 \text{ mol } \text{H}_2\text{O}} = 0.03593\end{aligned}$$

- 2B** First we need the amount of sucrose in solution. We use a 100.00-g sample of solution, in which there are 10.00 g sucrose and 90.00 g water.

$$\text{amount } \text{C}_{12}\text{H}_{22}\text{O}_{11} = 10.00 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}} = 0.02921 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}$$

- (a)** Molarity is amount of solute in moles per liter of solution. Convert the 100.00 g of solution to L with density as a conversion factor.

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ molarity} = \frac{0.02921 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{1000. \text{ g soln}} \times \frac{1.040 \text{ g soln}}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.3038 \text{ M}$$

- (b)** Molality is amount of solute in moles per kilogram of solvent. Convert 90.00 g of solute to kg.

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ molality} = \frac{0.02921 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{90.00 \text{ g } \text{H}_2\text{O}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 0.3246 \text{ m}$$

- (c)** Mole fraction is amount of solute per amount of solution. First compute the amount in 90.00 g  $\text{H}_2\text{O}$ .

$$\text{amount } \text{H}_2\text{O} = 90.00 \text{ g} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} = 4.994 \text{ mol } \text{H}_2\text{O}$$

$$\text{mole fraction } \text{C}_{12}\text{H}_{22}\text{O}_{11} = \frac{0.02921 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{0.02921 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11} + 4.994 \text{ mol } \text{H}_2\text{O}} = 0.005815$$

- 3A** Water is a polar, hydrogen bonding compound. It should mix well with other polar, hydrogen bonding compounds. (a) Toluene is nonpolar and should not be very soluble in water. (c) Benzaldehyde can form hydrogen bonds to water through its O atom. However, most of the molecule is non-polar and, as a result, it has limited solubility in water. (b) Oxalic acid is polar and can form hydrogen bonds. Oxalic acid should be the most readily soluble of these three compounds in water. Actual solubilities (w/w%) are: toluene (0.067%) < benzaldehyde (0.28%) < oxalic acid (14%).

**3B** Both  $I_2$  and  $CCl_4$  are nonpolar molecules. It does not take much energy to break the attractions among  $I_2$  molecules, or among  $CCl_4$  molecules. Also, there is not a strong  $I_2-CCl_4$  attraction created when a solution forms. The result is that  $I_2$  should dissolve well in  $CCl_4$  by simple mixing.  $H_2O$  is extensively hydrogen bonded with strong intermolecular forces requiring significant energy to break, but there is not a strong  $I_2-H_2O$  attraction created when a solution forms. We expect  $I_2$  to dissolve poorly in water. Actual solubilities are 2.603 g  $I_2$ /100 g  $CCl_4$  and 0.033 g  $I_2$ /100 g  $H_2O$ .

**4A** The two suggestions are quoted first, followed by the means of achieving each one.

- (1) Dissolve the 95 g  $NH_4Cl$  in just enough water to produce a saturated solution (55 g  $NH_4Cl$ /100 g  $H_2O$ ) at 60°C.

$$\text{mass of water needed} = 95 \text{ g } NH_4Cl \times \frac{100 \text{ g } H_2O}{55 \text{ g } NH_4Cl} = 173 \text{ g } H_2O$$

The mass of  $NH_4Cl$  in the saturated solution at 20°C now is smaller.

$$\text{mass } NH_4Cl \text{ dissolved} = 173 \text{ g } H_2O \times \frac{37 \text{ g } NH_4Cl}{100 \text{ g } H_2O} = 64 \text{ g } NH_4Cl \text{ dissolved}$$

$$\begin{aligned} \text{crystallized mass } NH_4Cl &= 95 \text{ g } NH_4Cl \text{ total} - 64 \text{ g } NH_4Cl \text{ dissolved at 20°C} \\ &= 31 \text{ g } NH_4Cl \text{ crystallized} \end{aligned}$$

- (2) Lower the final temperature to 0°C, rather than 20°C. From Figure 14-8, at 0°C the solubility of  $NH_4Cl$  is 28.5 g  $NH_4Cl$ /100 g  $H_2O$ . From this (and knowing that there is 173 g  $H_2O$  present in the solution) we calculate the mass of  $NH_4Cl$  dissolved at this lower temperature.

$$\text{mass dissolved } NH_4Cl = 173 \text{ g } H_2O \times \frac{28.5 \text{ g } NH_4Cl}{100 \text{ g } H_2O} = 49.3 \text{ g } NH_4Cl \text{ dissolved}$$

The mass of  $NH_4Cl$  recrystallized is 95 g - 49.3 g = 46 g

$$\text{yield} = (46/95) \times 100\% = 48\%$$

**4B** Percent yield for the recrystallization can be defined as:

$$\% \text{ yield} = \frac{\text{mass crystallized}}{\text{mass dissolved}(40^\circ C)} \times 100\%$$

$$\% \text{ yield} = \frac{\text{mass dissolved}(40^\circ C) - \text{mass dissolved}(20^\circ C)}{\text{mass dissolved}(40^\circ C)} \times 100\%$$

Figure 14-8 solubilities per 100 g  $H_2O$  are followed by percent yield calculations.

Solubility of  $KClO_4$ : 4.84 g at 40°C and 3.0 g at 20° C

$$\text{Percent yield of } KClO_4 = \frac{4.8 \text{ g } (40^\circ C) - 3.0 \text{ g } (20^\circ C)}{4.8 \text{ g } (40^\circ C)} \times 100\% = 38\% \text{ } KClO_4$$

Solubility of  $\text{KNO}_3$ : 60.7 g at 40°C and 32.3 g at 20°C

$$\text{Percent Yield of } \text{KNO}_3 = \frac{60.7 \text{ g (40°C)} - 32.3 \text{ g (20°C)}}{60.7 \text{ g (40°C)}} \times 100\% = 47\% \text{ KNO}_3$$

Solubility of  $\text{K}_2\text{SO}_4$ : 15.1 g at 40°C and 11.9 g at 20°C

$$\text{Percent yield of } \text{K}_2\text{SO}_4 = \frac{15.1 \text{ g (40°C)} - 11.9 \text{ g (20°C)}}{15.1 \text{ g (40°C)}} \times 100\% = 21\% \text{ K}_2\text{SO}_4$$

Ranked in order from highest to lowest percent yield:

$$\text{KNO}_3 (47\%) > \text{KClO}_4 (38\%) > \text{K}_2\text{SO}_4 (21\%)$$

- 5A** From Example 14-5, we know that the Henry's law constant for  $\text{O}_2$  dissolved in water is  $k = 2.18 \times 10^{-3} \text{ M atm}^{-1}$ . Consequently,

$$P_{\text{gas}} = \frac{C}{k} = \frac{8.23 \times 10^{-4} \text{ M}}{2.18 \times 10^{-3} \text{ M atm}^{-1}} = 0.378 \text{ atm } \text{O}_2 \text{ pressure}$$

- 5B** The pressure required must allow 0.0100 mol CO will dissolve in each liter of solution, which we take as 1000 mL  $\text{H}_2\text{O}$ . We know that at 1 atm pressure, 35.4 mL CO dissolves in each liter of solution (0.0354 mL CO/mL solution). Thus,  $[\text{CO}]$  at 1 atm CO pressure is

$$[\text{CO}] = \frac{35.4 \text{ mL CO at STP} \times \frac{1 \text{ mol CO}}{22,414 \text{ mL CO at STP}}}{1 \text{ L soln}} = 0.00158 \text{ M}$$

Now, Henry's law:

$$k = \frac{c}{P_{\text{gas}}} = \frac{0.00158 \text{ M}}{1 \text{ atm}} = \frac{0.0100 \text{ M}}{P} \quad P = \frac{0.0100 \text{ M} \times 1 \text{ atm}}{0.00158 \text{ M}} = 6.33 \text{ atm CO}$$

- 6A** Raoult's law enables us to determine the vapor pressure of each component.

$$P_{\text{hex}} = \chi_{\text{hex}} P^{\circ}_{\text{hex}} = 0.750 \times 149.1 \text{ mmHg} = 112 \text{ mmHg}$$

$$P_{\text{pen}} = \chi_{\text{pen}} P^{\circ}_{\text{pen}} = 0.250 \times 508.5 \text{ mmHg} = 127 \text{ mmHg}.$$

We use Dalton's law to determine the total vapor pressure:

$$P_{\text{total}} = P_{\text{hex}} + P_{\text{pen}} = 112 \text{ mmHg} + 127 \text{ mmHg} = 239 \text{ mmHg}$$

- 6B** Masses of solution components need to be converted to amounts in moles through the use of molar masses. Let us choose as our mass precisely 1.0000 mole of

$$\text{C}_6\text{H}_6 = 78.11 \text{ g } \text{C}_6\text{H}_6 \text{ and an equal mass of toluene.}$$

$$\text{amount of toluene} = 78.11 \text{ g } \text{C}_7\text{H}_8 \times \frac{1 \text{ mol } \text{C}_7\text{H}_8}{92.14 \text{ g } \text{C}_7\text{H}_8} = 0.8477 \text{ mol } \text{C}_7\text{H}_8$$

$$\text{mole fraction toluene} = \chi_{\text{tol}} = \frac{0.8477 \text{ mol } \text{C}_7\text{H}_8}{0.8477 \text{ mol } \text{C}_7\text{H}_8 + 1.0000 \text{ mol } \text{C}_6\text{H}_6} = 0.4588$$

$$\text{toluene vapor pressure} = \chi_{\text{tol}} P^{\circ}_{\text{tol}} = 0.4588 \times 28.4 \text{ mmHg} = 13.0 \text{ mmHg}$$

$$\text{benzene vapor pressure} = \chi_{\text{benz}} P^{\circ}_{\text{benz}} = (1.0000 - 0.4588) \times 95.1 \text{ mmHg} = 51.5 \text{ mmHg.}$$

$$\text{total vapor pressure} = 13.0 \text{ mmHg} + 51.5 \text{ mmHg} = 64.5 \text{ mmHg}$$

- 7A** The mole fraction composition of each component is that component's partial pressure divided by the total pressure. Again, we note that the vapor is richer in the more volatile component.

$$y_{\text{hexane}} = \frac{P_{\text{hexane}}}{P_{\text{total}}} = \frac{112 \text{ mmHg hexane}}{239 \text{ mmHg total}} = 0.469 \quad y_{\text{pentane}} = \frac{P_{\text{pentane}}}{P_{\text{total}}} = \frac{127 \text{ mmHg pentane}}{239 \text{ mmHg total}} = 0.531$$

or simply  $1.000 - 0.469 = 0.531$

- 7B** The mole fraction composition of each component is that component's partial pressure divided by the total pressure. Again we note that the vapor is richer in the more volatile component.

$$y_t = \frac{P_{\text{toluene}}}{P_{\text{total}}} = \frac{13.0 \text{ mmHg toluene}}{64.5 \text{ mmHg total}} = 0.202 \quad y_b = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{51.5 \text{ mmHg benzene}}{64.5 \text{ mmHg total}} = 0.798$$

or simply  $1.000 - 0.202 = 0.798$

- 8A** We use the osmotic pressure equation, converting the mass of solute to amount in moles, the temperature to Kelvin, and the solution volume to liters.

$$\pi = \frac{nRT}{V} = \frac{\left(1.50 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}\right) \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}}{125 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.857 \text{ atm}$$

- 8B** We use the osmotic pressure equation to determine the molarity of the solution.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{0.015 \text{ atm}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 6.1 \times 10^{-4} \text{ M}$$

Now, we can calculate the mass of urea.

$$\text{urea mass} = 0.225 \text{ L} \times \frac{6.1 \times 10^{-4} \text{ mol urea}}{1 \text{ L soln}} \times \frac{60.06 \text{ g CO(NH}_2\text{)}_2}{1 \text{ mol CO(NH}_2\text{)}_2} = 8.24 \times 10^{-3} \text{ g}$$

- 9A** We could substitute directly into the equation for molar mass derived in Example 14-9, but let us rather think our way through each step of the process. First, we find the concentration of the solution, by rearranging  $\pi = \frac{n}{V} RT$ . We need to convert the osmotic pressure to atmospheres.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{8.73 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}} = 4.70 \times 10^{-4} \text{ M}$$

Next we determine the amount in moles of dissolved solute.

$$\text{amount of solute} = 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{4.70 \times 10^{-4} \text{ mol solute}}{1 \text{ L solution}} = 4.70 \times 10^{-5} \text{ mol solute}$$

We use the mass of solute, 4.04 g, to determine the molar mass.  $\rightarrow M = \frac{4.04 \text{ g}}{4.70 \times 10^{-5} \text{ mol}} = 8.60 \times 10^4 \text{ g/mol}$

**9B** We use the osmotic pressure equation along with the molarity of the solution.

$$\pi = \frac{n}{V} RT = \frac{2.12 \text{ g} \times \frac{1 \text{ mol}}{6.86 \times 10^4 \text{ g}}}{75.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times (310.2) \text{ K} = 0.0105 \text{ atm} = 7.97 \text{ mmHg}$$

**10A (a)** The freezing point depression constant for water is  $K_f = 1.86 \text{ }^{\circ}\text{C m}^{-1}$ .

$$\text{molality} = \frac{\Delta T_f}{-K_f} = \frac{-0.227 \text{ }^{\circ}\text{C}}{-1.86 \text{ }^{\circ}\text{C m}^{-1}} = 0.122 \text{ m}$$

**(b)** Use the definition of molality to determine the number of moles of riboflavin in 0.833 g of dissolved riboflavin.

$$\text{amount of riboflavin} = 18.1 \text{ g solvent H}_2\text{O} \times \frac{1 \text{ kg solvent}}{1000 \text{ g}} \times \frac{0.122 \text{ mol solute}}{1 \text{ kg solvent}}$$

$$\text{amount of riboflavin} = 2.21 \times 10^{-3} \text{ mol riboflavin}$$

$$M = \frac{0.833 \text{ g riboflavin}}{2.21 \times 10^{-3} \text{ mol}} = 377 \text{ g/mol}$$

**(c)** Use the method of Chapter 3 to find riboflavin's empirical formula, starting with a 100.00-g sample.

$$54.25 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.517 \text{ mol C} \div 1.063 \rightarrow = 4.249 \text{ mol C}$$

$$5.36 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 5.32 \text{ mol H} \div 1.063 \rightarrow = 5.00 \text{ mol H}$$

$$25.51 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.594 \text{ mol O} \div 1.063 \rightarrow = 1.500 \text{ mol O}$$

$$14.89 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.063 \text{ mol N} \div 1.063 \rightarrow = 1.000 \text{ mol N}$$

If we multiply each of these amounts by 4 (because 4.249 is almost equal to  $4\frac{1}{4}$ ), the empirical formula is  $\text{C}_{17}\text{H}_{20}\text{O}_6\text{N}_4$  with a molar mass of 376 g/mol. The molecular formula is  $\text{C}_{17}\text{H}_{20}\text{O}_6\text{N}_4$ .

**10B** The boiling point of pure water at 760.0 mmHg is 100.000  $^{\circ}\text{C}$ . For higher pressures, the boiling point occurs at a higher temperature; for lower pressures, a lower boiling point is observed. The boiling point elevation of this urea solution is calculated as follows.

$$\Delta T_b = K_b \times m = 0.512 \text{ }^{\circ}\text{C m}^{-1} \times 0.205 \text{ m} = 0.105 \text{ }^{\circ}\text{C}$$

We would expect this urea solution to boil at  $(100.00 + 0.105) = 100.105^\circ\text{C}$  under 760.0 mmHg atmospheric pressure. Since it boils at a lower temperature, the atmospheric pressure must be lower than 760.0 mmHg.

- 11A** We assume a van't Hoff factor of  $i = 3.00$  and convert the temperature to Kelvin, 298 K.

$$\pi = iMRT = \frac{3.00 \text{ mol ions}}{1 \text{ mol MgCl}_2} \times \frac{0.0530 \text{ mol MgCl}_2}{1 \text{ L soln}} \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K} = 3.89 \text{ atm}$$

- 11B** We first determine the molality of the solution, and assume a van't Hoff factor of  $i = 2.00$ .

$$m = \frac{\Delta T_f}{-K_f \times i} = \frac{-0.100^\circ\text{C}}{-1.86^\circ\text{C m}^{-1} \times 2.00} = 0.0269 \text{ m} \approx 0.0269 \text{ M}$$

$$\text{volume of HCl(aq)} = 250.0 \text{ mL final soln} \times \frac{0.0269 \text{ mmol HCl}}{1 \text{ mL soln}} \times \frac{1 \text{ mL conc soln}}{12.0 \text{ mmol HCl}}$$

$$\text{volume of HCl(aq)} = 0.560 \text{ mL conc soln}$$

## REVIEW QUESTIONS

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- $\chi_B$  is the symbol for the mole fraction of component B: the amount in moles of B divided by the total amount in moles in the solution.
  - $P_A^\circ$  represents the vapor pressure of pure substance A.
  - $K_f$  is the freezing point depression constant, the amount by which the freezing point of a solvent is lowered by having one mole of dissolved particles present in a kilogram of solvent.
  - $i$  is the symbol for the van't Hoff factor, the measured value of a colligative property divided by the value calculated assuming that each mole of solute produces one mole of particles in solution.
  - The activity of a solute is its effective concentration, the concentration it would have to have if solute particles did not interact with each other in solution.
- Henry's law states that the solubility of a gas in a solution is directly proportional to the pressure of that gas above the solution.
  - Freezing point depression is the change in the freezing point of a liquid due to the presence of dissolved solute.
  - Recrystallization is a purification process. An impure solute is dissolved in a solvent. As solvent evaporates away, the less soluble pure solute crystallizes first. When this process is repeated with the crystals obtained they become purer still.
  - A hydrated ion is an ion surrounded by and attracted to water molecules.
  - Deliquescence is the absorbance by a solid of water vapor from the air to such an extent that a saturated solution is formed.

3. (a) Molarity is the amount of dissolved solute in moles per liter of solution, while molality is the amount of dissolved solute in moles per kilogram of solvent.
- (b) In an ideal solution the attractions among particles of all types are approximately the same in strength. In a nonideal solution, there is a disparity in the strengths of these attractive forces.
- (c) More solute can be dissolved in an unsaturated solution. The attempt to dissolve more solute in a supersaturated solution results in the precipitation of some solute.
- (d) Fractional crystallization is the process of first producing a concentrated and warm solution and then chilling it to a point of lower solute solubility to precipitate out some of that solute. Repetition of this process produces very pure solute. Fractional distillation is the repeated vaporization and condensation of a liquid mixture. This also produces quite pure components.
- (e) Osmosis is the motion of solute through a membrane permeable only to it. This creates an imbalance of pressures, if the solvent and solution volumes are limited, known as osmotic pressure. Reverse osmosis describes obtaining pure solvent by pushing a solution through a semipermeable membrane. This, of course, leaves the solute behind.

4. 
$$\% \text{ NaBr} = \frac{116 \text{ g NaBr}}{116 \text{ g NaBr} + 100 \text{ g H}_2\text{O}} \times 100\% = 53.7\% = 53.7 \text{ g NaBr/100 g solution}$$

5. (a) 
$$\% \text{ by volume} = \frac{12.8 \text{ mL CH}_3\text{CH}_2\text{CH}_2\text{OH}}{75.0 \text{ mL soln}} \times 100\% = 17.1\% \text{ CH}_3\text{CH}_2\text{CH}_2\text{OH}$$

(b) 
$$\text{percent by mass} = \frac{12.8 \text{ mL CH}_3\text{CH}_2\text{CH}_2\text{OH} \times \frac{0.803 \text{ g}}{1 \text{ mL}}}{75.0 \text{ mL} \times \frac{0.988 \text{ g}}{1 \text{ mL}}} \times 100\%$$

percent by mass = 13.9%  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  by mass

(c) 
$$\text{percent (mass/vol)} = \frac{12.8 \text{ mL CH}_3\text{CH}_2\text{CH}_2\text{OH} \times \frac{0.803 \text{ g}}{1 \text{ mL}}}{75.0 \text{ mL}} \times 100\%$$

percent (mass/vol) = 13.7  $\frac{\text{mass}}{\text{vol}}\%$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

6. 
$$\text{soln. volume} = 725 \text{ kg NaCl} \times \frac{1000 \text{ g NaCl}}{1 \text{ kg NaCl}} \times \frac{100.00 \text{ g soln}}{3.87 \text{ g NaCl}} \times \frac{75.0 \text{ mL soln}}{76.9 \text{ g soln}} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}}$$
  

$$= 1.83 \times 10^4 \text{ L soln}$$

7. 
$$\text{mass AgNO}_3 = 0.1250 \text{ L soln} \times \frac{0.0321 \text{ mol AgNO}_3}{1 \text{ L soln}} \times \frac{169.9 \text{ g AgNO}_3}{1 \text{ mol AgNO}_3} \times \frac{100.00 \text{ g mixt.}}{99.81 \text{ g AgNO}_3}$$

mass  $\text{AgNO}_3 = 0.683 \text{ g mixture}$

$$8. \text{ molality} = \frac{2.65 \text{ g C}_6\text{H}_4\text{Cl}_2 \times \frac{1 \text{ mol C}_6\text{H}_4\text{Cl}_2}{147.0 \text{ g C}_6\text{H}_4\text{Cl}_2}}{50.0 \text{ mL} \times \frac{0.879 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 0.410 \text{ m}$$

$$9. \text{ molarity} = \frac{6.00 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}}}{100.00 \text{ g soln} \times \frac{1 \text{ mL}}{0.988 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 1.85 \text{ M} = [\text{CH}_3\text{OH}]$$

$$10. \text{ total amount} = 1.28 \text{ mol C}_7\text{H}_{16} + 2.92 \text{ mol C}_8\text{H}_{18} + 2.64 \text{ mol C}_9\text{H}_{20} = 6.84 \text{ moles}$$

$$\begin{aligned} \text{(a)} \quad \chi_{\text{C}_7\text{H}_{16}} &= \frac{1.28 \text{ mol C}_7\text{H}_{16}}{6.84 \text{ moles total}} = 0.187 & \text{(b)} \quad \times 100\% &= 18.7 \text{ mol\% C}_7\text{H}_{16} \\ \chi_{\text{C}_8\text{H}_{18}} &= \frac{2.92 \text{ mol C}_8\text{H}_{18}}{6.84 \text{ moles total}} = 0.427 & \times 100\% &= 42.7 \text{ mol\% C}_8\text{H}_{18} \\ \chi_{\text{C}_9\text{H}_{20}} &= \frac{2.64 \text{ mol C}_9\text{H}_{20}}{6.84 \text{ moles total}} = 0.386 & \times 100\% &= 38.6 \text{ mol\% C}_9\text{H}_{20} \\ &\text{or } 1.00 - 0.187 - 0.427 = 0.386 & &\text{or } 100 - 18.7 - 42.7 = 38.6 \% \end{aligned}$$

$$11. \text{(a)} \quad [\text{C}_3\text{H}_8\text{O}_3] = \frac{62.0 \text{ g C}_3\text{H}_8\text{O}_3 \times \frac{1 \text{ mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3}}{100.0 \text{ g soln} \times \frac{1 \text{ mL soln}}{1.159 \text{ g soln}} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}}} = 7.80 \text{ M}$$

$$\text{(b)} \quad [\text{H}_2\text{O}] = \frac{38.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}}{100.0 \text{ g soln} \times \frac{1 \text{ mL soln}}{1.159 \text{ g soln}} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}}} = 24.4 \text{ M}$$

$$\text{(c)} \quad \text{H}_2\text{O molality} = \frac{38.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}}{62.0 \text{ g C}_3\text{H}_8\text{O}_3 \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 34.0 \text{ m}$$

$$\text{(d)} \quad \text{C}_3\text{H}_8\text{O}_3 \text{ mole fraction} = \frac{\frac{62.0 \text{ g C}_3\text{H}_8\text{O}_3 \times \frac{1 \text{ mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3}}{62.0 \text{ g C}_3\text{H}_8\text{O}_3} + \frac{38.0 \text{ g H}_2\text{O}}{92.09 \text{ g mol}^{-1} \text{ C}_3\text{H}_8\text{O}_3} + \frac{18.02 \text{ g mol}^{-1} \text{ H}_2\text{O}}{18.02 \text{ g mol}^{-1} \text{ H}_2\text{O}}}{\frac{0.674 \text{ mol C}_3\text{H}_8\text{O}_3}{0.674 \text{ mol C}_3\text{H}_8\text{O}_3 + 2.11 \text{ mol H}_2\text{O}}} = 0.242$$

$$(e) \quad \text{H}_2\text{O mole percent} = \frac{2.11 \text{ mol H}_2\text{O}}{0.674 \text{ mol C}_3\text{H}_8\text{O}_3 + 2.11 \text{ mol H}_2\text{O}} \times 100\% = 75.8 \text{ mol \% H}_2\text{O}$$

or  $(1.000 - 0.242) \times 100\% = 75.8 \% \text{ H}_2\text{O}$

12. Solubilities in Figure 14-8 are given as grams of solute per 100 g of solvent.

$$\text{mass NH}_4\text{Cl} = 1.12 \text{ mol NH}_4\text{Cl} \times \frac{53.49 \text{ g NH}_4\text{Cl}}{1 \text{ mol NH}_4\text{Cl}} = 59.9 \text{ g NH}_4\text{Cl}$$

$$\text{Mass of NH}_4\text{Cl} = \frac{59.9 \text{ g NH}_4\text{Cl}}{150.0 \text{ g H}_2\text{O}} \times 100 \text{ g H}_2\text{O} = 39.9 \text{ g NH}_4\text{Cl}$$

From Figure 14-8, the solubility of  $\text{NH}_4\text{Cl}$  in water at  $30^\circ\text{C}$  is 42 g/100 g water. The solution described in the problem is unsaturated.

13. Answer (d) is correct. An ideal solution is most likely to form when the solute and the solvent have similar polarities, and thus the forces between solvent and solute molecules are about the same strength as those among solute or among solvent molecules. In (a),  $\text{NaCl}$  is an ionic solid, while  $\text{H}_2\text{O}$  is a polar liquid. In (b),  $\text{C}_2\text{H}_5\text{OH}$  is a polar liquid, while  $\text{C}_6\text{H}_6(\text{l})$  is nonpolar. In (c),  $\text{C}_7\text{H}_{16}$  is nonpolar, while  $\text{H}_2\text{O}$  is highly polar. In (d), both  $\text{C}_7\text{H}_{16}$  and  $\text{C}_8\text{H}_{18}$  are nonpolar liquids.

14.  $\text{NH}_2\text{OH(s)}$  should be the most water soluble. Both  $\text{C}_6\text{H}_6(\text{l})$  and  $\text{C}_{10}\text{H}_8(\text{s})$  are composed of nonpolar molecules, which are barely (if at all) soluble in water. Both  $\text{NH}_2\text{OH(s)}$  and  $\text{CaCO}_3(\text{s})$  should be able to be attracted by water molecules. But  $\text{CaCO}_3(\text{s})$  contains ions of high charge, difficult to dissolve because of the high lattice energy. (Recall the solubility rules of Chapter 5: most carbonates are insoluble in water.)

15. Butyl alcohol should be moderately soluble in both water and benzene. A solute that is moderately soluble in both solvents will have some properties in common with each solvent. Both naphthalene and hexane are nonpolar molecules, like benzene, but have no properties in common with water molecules; they are soluble in benzene but not in water. Sodium chloride consists of charged ions, similar to the charges in the polar bonds of water. Thus, as expected  $\text{NaCl}$  is very soluble in water. Butyl alcohol, on the other hand, possesses both a nonpolar part ( $\text{C}_4\text{H}_9-$ ) like benzene, and a polar bond ( $-\text{O}-\text{H}$ ) like water. In fact, water and butyl alcohol can mutually hydrogen bond.

16. We first determine the number of moles of  $\text{O}_2$  that have dissolved.

$$\text{amount O}_2 = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 0.02831 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 1.16 \times 10^{-3} \text{ mol O}_2$$

$$[\text{O}_2] = \frac{1.16 \times 10^{-3} \text{ mol O}_2}{1.00 \text{ L soln}} = 1.16 \times 10^{-3} \text{ M}$$

The oxygen concentration now is computed at the higher pressure.

$$[\text{O}_2] = \frac{1.16 \times 10^{-3} \text{ M}}{1 \text{ atm O}_2} \times 3.86 \text{ atm O}_2 = 4.48 \times 10^{-3} \text{ M}$$

17. First determine the number of moles of each component, then its mole fraction in the solution, then the partial pressure due to that component above the solution, and finally the total pressure.

$$\text{amount benzene} = n_b = 35.8 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6} = 0.458 \text{ mol C}_6\text{H}_6$$

$$\text{amount toluene} = n_t = 56.7 \text{ g C}_7\text{H}_8 \times \frac{1 \text{ mol C}_7\text{H}_8}{92.14 \text{ g C}_7\text{H}_8} = 0.615 \text{ mol C}_7\text{H}_8$$

$$\chi_b = \frac{0.458 \text{ mol C}_6\text{H}_6}{(0.458 + 0.615) \text{ total moles}} = 0.427 \quad \chi_t = \frac{0.615 \text{ mol C}_7\text{H}_8}{(0.458 + 0.615) \text{ total moles}} = 0.573$$

$$P_b = 0.427 \times 95.1 \text{ mmHg} = 40.6 \text{ mmHg} \quad P_t = 0.573 \times 28.4 \text{ mmHg} = 16.3 \text{ mmHg}$$

$$\text{total pressure} = 40.6 \text{ mmHg} + 16.3 \text{ mmHg} = 56.9 \text{ mmHg}$$

18. vapor fraction of benzene =  $f_b = \frac{40.6 \text{ mmHg}}{56.9 \text{ mmHg}} = 0.714$

$$\text{vapor fraction of toluene} = f_t = \frac{16.3 \text{ mmHg}}{56.9 \text{ mmHg}} = 0.286$$

These are both pressure fractions, as calculated, and also are the mole fractions in the vapor phase.

19. The freezing point depression is proportional to the product of the solute's molality and the van't Hoff factor. For nonelectrolytes, such as  $\text{C}_2\text{H}_5\text{OH}$  ( $0.050 \text{ m}$ ),  $i = 1$ , and thus  $i \cdot m = 0.050 \text{ m}$ . For 1:1 electrolytes, such as  $\text{MgSO}_4$  and  $\text{NaCl}$ ,  $i = 2$ , and thus  $i \cdot m = 0.020 \text{ m}$  for ( $0.010 \text{ m}$ )  $\text{MgSO}_4$  and  $i \cdot m = 0.022 \text{ m}$  for ( $0.011 \text{ m}$ )  $\text{NaCl}$ . For 1:2 electrolytes, such as  $\text{MgI}_2$  ( $0.010 \text{ m}$ ),  $i = 3$ , and thus  $i \cdot m = 0.030 \text{ m}$ . The  $i \times m$  product is largest for  $\text{C}_2\text{H}_5\text{OH}$ ; thus it has the largest freezing point depression and lowest freezing point.

20. The solution with the largest freezing-point depression will have the lowest freezing point. Since  $\text{C}_2\text{H}_5\text{OH}$  is a nonelectrolyte, it will produce 1 mol of particles per mole of solute, and give the smallest freezing point depression, hence the highest freezing point.

$\text{HC}_2\text{H}_3\text{O}_2$  is a weak electrolyte and produces slightly more than 1 mole of particles per mole of solute; its freezing point is the second lowest.  $\text{NaCl}$ ,  $\text{MgBr}_2$ , and  $\text{Al}_2(\text{SO}_4)_3$  all are strong electrolytes, producing 2, 3, and 5 moles of particles per mole of solute. They are listed in order of decreasing value of the freezing points of their solutions. Thus, the solutes, listed in order of decreasing freezing points of their  $0.01 \text{ m}$  aqueous solutions, are:  $\text{C}_2\text{H}_5\text{OH} > \text{HC}_2\text{H}_3\text{O}_2 > \text{NaCl} > \text{MgBr}_2 > \text{Al}_2(\text{SO}_4)_3$

21. (a)  $[\text{Na}^+] = \frac{0.92 \text{ g NaCl}}{100 \text{ mL soln}} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{1 \text{ mol Na}^+}{1 \text{ mol NaCl}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} = 0.16 \text{ M Na}^+$

$$(b) [\text{ions}] = [\text{Na}^+] + [\text{Cl}^-] = 2 \times [\text{Na}^+] = 2 \times 0.16 \text{ M} = 0.32 \text{ M}$$

$$(c) \quad \pi = \frac{n}{V} RT = \frac{0.32 \text{ mol ions}}{1 \text{ L}} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 310 \text{ K} = 8.1 \text{ atm}$$

- (d) To determine freezing point depression, we first need molality, which means we need mass of solvent.

$$\text{molality} = \frac{0.92 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol NaCl}}}{\left( \left( 100 \text{ mL soln} \times \frac{1.005 \text{ g}}{1 \text{ mL soln}} \right) - 0.92 \text{ g NaCl} \right) \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 0.32 \text{ m}$$

$$\Delta T_f = -K_f \times m = -1.86^\circ\text{C} / \text{m} \times 0.32 \text{ m} = -0.60^\circ\text{C} \quad T_f = -0.60^\circ\text{C}$$

22. We compute the concentration of the solution. Then, assuming that the solution volume is the same as that of the solvent (0.2500 L), we determine the amount of solute dissolved, and finally the molar mass.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{1.67 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 8.98 \times 10^{-5} \text{ M}$$

$$\text{solute amount} = 0.2500 \text{ L} \times \frac{8.98 \times 10^{-5} \text{ mol}}{1 \text{ L}} = 2.25 \times 10^{-5} \text{ mol}$$

$$M = \frac{0.72 \text{ g}}{2.25 \times 10^{-5} \text{ mol}} = 3.2 \times 10^4 \text{ g/mol}$$

23. First compute the molality of the benzene solution, then the number of moles of solute dissolved, and finally the molar mass of the unknown compound.

$$m = \frac{\Delta T_f}{-K_f} = \frac{4.92^\circ\text{C} - 5.53^\circ\text{C}}{-5.12^\circ\text{C}/\text{m}} = 0.12 \text{ m}$$

$$\text{amount solute} = 0.07522 \text{ kg benzene} \times \frac{0.12 \text{ mol solute}}{1 \text{ kg benzene}} = 9.0 \times 10^{-3} \text{ mol solute}$$

$$M = \frac{1.10 \text{ g unknown compound}}{9.0 \times 10^{-3} \text{ mol}} = 1.2 \times 10^2 \text{ g/mol}$$

24. We compute the value of the van't Hoff factor, then use this value to compute the boiling point elevation.

$$i = \frac{\Delta T_b}{-K_b m} = \frac{-0.072^\circ\text{C}}{-1.86^\circ\text{C}/\text{m} \times 0.010 \text{ m}} = 3.9$$

$$\Delta T_b = i K_b m = 3.9 \times 0.512^\circ\text{C} \text{ m}^{-1} \times 0.010 \text{ m} = 0.020^\circ\text{C}$$

The solution begins to boil at 100.02 °C.

## EXERCISES

### Homogeneous and Heterogeneous Mixtures

- 25.** (b) salicyl alcohol probably is moderately soluble in both benzene and water. The reason for this assertion is that salicyl alcohol contains a benzene ring, which would make it soluble in benzene, and also can use its  $-\text{OH}$  groups to hydrogen bond to water molecules. On the other hand, (c) diphenyl contains only nonpolar benzene rings; it should be soluble in benzene but not in water. (a) *para*-dichlorobenzene contains a benzene ring, making it soluble in benzene, and two polar C–Cl bonds, which oppose each other, producing a nonpolar—and thus water-insoluble—molecule. (d) hydroxyacetic acid is a very polar molecule with many opportunities for hydrogen bonding. Its polar nature would make it insoluble in benzene, while the prospective hydrogen bonds will enhance aqueous solubility.
- 27.** (c) formic acid and (f) propylene glycol are soluble in water. They both can form hydrogen bonds with water, and they both have small nonpolar portions. (b) benzoic acid and (d) butyl alcohol are only slightly soluble in water. Although they both can form hydrogen bonds with water, both molecules contain reasonably large nonpolar portions, which will not interact strongly with water. (a) iodoform and (e) chlorobenzene are insoluble in water. Although both molecules have polar groups, their influence is too small to enable the molecules to disrupt the hydrogen bonds in water and form a homogeneous liquid mixture.
- 29.** We expect small, highly charged ions to form crystals with large lattice energies, a factor that decreases their solubility. Based on this information, we would expect  $\text{MgF}_2$  to be insoluble and  $\text{KF}$  to be soluble. It is probable that  $\text{CaF}_2$  is insoluble due to a high lattice energy, but that  $\text{NaF}$ , with a smaller lattice energy, is soluble.  $\text{KF}$  is probably the most water soluble. Actual solubilities at  $25^\circ\text{C}$  are:  $0.00020\text{ M CaF}_2 < 0.0021\text{ M MgF}_2 < 0.95\text{ M NaF} < 16\text{ M KF}$ .

### Percent Concentration

- 31.** For water, the mass in grams and the volume in mL are about equal; the density of water is close to  $1.0\text{ g/mL}$ . For ethanol, on the other hand, the density is about  $0.8\text{ g/mL}$ . As long as the final solution volume after mixing is close to sum of the volumes for the two pure liquids, the percent by volume of ethanol will have to be larger than its percent by mass. This would not necessarily be true of other ethanol solutions. It would only be true in those cases where the density of the other component is greater than the density of ethanol.
- 33.**  $\text{mass HC}_2\text{H}_3\text{O}_2 = 355\text{ mL vinegar} \times \frac{1.01\text{ g vinegar}}{1\text{ mL}} \times \frac{6.02\text{ g HC}_2\text{H}_3\text{O}_2}{100.00\text{ g vinegar}}$
- $$\text{mass HC}_2\text{H}_3\text{O}_2 = 21.6\text{ g HC}_2\text{H}_3\text{O}_2$$

35.  $46.1 \text{ ppm} = \frac{46.1 \text{ mg SO}_4^{2-}}{1 \text{ L solution}} \text{ (Assumes density of water } \sim 1.00 \text{ g mL}^{-1}\text{)}$

$$[\text{SO}_4^{2-}] = \frac{46.1 \text{ mg SO}_4^{2-}}{1 \text{ L solution}} \times \frac{1 \text{ g SO}_4^{2-}}{1000 \text{ mg SO}_4^{2-}} \times \frac{1 \text{ mol SO}_4^{2-}}{96.06 \text{ g SO}_4^{2-}} = 4.80 \times 10^{-4} \text{ M}$$

## Molarity

37. The solution of Example 14-1 is 1.71 M  $\text{C}_2\text{H}_5\text{OH}$ , or 1.71 mmol  $\text{C}_2\text{H}_5\text{OH}$  in each mL of solution.

$$\text{volume conc. soln} = 825 \text{ mL} \times \frac{0.235 \text{ mmol C}_2\text{H}_5\text{OH}}{1 \text{ mL soln}} \times \frac{1 \text{ mL conc. soln}}{1.71 \text{ mmol C}_2\text{H}_5\text{OH}}$$

$$\text{volume conc. soln} = 113 \text{ mL conc. soln}$$

## Molality

39. The mass of solvent in kg multiplied by the molality gives the amount in moles of the solute.

$$\text{mass I}_2 = \left( 725.0 \text{ mL CS}_2 \times \frac{1.261 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \right) \times \frac{0.236 \text{ mol I}_2}{1 \text{ kg CS}_2} \times \frac{253.8 \text{ g I}_2}{1 \text{ mol I}_2} = 54.8 \text{ g I}_2$$

41.  $\text{H}_3\text{PO}_4$  molarity =  $\frac{34.0 \text{ g H}_3\text{PO}_4 \times \frac{1 \text{ mol H}_3\text{PO}_4}{98.00 \text{ g H}_3\text{PO}_4}}{100.0 \text{ g soln} \times \frac{1 \text{ mL}}{1.209 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 4.19 \text{ M}$

$$\text{molality} = \frac{34.0 \text{ g H}_3\text{PO}_4 \times \frac{1 \text{ mol H}_3\text{PO}_4}{98.00 \text{ g H}_3\text{PO}_4}}{66.0 \text{ g solvent} \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 5.26 \text{ m}$$

## Mole Fraction, Mole Percent

43. (a) amount  $\text{C}_2\text{H}_5\text{OH} = 21.7 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} = 0.471 \text{ mol C}_2\text{H}_5\text{OH}$

$$\text{amount H}_2\text{O} = 78.3 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 4.35 \text{ mol H}_2\text{O}$$

$$\chi_{\text{ethanol}} = \frac{0.471 \text{ mol C}_2\text{H}_5\text{OH}}{(0.471 + 4.34) \text{ total moles}} = 0.0979$$

(b) amount  $\text{H}_2\text{O} = 1000. \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 55.49 \text{ mol H}_2\text{O}$

$$\chi_{\text{urea}} = \frac{0.684 \text{ mol urea}}{(55.49 + 0.684) \text{ total moles}} = 0.0122$$

45. Solve the following relationship for  $n_{\text{ethanol}}$ , the number of moles of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ . The number of moles of water calculated in the Example is 5.01 moles, that of ethanol is 0.171 moles.

$$\chi_{\text{ethanol}} = \frac{n_{\text{ethanol}}}{n_{\text{ethanol}} + 5.01 \text{ mol H}_2\text{O}} = 0.0525 \quad n_{\text{ethanol}} = 0.0525 n_{\text{ethanol}} + 0.263$$

$$n_{\text{ethanol}} = \frac{0.263}{1.0000 - 0.0525} = 0.278 \text{ mol ethanol}$$

$$\text{moles of added ethanol} = (0.278 - 0.171) \text{ mol C}_2\text{H}_5\text{OH} = 0.107 \text{ mol C}_2\text{H}_5\text{OH}$$

$$\text{mass added ethanol} = 0.107 \text{ mol C}_2\text{H}_5\text{OH} \times \frac{46.07 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ mol C}_2\text{H}_5\text{OH}} = 4.93 \text{ g C}_2\text{H}_5\text{OH}$$

## Solubility Equilibrium

47. At 40 °C the solubility of  $\text{NH}_4\text{Cl}$  is 46.3 g per 100 g of  $\text{H}_2\text{O}$ . To determine molality, we calculate amount in moles of the solute and the solvent mass in kg.

$$\text{molarity} = \frac{46.3 \text{ g} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}}}{100 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 8.66 \text{ m}$$

49. (a) The concentration for  $\text{KClO}_4$  in this mixture is calculated first.

$$\frac{\text{mass solute}}{100 \text{ g H}_2\text{O}} = 100 \text{ g H}_2\text{O} \times \frac{20.0 \text{ g KClO}_4}{500.0 \text{ g water}} = 4.00 \text{ g KClO}_4$$

At 40 °C a saturated  $\text{KClO}_4$  solution has a concentration of about 4.6 g  $\text{KClO}_4$  dissolved in 100 g water. Thus, the solution is unsaturated.

- (b) The mass of  $\text{KClO}_4$  that must be added is the difference between the mass now present in the mixture and the mass that is dissolved in 500 g  $\text{H}_2\text{O}$  to produce a saturated solution.

$$\text{mass to be added} = \left( 500.0 \text{ g H}_2\text{O} \times \frac{4.6 \text{ g KClO}_4}{100 \text{ g H}_2\text{O}} \right) - 20.0 \text{ g KClO}_4 = 3.0 \text{ g KClO}_4$$

## Solubility of Gases

51. mass of  $\text{CH}_4 = 1.00 \times 10^3 \text{ kg H}_2\text{O} \times \frac{0.02 \text{ g CH}_4}{1 \text{ kg H}_2\text{O} \cdot \text{ atm}} \times 20 \text{ atm} = 4 \times 10^2 \text{ g CH}_4$  (natural gas)

53. We use the STP molar volume (22.414 L = 22,414 mL) to determine the molarity of Ar under 1 atm pressure and then the Henry's law constant.

$$k_{\text{Ar}} = \frac{C}{P_{\text{Ar}}} = \frac{\frac{33.7 \text{ mL Ar}}{1 \text{ L soln}} \times \frac{1 \text{ mol Ar}}{22,414 \text{ mL at STP}}}{1 \text{ atm pressure}} = \frac{0.00150 \text{ M}}{\text{atm}}$$

In the atmosphere, the partial pressure of argon is  $P_{\text{Ar}} = 0.00934 \text{ atm}$ . (Recall that pressure fractions equal volume fractions for ideal gases.) We now compute the concentration of argon in aqueous solution.

$$C = k_{\text{Ar}} P_{\text{Ar}} = \frac{0.00150 \text{ M}}{\text{atm}} \times 0.00934 \text{ atm} = 1.40 \times 10^{-5} \text{ M}$$

55. Equation 14.2 is  $c = kP_{\text{gas}}$ . Concentration,  $c$ , is the number of moles of gas dissolved in a fixed volume of solution. But gas solubilities are quite low and thus the volume of solution is almost exactly the same as volume of solvent. Of course the amount of gas in moles is directly proportional to its mass. Therefore the two statements are equivalent.

## Raoult's Law and Liquid-Vapor Equilibrium

57. We determine the mole fraction of water in this solution.

$$n_{\text{glucose}} = 165 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.916 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$n_{\text{water}} = 685 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 38.0 \text{ mol H}_2\text{O} \quad \chi_{\text{water}} = \frac{38.0 \text{ mol H}_2\text{O}}{(38.0 + 0.916) \text{ total moles}} = 0.976$$

$$P_{\text{soln}} = \chi_{\text{water}} P_{\text{water}} = 0.976 \times 23.8 \text{ mmHg} = 23.2 \text{ mmHg}$$

59. We consider a sample of 100.0 g of the solution and determine the number of moles of each component in this sample. From this information and the given vapor pressures, we determine the vapor pressure of each component.

$$\text{amount styrene} = n_s = 38 \text{ g styrene} \times \frac{1 \text{ mol C}_8\text{H}_8}{104 \text{ g C}_8\text{H}_8} = 0.37 \text{ mol C}_8\text{H}_8$$

$$\text{amount ethylbenzene} = n_e = 62 \text{ g ethylbenzene} \times \frac{1 \text{ mol C}_8\text{H}_{10}}{106 \text{ g C}_8\text{H}_{10}} = 0.58 \text{ mol C}_8\text{H}_{10}$$

$$\chi_s = \frac{n_s}{n_s + n_e} = \frac{0.37 \text{ mol styrene}}{(0.37 + 0.58) \text{ total moles}} = 0.39; \quad P_s = 0.39 \times 134 \text{ mmHg} = 52 \text{ mmHg for C}_8\text{H}_8$$

$$\chi_e = \frac{n_e}{n_s + n_e} = \frac{0.58 \text{ mol ethylbenzene}}{(0.37 + 0.58) \text{ total moles}} = 0.61; \quad P_e = 0.61 \times 182 \text{ mmHg} = 111 \text{ mmHg for C}_8\text{H}_{10}$$

Then the mole fraction in the vapor can be determined.

$$y_e = \frac{P_e}{P_e + P_s} = \frac{111 \text{ mmHg}}{(111 + 52) \text{ mmHg}} = 0.68 \quad y_s = 1.00 - 0.68 = 0.32$$

61. The total vapor pressure above the solution at its normal boiling point is 760 mm Hg. The vapor pressure due to toluene is given by the following equation.

$$P_{\text{toluene}} = \chi_{\text{toluene}} \cdot P^{\circ}_{\text{toluene}} = 0.700 \times 533 \text{ mm Hg} = 373 \text{ mm Hg}$$

Next, the vapor pressure due to benzene is determined, followed by the vapor pressure of pure benzene.

$$P_{\text{benzene}} = P_{\text{total}} - P_{\text{toluene}} = 760 \text{ mm Hg} - 373 \text{ mm Hg} = 387 \text{ mm Hg} = \chi_{\text{benzene}} \cdot P^{\circ}_{\text{benzene}}$$

$$387 \text{ mm Hg} = 0.300 \times P^{\circ}_{\text{benzene}} \text{ and hence, } P^{\circ}_{\text{benzene}} = 1.29 \times 10^3 \text{ mm Hg}$$

## Osmotic Pressure

63. Both the flowers and the cucumber contain solutions (plant sap), but both of these solutions are less concentrated than the salt solution. Thus, the solution in the plant material moves across the semipermeable membrane in an attempt to dilute the salt solution, leaving behind wilted flowers and shriveled pickles (less water in their tissues).
65. We first determine the molarity of the solution. Let's work the problem with three significant figures.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{1.00 \text{ atm}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}} = 0.0446 \text{ M}$$

$$\text{volume} = 1 \text{ mol} \times \frac{1 \text{ L}}{0.0446 \text{ mol solute}} = 22.4 \text{ L solution} \approx 22.4 \text{ L solvent}$$

We have assumed that the solution is so dilute that its volume closely approximates the volume of the solvent constituting it. Note that this volume corresponds to the STP molar volume of an ideal gas. The osmotic pressure equation also resembles the ideal gas equation.

67. First determine the concentration of the solution from the osmotic pressure, then the amount of solute dissolved, and finally the molar mass of that solute.

$$\pi = 5.1 \text{ mm soln} \times \frac{0.88 \text{ mmHg}}{13.6 \text{ mm soln}} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 4.3 \times 10^{-4} \text{ atm}$$

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{4.3 \times 10^{-4} \text{ atm}}{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{amount solute} = 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 1.8 \times 10^{-5} \text{ M} = 1.8 \times 10^{-6} \text{ mol solute}$$

$$M = \frac{0.50 \text{ g}}{1.8 \times 10^{-6} \text{ mol}} = 2.8 \times 10^5 \text{ g / mol}$$

- 69.** The reverse osmosis process requires a pressure equal to or slightly greater than the osmotic pressure of the solution. We assume that this solution has a density of 1.00 g/mL. First, we determine the molar concentration of ions in the solution.

$$[\text{ions}] = \frac{2.5 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol NaCl}}}{100.0 \text{ mL soln} \times \frac{1 \text{ mL soln}}{1.00 \text{ g}} \times \frac{1 \text{ L soln}}{1000 \text{ mL}}} = 0.86 \text{ M}$$

$$\pi = \frac{n}{V} RT = 0.86 \frac{\text{mol}}{\text{L}} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times (25 + 273.2) \text{ K} = 21 \text{ atm}$$

## Freezing Point Depression and Boiling Point Elevation

- 71. (a)** First determine the molality of the solution, then the value of the freezing-point depression constant.

$$m = \frac{1.00 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6}}{80.00 \text{ g solvent} \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 0.160 \text{ m} \quad K_f = \frac{\Delta T_f}{-m} = \frac{3.3^\circ\text{C} - 6.5^\circ\text{C}}{-0.160 \text{ m}} = 20.^\circ\text{C/m}$$

- (b)** For benzene,  $K_f = 5.12 \text{ }^\circ\text{C m}^{-1}$ . Cyclohexane is the better solvent for freezing point depression determinations of molar mass, since a less concentrated solution will still give a substantial freezing-point depression. For the same concentration, cyclohexane solutions will show a freezing point depression approximately four times that of benzene. (Another factor is that benzene is labeled as a carcinogen and should be avoided.)

- 73.** We determine the molality of the solution, then the number of moles of solute present, and then the molar mass of the solute. Then we determine the compound's empirical formula, and combine this with the molar mass to determine the molecular formula.

$$m = \frac{\Delta T_f}{-K_f} = \frac{1.37 \text{ }^\circ\text{C} - 5.53 \text{ }^\circ\text{C}}{-5.12 \text{ }^\circ\text{C/m}} = 0.813 \text{ m}$$

$$\text{amount} = \left( 50.0 \text{ mL C}_6\text{H}_6 \times \frac{0.879 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \right) \times \frac{0.813 \text{ mol solute}}{1 \text{ kg C}_6\text{H}_6} = 3.57 \times 10^{-2} \text{ mol}$$

$$M = \frac{6.45 \text{ g}}{3.57 \times 10^{-2} \text{ mol}} = 181 \text{ g/mol}$$

$$42.9 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.57 \text{ mol C} \quad \div 1.19 \rightarrow 3.00 \text{ mol C}$$

$$2.4 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 2.4 \text{ mol H} \quad \div 1.19 \rightarrow 2.0 \text{ mol H}$$

$$16.7 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.19 \text{ mol N} \quad \div 1.19 \rightarrow 1.00 \text{ mol N}$$

$$38.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.38 \text{ mol O} \quad \div 1.19 \rightarrow 2.00 \text{ mol O}$$

The empirical formula is  $\text{C}_3\text{H}_2\text{NO}_2$ , with a formula mass of 84.0 g/mol. This is one-half the experimentally determined molar mass. Thus, the molecular formula is  $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ .

75. We determine the molality of the benzene solution first, then the molar mass of the solute.

$$m = \frac{\Delta T_f}{-K_f} = \frac{-1.183^\circ\text{C}}{-5.12^\circ\text{C/m}} = 0.231 \text{ m}$$

$$\text{amount solute} = 0.04456 \text{ kg benzene} \times \frac{0.231 \text{ mol solute}}{1 \text{ kg benzene}} = 0.0103 \text{ mol solute}$$

$$M = \frac{0.867 \text{ g thiophene}}{0.0103 \text{ mol thiophene}} = 84.2 \text{ g/mol}$$

Next, we determine the empirical formula from the masses of the combustion products.

$$\text{amount C} = 4.913 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.1116 \text{ mol C} \div 0.02791 \rightarrow 4.000 \text{ mol C}$$

$$\text{amount H} = 1.005 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.1116 \text{ mol H} \div 0.02791 \rightarrow 4.000 \text{ mol H}$$

$$\text{amount S} = 1.788 \text{ g SO}_2 \times \frac{1 \text{ mol SO}_2}{64.065 \text{ g SO}_2} \times \frac{1 \text{ mol S}}{1 \text{ mol SO}_2} = 0.02791 \text{ mol S} \div 0.02791 \rightarrow 1.000 \text{ mol S}$$

A reasonable empirical formula is  $\text{C}_4\text{H}_4\text{S}$ , which has an empirical mass of 84.1 g/mol.

Since this is the same as the experimentally determined molar mass, the molecular formula of thiophene is  $\text{C}_4\text{H}_4\text{S}$ .

77. The boiling point must go up by 2 degrees, so  $\Delta T_b = 2^\circ\text{C}$ . We know that  $K_b = 0.512^\circ\text{C/m}$  for water. We assume that the mass of a litre of water is 1.000 kg and that the van't Hoff factor for NaCl is  $i = 2.00$ . We first determine the molality of the saltwater solution and then the mass of solute needed.

$$m = \frac{\Delta T_b}{i K_b} = \frac{2^\circ\text{C}}{2.00 \times 0.512^\circ\text{C/m}} = 2 \text{ m}$$

$$\text{solute mass} = 1.00 \text{ L H}_2\text{O} \times \frac{1 \text{ kg H}_2\text{O}}{1 \text{ L H}_2\text{O}} \times \frac{2 \text{ mol NaCl}}{1 \text{ kg H}_2\text{O}} \times \frac{58.4 \text{ g NaCl}}{1 \text{ mol NaCl}} = 120 \text{ g NaCl}$$

This is at least ten times the amount of salt one would typically add to a liter of water for cooking purposes.

## Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes

79. The freezing point depression is given by  $\Delta T_f = -iK_f m$ . Since  $K_f = 1.86^\circ\text{C/m}$  for water,  $\Delta T_f = -i0.186^\circ\text{C}$  for this group of 0.10m solutions.

(a)  $T_f = -0.19^\circ\text{C}$  Urea is a nonelectrolyte, and  $i = 1$ .

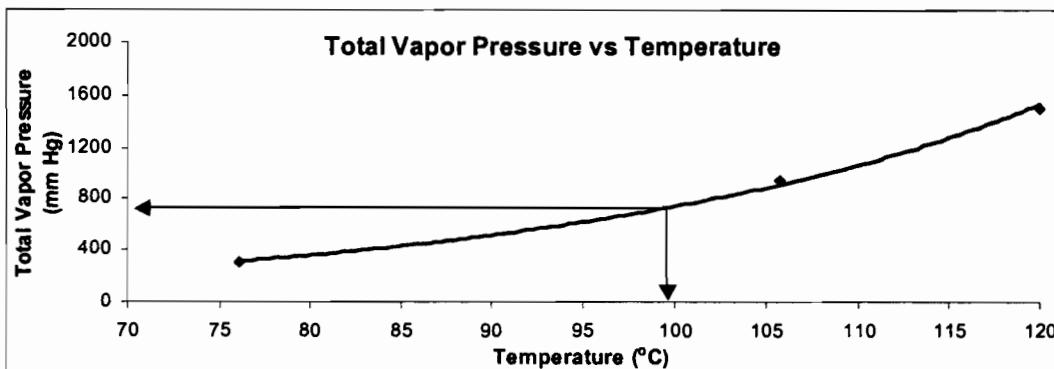
- (b)  $T_f = -0.37^\circ\text{C}$   $\text{NH}_4\text{NO}_3$  is a strong electrolyte, composed of two ions per formula unit;  $i = 2$ .
- (c)  $T_f = -0.37^\circ\text{C}$   $\text{HCl}$  is a strong electrolyte, composed of two ions per formula unit;  $i = 2$ .
- (d)  $T_f = -0.56^\circ\text{C}$   $\text{CaCl}_2$  is a strong electrolyte, composed of three ions per formula unit;  $i = 3$ .
- (e)  $T_f = -0.37^\circ\text{C}$   $\text{MgSO}_4$  is a strong electrolyte, composed of two ions per formula unit;  $i = 2$ .
- (f)  $T_f = -0.19^\circ\text{C}$  Ethanol is a nonelectrolyte;  $i = 1$ .
- (g)  $T_f < -0.19^\circ\text{C}$   $\text{HC}_2\text{H}_3\text{O}_2$  is a weak electrolyte;  $i$  is somewhat larger than 1.
- 81.** The combination of  $\text{NH}_3\text{(aq)}$  with  $\text{HC}_2\text{H}_3\text{O}_2\text{(aq)}$ , results in the formation of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2\text{(aq)}$ , a solution of an ionic substance and a strong electrolyte.
- $$\text{NH}_3\text{(aq)} + \text{HC}_2\text{H}_3\text{O}_2\text{(aq)} \rightarrow \text{NH}_4\text{C}_2\text{H}_3\text{O}_2\text{(aq)} \rightarrow \text{NH}_4^+\text{(aq)} + \text{C}_2\text{H}_3\text{O}_2^-\text{(aq)}$$
- This solution of strong electrolyte conducts a current very well.

## FEATURE PROBLEMS

- 105. (a)** The temperature at which the total vapor pressure is equal to 760 mm Hg corresponds to the boiling point for the cinnamaldehyde/ $\text{H}_2\text{O}$  mixture. Consequently, to find the temperature at which steam distillation begins under 1 atm pressure, we must construct a plot of  $P_{\text{total}}$  against the temperature. The data needed for this graph and a separate graph required for the answer to part (c) are given in the table below.

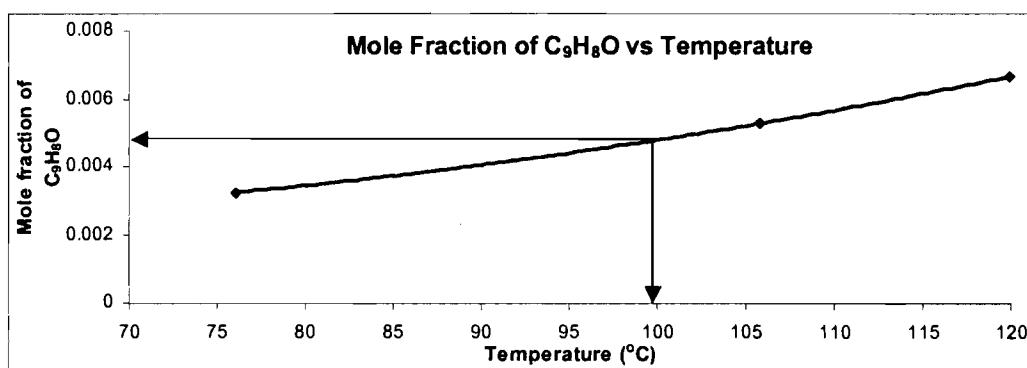
Temperature (°C)	$P_{\text{H}_2\text{O}}$ (mmHg)	$P_{\text{C}_9\text{H}_8\text{O}}$ (mmHg)	$P_{\text{total}}$ (mmHg)	Mole fraction of $\text{C}_9\text{H}_8\text{O}$
76.1	308	1	309	$3.24 \times 10^{-3}$
105.8	942	5	947	$5.28 \times 10^{-3}$
120.0	1489	10	1499	$6.67 \times 10^{-3}$

The graph of total vapor pressure vs temperature is drawn below:



According to this plot, when the barometric pressure is 1 atm. (i.e. 760 mmHg), distillation occurs at 99.6 °C. Thus, as one would expect for a steam distillation, the boiling point for the mixture is below the boiling point for the lower boiling point component, viz. water. Moreover, the graph shows that the boiling point for this mixture is close to that for pure water and, once again, this is the anticipated result since the mixture contains very little cinnamaldehyde.

- (b) The condensate that is collected in a steam distillation is the liquefied form of the gaseous mixture generated in the distillation pot. The composition of the gaseous mixture and that of the derived condensate is determined not by the composition of the liquid mixture but rather by the vapor pressure for each component at the boiling point. The boiling point of the cinnamaldehyde/H<sub>2</sub>O mixture will stay fixed at 99.6 °C and the composition will remain at 99.54 mole % H<sub>2</sub>O and 0.464 % cinnamaldehyde as long as there is at least a modicum of each component present.
- (c) To answer this part of the question we must construct a plot of the mole fraction of cinnamaldehyde against temperature. The graph, which is drawn below, shows that the mole fraction for cinnamaldehyde at the boiling point (99.6 °C) is 0.00464.



Because the concentration of each component in the vapor is directly proportional to its vapor pressure, the number of moles of component A divided by the moles of component B is equal to the partial pressure for component A divided by the partial pressure of component B.

$$\frac{\text{# moles component A}}{\text{# moles component B}} = \frac{P_{\text{component A}}}{P_{\text{component B}}}$$

$$\text{Expressed another way, } \frac{\text{Mass A}}{\text{Mass B}} = \frac{P_{\text{component A}}}{P_{\text{component B}}} \times \frac{\text{Molar Mass component A}}{\text{Molar Mass component B}}$$

If we make cinnamaldehyde component A and water component B, and then plug in the appropriate numbers into the second equation involving masses, we obtain

$$P_{\text{cinn}} = 0.00464 \times (760 \text{ mmHg}) = \sim 3.53 \text{ mmHg};$$

$$P_{\text{H}_2\text{O}} = (760 - 3.53) \text{ mmHg} = \sim 756 \text{ mmHg}$$

$$\frac{\text{Mass C}_9\text{H}_8\text{O}}{\text{Mass H}_2\text{O}} = \frac{3.53 \text{ mmHg}}{756 \text{ mm Hg}} \times \frac{\frac{132 \text{ g C}_9\text{H}_8\text{O}}{1 \text{ mol C}_9\text{H}_8\text{O}}}{\frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}} = 3.42 \times 10^{-2}$$

Clearly then, water condenses in the greater quantity by mass. In fact, every gram of cinnamaldehyde that condenses is accompanied by  $\sim 29$  g of water in the collection flask!

- 106. (a)** A solution with  $\chi_{\text{HCl}} = 0.50$  begins to boil at about  $18^\circ \text{ C}$ . At that temperature the composition of the vapor is about  $\chi_{\text{HCl}} = 0.63$ , reading directly across the tie line at  $18^\circ \text{ C}$ . The vapor has  $\chi_{\text{HCl}} > 0.50$ .
- (b)** The composition of  $\text{HCl}(\text{aq})$  changes as the solution boils in an open container because the vapor has a different composition than does the liquid. Thus, the component with the lower boiling point is depleted as the solution boils.
- (c)** The azeotrope occurs at the maximum of the curve: at  $\chi_{\text{HCl}} = 0.12$  and a boiling temperature of  $110^\circ \text{ C}$ .
- (d)** We first determine the amount of  $\text{HCl}$  in the sample.

$$\text{amount HCl} = 30.32 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.006 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}}$$

$$\text{amount HCl} = 0.03050 \text{ mol HCl}$$

The mass of water is the difference between the mass of solution and that of  $\text{HCl}$ .

$$\text{mass H}_2\text{O} = \left( 5.00 \text{ mL soln} \times \frac{1.099 \text{ g}}{1 \text{ mL}} \right) - \left( 0.03050 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} \right) = 4.38 \text{ g}$$

Now we determine the amount of  $\text{H}_2\text{O}$  and then the mole fraction of  $\text{HCl}$ .

$$\text{amount H}_2\text{O} = 4.38 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 0.243 \text{ mol H}_2\text{O}$$

$$\chi_{\text{HCl}} = \frac{0.03050 \text{ mol HCl}}{0.03050 \text{ mol HCl} + 0.243 \text{ mol H}_2\text{O}} = 0.111$$

- 107. (a)** At  $20^\circ \text{ C}$ , the solubility of  $\text{NaCl}$  is  $35.9 \text{ g NaCl} / 100 \text{ g H}_2\text{O}$ . We determine the mole fraction of  $\text{H}_2\text{O}$  in this solution

$$\text{amount H}_2\text{O} = 100 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 5.549 \text{ mol H}_2\text{O}$$

$$\text{amount NaCl} = 35.9 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.614 \text{ mol NaCl}$$

$$\chi_{\text{water}} = \frac{5.549 \text{ mol H}_2\text{O}}{0.614 \text{ mol NaCl} + 5.549 \text{ mol H}_2\text{O}} = 0.9004$$

The approximate relative humidity then will be 90% (90.04 %), because the water vapor pressure above the NaCl saturated solution will be 90.04% of the vapor pressure of pure water at 20° C.

- (b)  $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$  deliquesces if the relative humidity is over 32%. Thus,  $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$  will deliquesce.
- (c) If the substance in the bottom of the dessicator has a high water solubility its saturated solution will have a low  $\chi_{\text{water}}$ , which in turn will produce a low relative humidity. Relative humidity lower than 32% is needed to keep  $\text{CaCl}_2 \cdot 6 \text{ H}_2\text{O}$  dry.

- 108. (a)** We first compute the molality of a 0.92% mass/volume solution, assuming a solution density of about 1.00 g/mL, meaning that 100.0 mL solution has a mass of 100.0 g.

$$\text{molality} = \frac{0.92 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}}}{(100.0 \text{ g soln} - 0.92 \text{ g NaCl}) \times \frac{1 \text{ kg solvent}}{1000 \text{ g}}} = 0.16 \text{ m}$$

Then we compute the freezing point depression of this solution.

$$\Delta T_f = -iK_f m = \frac{-2.0 \text{ mol ions}}{\text{mol NaCl}} \times \frac{1.86^\circ\text{C}}{\text{m}} \times 0.16 \text{ m} = -0.61^\circ\text{C}$$

The van't Hoff factor of NaCl most likely is not equal to 2.0, but a bit less and thus the two definitions are in fair agreement.

- (b) We calculate the amount of each solute, assume 1.00 L of solution has a mass of 1000 g, and subtract the mass of all solutes to determine the mass of solvent.

$$\text{amount NaCl ions} = 3.5 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol NaCl}} = 0.12 \text{ mol ions}$$

$$\text{amount KCl ions} = 1.5 \text{ g} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol KCl}} = 0.040 \text{ mol ions}$$

$$\text{amount Na}_3\text{C}_6\text{H}_5\text{O}_7 \text{ ions} = 2.9 \text{ g} \times \frac{1 \text{ mol Na}_3\text{C}_6\text{H}_5\text{O}_7}{258.07 \text{ g Na}_3\text{C}_6\text{H}_5\text{O}_7} \times \frac{4 \text{ mol ions}}{1 \text{ mol Na}_3\text{C}_6\text{H}_5\text{O}_7}$$

$$\text{amount Na}_3\text{C}_6\text{H}_5\text{O}_7 \text{ ions} = 0.045 \text{ mol ions}$$

$$\text{amount C}_6\text{H}_{12}\text{O}_6 = 20.0 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.111 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$\text{solvent mass} = 1000.0 \text{ g} - (3.5 \text{ g} + 1.5 \text{ g} + 2.9 \text{ g} + 20.0 \text{ g}) = 972.1 \text{ g H}_2\text{O}$$

$$\text{solvent mass} = 0.9721 \text{ kg H}_2\text{O}$$

$$\text{solution molality} = \frac{(0.120 + 0.040 + 0.045 + 0.111) \text{ mol}}{0.9721 \text{ kg H}_2\text{O}} = 0.325 \text{ m}$$

$$\Delta T_f = -K_f m = -1.86^\circ\text{C/m} \times 0.325 \text{ m} = -0.60^\circ\text{C}$$

This again is close to the defined freezing point of  $-0.52^\circ\text{C}$ , with the error most likely arising from the van't Hoff factors not being integral.

# CHAPTER 15

## CHEMICAL KINETICS

### PRACTICE EXAMPLES

- 1A** The rate of reaction for a reactant is expressed as the negative of the change in molarity divided by the time interval. Thus rate of reaction of A

$$= \frac{-\Delta[A]}{\Delta t} = \frac{-(0.3187 \text{ M} - 0.3629 \text{ M})}{8.25 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ sec}} = 8.93 \times 10^{-5} \text{ M sec}^{-1}$$

- 1B** We use the rate of reaction of A to determine the rate of formation of B, noting from the balanced equation that 3 moles of B form (+3 moles B) when 2 moles of A react (-2 moles A). (Recall that "M" means "moles per liter.")

$$\text{rate of B formation} = \frac{0.5522 \text{ M A} - 0.5684 \text{ M A}}{2.50 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}} \times \frac{+3 \text{ moles B}}{-2 \text{ moles A}} = 1.62 \times 10^{-4} \text{ M s}^{-1}$$

- 2A (a)** The 2400-s tangent line intersects the 1200-s vertical line at 0.75 M and reaches 0 M at 3500 s. The slope of that tangent line is thus

$$\text{slope} = \frac{0 \text{ M} - 0.75 \text{ M}}{3500 \text{ s} - 1200 \text{ s}} = -3.3 \times 10^{-4} \text{ M s}^{-1} = -\text{instantaneous rate of reaction}$$

The instantaneous rate of reaction =  $3.3 \times 10^{-4} \text{ M s}^{-1}$

- (b)** At 2400 s,  $[\text{H}_2\text{O}_2] = 0.39 \text{ M}$ . At 2450 s,  $[\text{H}_2\text{O}_2] = 0.39 \text{ M} + \text{rate} \times \Delta t$

$$\begin{aligned} \text{At 2450 s, } [\text{H}_2\text{O}_2] &= 0.39 \text{ M} + [-3.3 \times 10^{-4} \text{ mol H}_2\text{O}_2 \text{ L}^{-1}\text{s}^{-1} \times 50 \text{ s}] \\ &= 0.39 \text{ M} - 0.017 \text{ M} = 0.37 \text{ M} \end{aligned}$$

- 2B** With only the data of Table 15.2 we can use only the reaction rate during the first 400 s,  $-\Delta[\text{H}_2\text{O}_2]/\Delta t = 15.0 \times 10^{-4} \text{ M s}^{-1}$ , and the initial concentration,  $[\text{H}_2\text{O}_2]_0 = 2.32 \text{ M}$ .

We calculate the change in  $[\text{H}_2\text{O}_2]$  and add it to  $[\text{H}_2\text{O}_2]_0$  to determine  $[\text{H}_2\text{O}_2]_{100}$ .

$$\Delta[\text{H}_2\text{O}_2] = \text{rate of reaction of H}_2\text{O}_2 \times \Delta t = -15.0 \times 10^{-4} \text{ M s}^{-1} \times 100 \text{ s} = -0.15 \text{ M}$$

$$[\text{H}_2\text{O}_2]_{100} = [\text{H}_2\text{O}_2]_0 + \Delta[\text{H}_2\text{O}_2] = 2.32 \text{ M} + (-0.15 \text{ M}) = 2.17 \text{ M}$$

This value differs from the value of 2.15 M determined in *text* Example 15-2b because the *text* used the initial rate of reaction ( $17.1 \times 10^{-4} \text{ M s}^{-1}$ ), which is a bit faster than the average rate over the first 400 seconds.

- 3A** We write the equation for each rate, divide them into each other, and solve for  $n$ .

$$R_1 = k \times [N_2O_5]_1^n = 5.45 \times 10^{-5} \text{ M s}^{-1} = k(3.15 \text{ M})^n$$

$$R_2 = k \times [N_2O_5]_2^n = 1.35 \times 10^{-5} \text{ M s}^{-1} = k(0.78 \text{ M})^n$$

$$\frac{R_1}{R_2} = \frac{5.45 \times 10^{-5} \text{ M s}^{-1}}{1.35 \times 10^{-5} \text{ M s}^{-1}} = 4.04 = \frac{k \times [N_2O_5]_1^n}{k \times [N_2O_5]_2^n} = \frac{k(3.15 \text{ M})^n}{k(0.78 \text{ M})^n} = \left(\frac{3.15}{0.78}\right)^n = (4.04)^n$$

We kept an extra significant figure (4) to emphasize that the value of  $n = 1$ ; the reaction is first-order in  $N_2O_5$ .

- 3B** For the reaction, we know that  $\text{rate} = k[HgCl_2]^1[C_2O_4^{2-}]^2$ . Compare Expt. 4 to Expt. 1:

$$\frac{\text{rate}_4}{\text{rate}_1} = \frac{k[HgCl_2]^1[C_2O_4^{2-}]^2}{k[HgCl_2]^1[C_2O_4^{2-}]^2} = \frac{0.025 \text{ M} \times (0.045 \text{ M})^2}{0.105 \text{ M} \times (0.150 \text{ M})^2} = 0.0214 = \frac{\text{rate}_4}{1.8 \times 10^{-5} \text{ M min}^{-1}}$$

The desired rate is  $\text{rate}_4 = 0.0214 \times 1.8 \times 10^{-5} \text{ M min}^{-1} = 3.9 \times 10^{-7} \text{ M min}^{-1}$

- 4A** We substitute into the rate law and solve for  $k$ .

$$\text{rate} = k[A]^2[B] = 4.78 \times 10^{-2} \text{ M s}^{-1} = k(1.12 \text{ M})^2(0.87 \text{ M})$$

$$k = \frac{4.78 \times 10^{-2} \text{ M s}^{-1}}{(1.12 \text{ M})^2 0.87 \text{ M}} = 4.4 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$$

- 4B** We already know that  $\text{rate} = k[HgCl_2]^1[C_2O_4^{2-}]^2$  and  $k = 7.6 \times 10^{-3} \text{ M}^{-2} \text{ min}^{-1}$ .

Thus, substitution yields:

$$\text{Rate} = 7.6 \times 10^{-3} \text{ M}^{-2} \text{ min}^{-1} (0.050 \text{ M})^1 (0.025 \text{ M})^2 = 2.4 \times 10^{-7} \text{ M min}^{-1}$$

- 5A** We substitute directly into the integrated rate equation.

$$\ln[A]_t = -kt + \ln[A]_0 = -3.02 \times 10^{-3} \text{ s}^{-1} \times 325 \text{ s} + \ln(2.80) = -0.982 + 1.030 = 0.048$$

$$[A]_t = e^{0.048} = 1.0 \text{ M}$$

- 5B** We substitute the suggested values into text equation (15.12).

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt = -k \times 600 \text{ s} = \ln \frac{1.49 \text{ M}}{2.32 \text{ M}} = -0.443 \quad k = \frac{-0.443}{-600 \text{ s}} = 7.38 \times 10^{-4} \text{ s}^{-1}$$

$$\text{Now we choose } [H_2O_2]_0 = 1.49 \text{ M}, [H_2O_2]_t = 0.62, \quad t = 1800 \text{ s} - 600 \text{ s} = 1200 \text{ s}$$

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt = -k \times 1200 \text{ s} = \ln \frac{0.62 \text{ M}}{1.49 \text{ M}} = -0.88 \quad k = \frac{-0.88}{-1200 \text{ s}} = 7.3 \times 10^{-4} \text{ s}^{-1}$$

These two values agree within the limits of the experimental measurement.

- 6A** We can use the integrated rate equation to find the ratio of the final and initial concentrations. This ratio equals the fraction of the initial concentration that remains.

$$\ln \frac{[A]_t}{[A]_0} = -kt = -2.95 \times 10^{-3} \text{ s}^{-1} \times 150 \text{ s} = -0.443$$

$$\frac{[A]_t}{[A]_0} = e^{-0.443} = 0.642; \quad 64.2\% \text{ of } [A]_0 \text{ remains.}$$

- 6B** After two-thirds of the sample has decomposed, one-third of the sample remains.

Thus  $[H_2O_2]_t = [H_2O_2]_0 / 3$ , and we have

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt = \ln \frac{[H_2O_2]_0 / 3}{[H_2O_2]_0} = \ln (1/3) = -1.099 = -7.30 \times 10^{-4} \text{ s}^{-1} t$$

$$t = \frac{-1.099}{-7.30 \times 10^{-4} \text{ s}^{-1}} = 1.51 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 25.2 \text{ min}$$

- 7A** At the end of one half-life the pressure of DTBP will have halved, to 400 mmHg. At the end of another half-life, at 160 min, the pressure of DTBP will have halved again, to 200 mmHg. Thus, the pressure of DTBP at 125 min will be intermediate between the pressure at 80.0 min (400 mmHg) and that at 160 min (200 mmHg). To obtain an exact answer, first we determine the value of the rate constant from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{80.0 \text{ min}} = 0.00866 \text{ min}^{-1}$$

$$\ln \frac{(P_{DTBP})_t}{(P_{DTBP})_0} = -kt = -0.00866 \text{ min}^{-1} \times 125 \text{ min} = -1.08$$

$$\frac{(P_{DTBP})_t}{(P_{DTBP})_0} = e^{-1.08} = 0.340$$

$$(P_{DTBP})_t = 0.340 \times (P_{DTBP})_0 = 0.340 \times 800 \text{ mmHg} = 272 \text{ mmHg}$$

- 7B (a)** We use partial pressures in place of concentrations in the integrated first-order rate equation. Notice first that more than 30 half-lives have elapsed, and thus the ethylene oxide pressure has declined to at most  $(0.5)^{30} = 9 \times 10^{-10}$  of its initial value.

$$\ln \frac{P_{30}}{P_0} = -kt = -2.05 \times 10^{-4} \text{ s}^{-1} \times 30.0 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} = -22.1 \quad \frac{P_{30}}{P_0} = e^{-22.1} = 2.4 \times 10^{-10}$$

$$P_{30} = 2.4 \times 10^{-10} P_0 = 2.4 \times 10^{-10} \times 782 \text{ mmHg} = 1.9 \times 10^{-7} \text{ mmHg}$$

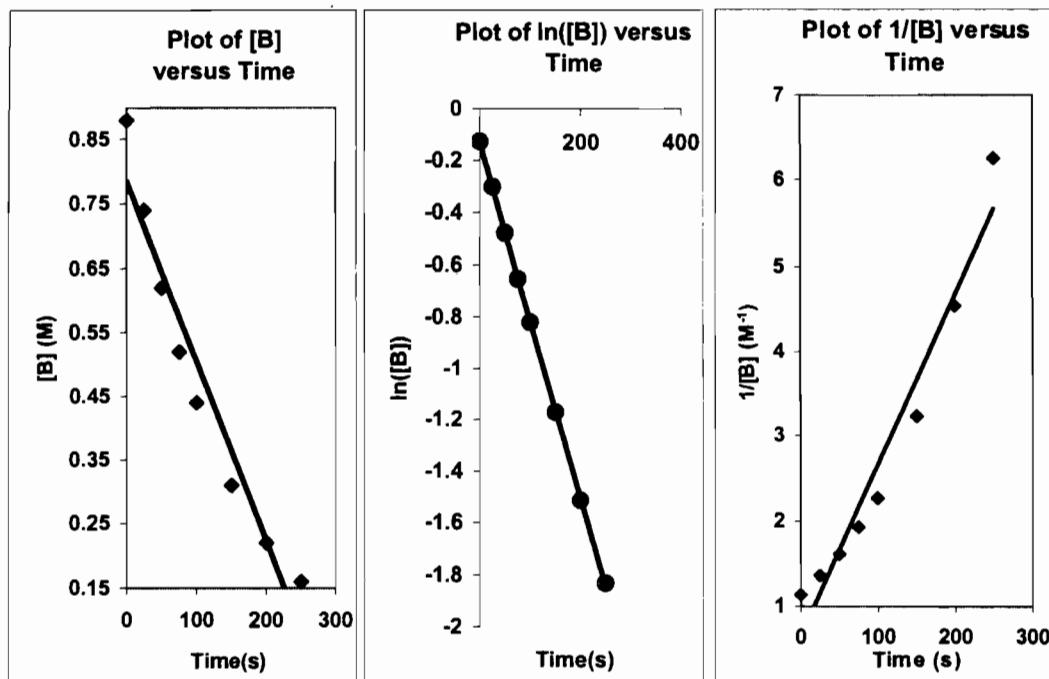
- (b)**  $P_{\text{ethylene oxide}}$  initially 782 mmHg  $\rightarrow 1.9 \times 10^{-7} \text{ mmHg} (\sim 0)$ . Essentially all of the ethylene oxide is converted to  $\text{CH}_4$  and  $\text{CO}$ . Since pressure is proportional to moles, the final pressure will be twice the initial pressure (1 mole  $\rightarrow$  2 moles; 782 mmHg  $\rightarrow$  1564 mmHg). The final pressure will be  $1.56 \times 10^3 \text{ mmHg}$ .

- 8A** We first begin by looking for a constant rate, indicative of a zero-order reaction. If the rate is constant, the concentration will decrease by the same quantity during the same time period. If we choose a 25-s time period, we note that the concentration decreases  $(0.88 \text{ M} - 0.74 \text{ M}) = 0.14 \text{ M}$  during the first 25 s,  $(0.74 \text{ M} - 0.62 \text{ M}) = 0.12 \text{ M}$  during the second 25 s,  $(0.62 \text{ M} - 0.52 \text{ M}) = 0.10 \text{ M}$  during the third 25 s, and  $(0.52 \text{ M} - 0.44 \text{ M}) = 0.08 \text{ M}$  during the fourth 25 s period. This is hardly a constant rate and we conclude that the reaction is not zero-order.

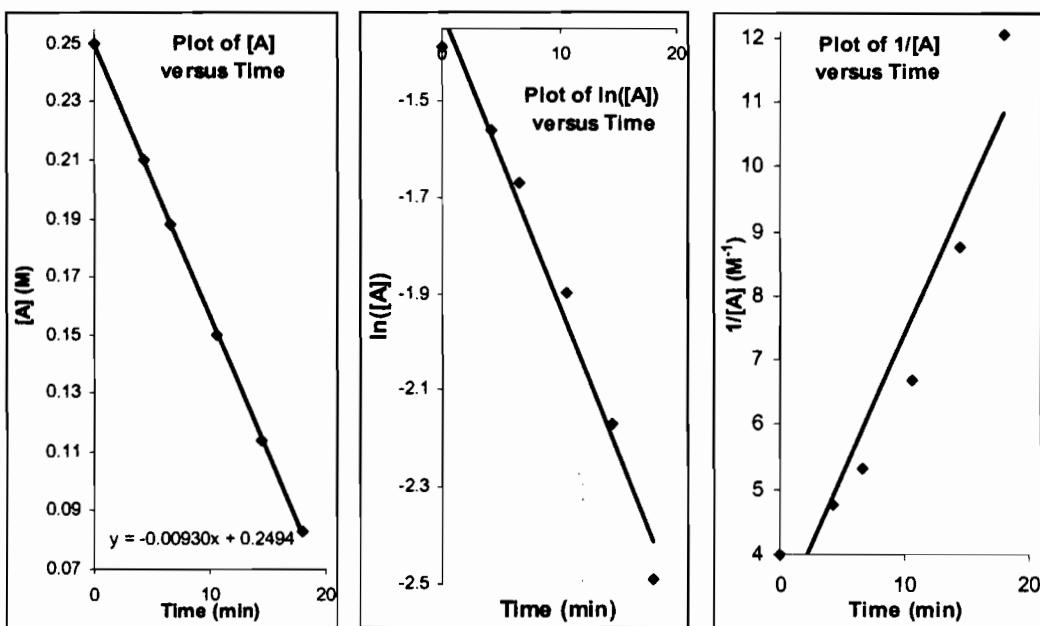
We next look for a constant half-life, indicative of a first-order reaction. The initial concentration of 0.88 M decreases to one half of that value, 0.44 M, during the first 100 s, indicating a 100-s half-life. The concentration halves again to 0.22 M in the second 100 s, another 100-s half-life. Finally, we note that the concentration halves also from 0.62 M at 50 s to 0.31 M at 150 s, yet another 100-s half-life. The rate is established as first-order.

The rate constant is  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100 \text{ s}} = 6.93 \times 10^{-3} \text{ s}^{-1}$

We can easily see that the reaction is first-order in the plots below,  $k = 6.85 \times 10^{-3} \text{ s}^{-1}$



- 8B** We plot the data in three ways to determine the order. (1) A plot of  $[A]$  vs. time is linear if the reaction is zero-order. (2) A plot of  $\ln [A]$  vs. time is linear if the reaction is first-order. (3) A plot of  $1/[A]$  vs. time is linear if the reaction is second-order. It is obvious from the plots below that the reaction is zero-order. The negative of the slope of the line equals  $k = -(0.083 \text{ M} - 0.250 \text{ M}) \div 18.00 \text{ min} = 9.28 \times 10^{-3} \text{ M/min}$  ( $k = 9.30 \times 10^{-3} \text{ M/min}$  using a graphical approach (next page)).



- 9A** First we compute the value of the rate constant at 75.0 °C with the Arrhenius equation. We know that the activation energy is  $E_a = 1.06 \times 10^5$  J/mol, and that  $k = 3.46 \times 10^{-5}$  s<sup>-1</sup> at 298 K. The temperature of 75.0 °C = 348.2 K.

$$\ln \frac{k_2}{k_1} = \ln \frac{k_2}{3.46 \times 10^{-5} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{1.06 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298.2 \text{ K}} - \frac{1}{348.2 \text{ K}} \right) = 6.14$$

$$k_2 = 3.46 \times 10^{-5} \text{ s}^{-1} \times e^{+6.14} = 3.46 \times 10^{-5} \text{ s}^{-1} \times 4.6 \times 10^2 = 0.016 \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.016 \text{ s}^{-1}} = 43 \text{ s at 75 } ^\circ\text{C}$$

- 9B** We use the integrated rate equation to determine the rate constant, realizing that one-third remains when two-thirds have decomposed.

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = \ln \frac{[\text{N}_2\text{O}_5]_0 \div 3}{[\text{N}_2\text{O}_5]_0} = \ln \frac{1}{3} = -kt = -k(1.50 \text{ h}) = -1.099$$

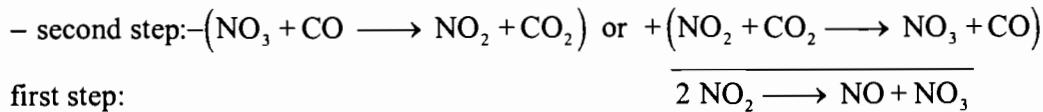
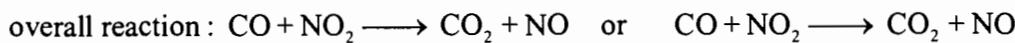
$$k = \frac{1.099}{1.50 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 2.04 \times 10^{-4} \text{ s}^{-1}$$

Now use the Arrhenius equation to determine the temperature at which the rate constant is  $2.04 \times 10^{-4}$  s<sup>-1</sup>.

$$\ln \frac{k_2}{k_1} = \ln \frac{2.04 \times 10^{-4} \text{ s}^{-1}}{3.46 \times 10^{-5} \text{ s}^{-1}} = 1.77 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{1.06 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{T_2} \right)$$

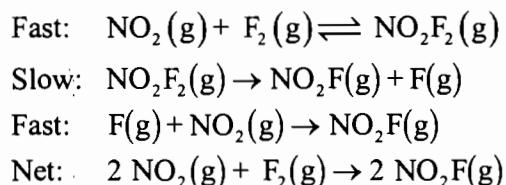
$$\frac{1}{T_2} = \frac{1}{298 \text{ K}} - \frac{1.77 \times 8.3145 \text{ K}^{-1}}{1.06 \times 10^5} = 3.22 \times 10^{-3} \text{ K}^{-1} \quad T_2 = 311 \text{ K}$$

- 10A** The two steps of the mechanism must add, in a Hess's law fashion, to produce the overall reaction.



If the first step is the slow step, then it will be the rate-determining step, and the rate of that step will be the rate of the reaction: rate of reaction =  $k_1 [\text{NO}_2]^2$

- 10B** (1) The steps of the mechanism must add, in a Hess's law fashion, to produce the overall reaction. This is done at right. The two intermediates,  $\text{NO}_2\text{F}_2(\text{g})$  and  $\text{F}(\text{g})$ , are each produced in one step and consumed in the next one.



- (2) The proposed mechanism must agree with the rate law. We expect the rate-determining step to determine the reaction rate: Rate =  $k_3 [\text{NO}_2\text{F}_2]$ . To eliminate  $[\text{NO}_2\text{F}_2]$ , we recognize that the first elementary reaction is very fast and will have the same rate forward as reverse:  $R_f = k_1 [\text{NO}_2][\text{F}_2] = k_2 [\text{NO}_2\text{F}_2] = R_r$ . We solve for the concentration of intermediate:  $[\text{NO}_2\text{F}_2] = k_1 [\text{NO}_2][\text{F}_2]/k_2$ . We now substitute this expression for  $[\text{NO}_2\text{F}_2]$  into the rate equation: Rate =  $(k_1 k_3/k_2)[\text{NO}_2][\text{F}_2]$ . The predicted rate law agrees with the experimental rate law.

## REVIEW QUESTIONS

- (a)  $[\text{A}]_0$  symbolizes the concentration of species A, usually a reactant, at time = 0.
- (b)  $k$  is the symbol for the specific rate constant of a reaction, the speed of the reaction if all rate-determining species were present at unit molarity.
- (c)  $t_{1/2}$  is the symbol for the half-life of a reaction, the time during which the concentration of the reactant drops to one-half of its initial value.
- (d) A zero-order reaction is one whose rate is independent of the concentration of reactant.
- (e) A catalyst is a substance that is added to increase the rate of a chemical reaction. The catalyst takes part in the chemical reaction, without being consumed by the reaction (it is regenerated). Catalysts work by providing an alternate reaction pathways with a lower activation energy than the uncatalyzed reaction.

2. (a) The method of initial rates is used to determine the overall reaction order and the rate constant for a reaction by measuring the effect of different reactant concentrations on the initial rate of reaction.
- (b) An activated complex is a high-energy species that is formed as a result of the collision of two reacting particles.
- (c) The reaction mechanism is the series of molecular processes that accounts for the overall reaction and its observed kinetics.
- (d) Heterogeneous catalysis refers to catalytic activity that occurs at the interface between two phases, usually a liquid or a gas in contact with a solid catalytic surface.
- (e) The rate-determining step is the slowest step of a reaction mechanism (i.e. the step with the highest activation energy).
3. (a) The rate of a first-order reaction depends on the first power of the concentration of a reactant; a second-order reaction's rate depends on the second power of the concentration of a reactant, or on the first power of each of the two reactants.
- (b) A rate equation or rate law is the relationship between the instantaneous rate of a reaction and the powers, (orders), of concentrations of the reactants. An integrated rate equation provides the mathematical relationship between the concentration of reactant and elapsed time.
- (c) The activation energy is the energy that must be supplied to energize reactants to the level of the activated complex; it is almost always endothermic. The enthalpy of reaction is the energy released or absorbed as the overall reaction occurs, i.e., it may be exothermic or endothermic, respectively.
- (d) An elementary process is a description of how molecules interact with each other. The net reaction is the result of the several elementary processes that constitute it.
- (e) An enzyme is a biological catalyst. A substrate is the reactant whose reaction the catalyst promotes.

4. (a)  $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{(0.1832 \text{ M} - 0.2643 \text{ M})}{35 \text{ min}} = 2.3 \times 10^{-3} \text{ M min}^{-1}$

(b)  $\text{Rate} = 2.3 \times 10^{-3} \frac{\text{mol}}{\text{L min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 3.8 \times 10^{-5} \text{ M sec}^{-1}$

5.  $2\text{A} + \text{B} \rightarrow \text{C} + 3\text{D} \quad -\frac{\Delta[\text{A}]}{\Delta t} = 6.2 \times 10^{-4} \text{ M s}^{-1}$

(a)  $\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{A}]}{\Delta t} = 1/2(6.2 \times 10^{-4} \text{ M s}^{-1}) = 3.1 \times 10^{-4} \text{ M s}^{-1}$

(b)  $\text{Rate of disappearance of B} = -\frac{1}{2} \frac{\Delta[\text{A}]}{\Delta t} = 1/2(6.2 \times 10^{-4} \text{ M s}^{-1}) = 3.1 \times 10^{-4} \text{ M s}^{-1}$

(c)  $\text{Rate of appearance of D} = -\frac{3}{2} \frac{\Delta[\text{A}]}{\Delta t} = 3(6.2 \times 10^{-4} \text{ M s}^{-1}) = 9.3 \times 10^{-4} \text{ M s}^{-1}$

6. In each case, we draw the tangent line to the plotted curve.

(a) The slope of the line is  $\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1.7 \text{ M} - 0.6 \text{ M}}{400 \text{ s} - 1600 \text{ s}} = -9.2 \times 10^{-4} \text{ M s}^{-1}$

$$\text{Reaction rate} = -\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = 9.2 \times 10^{-4} \text{ M s}^{-1}$$

- (b) Read the value where the horizontal line  $[\text{H}_2\text{O}_2] = 0.50 \text{ M}$ , intersects the curve  
 $\approx 2150 \text{ s}$  or  $\approx 36 \text{ minutes}$

7. Statement (b) is correct. After each half-life—that is, after each 75 s—the amount of reactant remaining is half of the amount that was present at the beginning of that half-life. Statement (a) is incorrect; the quantity of A remaining after 150 s is half of what was present after 75 s. Statement (c) is incorrect because different quantities of A are consumed in each 75 s of the reaction: 1/2 of the original amount in the first 75 s, 1/4 of the original amount in the second 75 s, 1/8 of the original amount in the third 75 s, and so on. Statement (d) is incorrect; it implies a constant rate during the first half-life. The rate of a first-order reaction actually decreases as time passes and reactant is consumed.

8. Substitute the given values into the rate equation to obtain the rate of reaction.

$$\text{Rate} = k[A]^2[B]^0 = (0.0103 \text{ M}^{-1}\text{min}^{-1})(0.116 \text{ M})^2(3.83 \text{ M})^0 = 1.39 \times 10^{-4} \text{ M / min}$$

Recall that  $(\text{any quantity})^0 = 1$ .

9. The rate constant is determined as  $k = 0.693 / t_{1/2} = 0.693 / 19.8 \text{ min} = 0.0350 \text{ min}^{-1}$

Then the rate can be determined.  $\text{Rate} = k[A] = 0.0350 \text{ min}^{-1} \times 0.632 \text{ M} = 0.0221 \text{ M min}^{-1}$

10. (a) A first-order reaction has a constant half-life. Thus, half of the initial concentration remains after 30.0 minutes, and at the end of another half-life—60.0 minutes total—half of the concentration present at 30.0 minutes will have reacted: the concentration has decreased to one-quarter of its initial value. Or, we could say that the reaction is 75% complete after two half-lives—60.0 minutes.

- (b) A zero-order reaction proceeds at a constant rate. Thus, if the reaction is 50% complete in 30.0 minutes, in twice the time—60.0 minutes—the reaction will be 100% complete. (And in one-fifth the time—6.0 minutes—the reaction will be 10% complete. Alternatively, we can say that the rate of reaction is 10%/6.0 min.) Time to be 75% complete =  $75\% \times \frac{60.0 \text{ min}}{100\%} = 45 \text{ min}$

- 11. (a)** Although we might be tempted to apply equation (15.12) to the given data, and calculate  $k$  first, there is an easier method. During one half-life,  $[A]$  decreases from 2.00 M to 1.00 M. Then, during the second half-life,  $[A]$  decreases from 1.00 M to 0.500 M. And finally, during the third half-life,  $[A]$  decreases 0.500 M to 0.250 M. Consequently, three half-lives must have elapsed while  $[A]$  has decreased from 2.00 M to 0.250 M.  $3t_{1/2} = 126 \text{ min} \quad t_{1/2} = 126 \text{ min} \div 3 = 42.0 \text{ min}$

$$\mathbf{(b)} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{42.0 \text{ min}} = 0.0165 \text{ min}^{-1}$$

- 12. (a)** The mass of A has decreased to one fourth of its original value, from 1.60 g to 0.40 g. Since  $\frac{1}{4} = \frac{1}{2} \times \frac{1}{2}$ , we see that two half-lives have elapsed. Thus,  $2 \times t_{1/2} = 38 \text{ min}$ , or  $t_{1/2} = 19 \text{ min}$ .

$$\mathbf{(b)} \quad k = 0.693/t_{1/2} = \frac{0.693}{19 \text{ min}} = 0.036 \text{ min}^{-1} \quad \ln \frac{[A]_t}{[A]_0} = -kt = -0.036 \text{ min}^{-1} \times 60 \text{ min} = -2.2$$

$$\frac{[A]_t}{[A]_0} = e^{-2.2} = 0.11 \quad \text{or} \quad [A]_t = [A]_0 e^{-kt} = 1.60 \text{ g A} \times 0.11 = 0.2 \text{ g A}$$

$$\mathbf{13. (a)} \quad \ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.632 \text{ M}}{0.816 \text{ M}} = -0.256 \quad k = -\frac{-0.256}{16.0 \text{ min}} = 0.0160 \text{ min}^{-1}$$

$$\mathbf{(b)} \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0160 \text{ min}^{-1}} = 43.3 \text{ min}$$

- (c)** Solve the integrated rate equation for the elapsed time.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.235 \text{ M}}{0.816 \text{ M}} = -1.245 = -0.0160 \text{ min}^{-1} \times t$$

$$t = \frac{-1.245}{-0.0160 \text{ min}^{-1}} = 77.8 \text{ min}$$

- (d)**  $\ln \frac{[A]}{[A]_0} = -kt$  becomes  $\frac{[A]}{[A]_0} = e^{-kt}$  which in turn becomes

$$[A] = [A]_0 e^{-kt} = 0.816 \text{ M} \exp \left( -0.0160 \text{ min}^{-1} \times 2.5 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \right) = 0.816 \times 0.0907 = 0.074 \text{ M}$$

14. (a) From Expt. 1 to Expt. 3, when [B] remains constant and [A] doubles, the rate

$$\text{increases by a factor of } \frac{6.75 \times 10^{-4} \text{ M s}^{-1}}{3.35 \times 10^{-4} \text{ M s}^{-1}} = 2.01 \approx 2$$

Thus, the reaction is first-order with respect to A.

From Expt 1 to Expt. 2, when [A] remains constant and [B] doubles, the rate

$$\text{increases by a factor of } \frac{1.35 \times 10^{-3} \text{ M s}^{-1}}{3.35 \times 10^{-4} \text{ M s}^{-1}} = 4.03 \approx 4$$

Thus, the reaction is second-order with respect to B.

- (b) Overall reaction order = order with respect to A + order with respect to B = 1 + 2 = 3  
The reaction is third-order overall.

(c) Rate =  $3.35 \times 10^{-4} \text{ M s}^{-1} = k(0.185 \text{ M})(0.133 \text{ M})^2$

$$k = \frac{3.35 \times 10^{-4} \text{ M s}^{-1}}{(0.185 \text{ M})(0.133 \text{ M})^2} = 0.102 \text{ M}^{-2} \text{ s}^{-1}$$

15. In the first 500 s, [A] decreases from 2.00 M to 1.00 M; this is the first half-life. From 500 s to 1500 s, an elapsed period of 1000 s, [A] decreases by half again, from 1.00 M to 0.50 M; this is the second half-life. Since the half-life is not constant, the reaction is not first-order.

During the first 500 s, Rate =  $-\frac{1.00 \text{ M} - 2.00 \text{ M}}{500 \text{ s}} = 0.00200 \text{ M/s}$ . Then during the first

1500 s, the rate is computed as Rate =  $-\frac{0.50 \text{ M} - 2.00 \text{ M}}{1500 \text{ s}} = 0.00100 \text{ M/s}$ .

Since the rate is not constant, this reaction is not zero-order.

We conclude that the reaction is second-order, by the process of elimination. We confirm this conclusion by computing values of the second-order rate constant with the equation

$$1/[A]_t - 1/[A]_0 = kt$$

$$\frac{1}{1.00 \text{ M}} - \frac{1}{2.00 \text{ M}} = 0.500 \text{ M}^{-1} = k \times 500 \text{ s} \quad k = \frac{0.500 \text{ M}^{-1}}{500 \text{ s}} = 0.0010 \text{ M}^{-1} \text{ s}^{-1}$$

$$\frac{1}{0.50 \text{ M}} - \frac{1}{2.00 \text{ M}} = 1.50 \text{ M}^{-1} = k \times 1500 \text{ s} \quad k = \frac{1.50 \text{ M}^{-1}}{1500 \text{ s}} = 0.0010 \text{ M}^{-1} \text{ s}^{-1}$$

$$\frac{1}{0.25 \text{ M}} - \frac{1}{2.00 \text{ M}} = 3.50 \text{ M}^{-1} = k \times 3500 \text{ s} \quad k = \frac{3.50 \text{ M}^{-1}}{3500 \text{ s}} = 0.0010 \text{ M}^{-1} \text{ s}^{-1}$$

The constant value of the second-order rate constant indicates that this reaction indeed is second-order.

- 16.** Statement (d) is correct; the activation energy of an endothermic reaction must at least equal the value of  $\Delta H$  for that reaction. However, if  $E_a = \Delta H_{rxn}$ , the products will readily "slip back down the hill" to reactants; that is, no net reaction will occur. (There will be no activation energy for the reverse reaction, nothing to prevent that reaction from occurring regardless of the energy of its reactants.) Thus,  $E_a$  should be at least a slight bit greater than  $\Delta H_{rxn}$ .

**17. (a)** 
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \frac{5.4 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}}{2.8 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{683 \text{ K}} - \frac{1}{599 \text{ K}} \right)$$

$$-3.95R = -E_a \times 2.05 \times 10^{-4}$$

$$E_a = \frac{3.95 R}{2.05 \times 10^{-4}} = 1.93 \times 10^4 \text{ K}^{-1} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 1.60 \times 10^5 \text{ J / mol} = 160 \text{ kJ / mol}$$

**(b)** 
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \frac{5.0 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}}{2.8 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}} = \frac{1.60 \times 10^5 \text{ J / mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{683 \text{ K}} - \frac{1}{T} \right)$$

$$-1.72 = 1.92 \times 10^4 \left( \frac{1}{683 \text{ K}} - \frac{1}{T} \right) \quad \left( \frac{1}{683 \text{ K}} - \frac{1}{T} \right) = \frac{-1.72}{1.92 \times 10^4} = -8.96 \times 10^{-5}$$

$$\frac{1}{T} = 8.96 \times 10^{-5} + 1.46 \times 10^{-3} = 1.55 \times 10^{-3} \quad T = 645 \text{ K}$$

- 18. (a)** Set II is data from a zero-order reaction. We know this because the rate of set II is constant.  $0.25 \text{ M}/25 \text{ s} = 0.010 \text{ M s}^{-1}$ . A zero-order reaction has a constant rate.
- (b)** A first-order reaction has a constant half-life. In set I, the first half-life is slightly less than 75 sec, since the concentration decreases by slightly more than half (from 1.00 M to 0.47 M) in 75 s. Again, from 75 s to 150 s the concentration decreases from 0.47 M to 0.22 M, again by slightly more than half, in a time of 75 s. Finally, two half-lives should see the concentration decrease to one-fourth of its initial value. This is what we see: from 100 s to 250 sec, 150 s of elapsed time, the concentration decreases from 0.37 M to 0.08 M; that is, to slightly less than one-fourth of its initial value. Notice that we cannot make the same statement of constancy of half-life regarding set III. The first half-life is 100 s, but it takes more than 150 s (from 100 s to 250 s) for [A] to again decrease by half.
- (c)** For a second-order reaction,  $1/[A]_t - 1/[A]_0 = kt$ . For the initial 100 s in set III, we have

$$\frac{1}{0.50 \text{ M}} - \frac{1}{1.00 \text{ M}} = 1.0 \text{ L mol}^{-1} = k 100 \text{ s}, \quad k = 0.010 \text{ L mol}^{-1} \text{ s}^{-1}$$

For the initial 200 s, we have

$$\frac{1}{0.33 \text{ M}} - \frac{1}{1.00 \text{ M}} = 2.0 \text{ L mol}^{-1} = k \text{ 200 s}, \quad k = 0.010 \text{ L mol}^{-1} \text{ s}^{-1}$$

Since we obtain the same value of the rate constant using the equation for second-order kinetics, set III must be second-order.

19. For a zero-order reaction (set II), the slope equals the rate constant:

$$k = -\Delta[A]/\Delta t = 1.00 \text{ M}/100 \text{ s} = 0.0100 \text{ M/s}$$

20. Set I is the data for a first-order reaction; we can analyze those items of data to determine the half-life. In the first 75 s, the concentration decreases by a bit more than half. This implies a half-life slightly less than 75 s, perhaps 70 s. This is consistent with the other time periods noted in the answer to Review Question 18 (b) and also to the fact that in the 150 s from 50 s to 200 s, the concentration decreases from 0.61 M to 0.14 M, a bit more than a factor-of-four decrease. The factor-of-four decrease, to one-fourth of the initial value, is what we would expect of two successive half-lives. We can determine the half-life more accurately, by obtaining a value of  $k$  from the relation  $\ln([A]_t/[A]_0) = -kt$  followed by  $t_{1/2} = 0.693/k$

21. We can determine an approximate initial rate by using data from the first 25 s.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.80 \text{ M} - 1.00 \text{ M}}{25 \text{ s} - 0 \text{ s}} = 0.0080 \text{ M s}^{-1}$$

22. The approximate rate at 75 s can be taken as the rate over the time period from 50 s to 100 s.

$$(a) \quad \text{Rate}_{II} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.00 \text{ M} - 0.50 \text{ M}}{100 \text{ s} - 50 \text{ s}} = 0.010 \text{ M s}^{-1}$$

$$(b) \quad \text{Rate}_{I} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.37 \text{ M} - 0.61 \text{ M}}{100 \text{ s} - 50 \text{ s}} = 0.0048 \text{ M s}^{-1}$$

$$(c) \quad \text{Rate}_{III} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.50 \text{ M} - 0.67 \text{ M}}{100 \text{ s} - 50 \text{ s}} = 0.0034 \text{ M s}^{-1}$$

Alternatively we can use  $[A]$  at 75 s (the values given in the table) in the relationship  $\text{Rate} = k[A]^m$ , where  $m = 0, 1$ , or  $2$ .

$$(a) \quad \text{Rate}_{II} = 0.010 \text{ M s}^{-1} \times (0.25 \text{ mol/L})^0 = 0.010 \text{ M s}^{-1}$$

$$(b) \quad \text{Since } t_{1/2} = 70 \text{ s}, \quad k = 0.693/70 \text{ s} = 0.0099 \text{ s}^{-1}$$

$$\text{Rate}_I = 0.0099 \text{ s}^{-1} \times (0.47 \text{ mol/L})^1 = 0.0047 \text{ M s}^{-1}$$

$$(c) \quad \text{Rate}_{III} = 0.010 \text{ L mol}^{-1} \text{ s}^{-1} \times (0.57 \text{ mol/L})^2 = 0.0032 \text{ M s}^{-1}$$

- 23.** We can combine the approximate rates from Review Question 22, with the fact that 10 s have elapsed, and the concentration at 100 s.

- (a)  $[A]_{II} = 0.00 \text{ M}$  There is no reactant left after 100 s.
- (b)  $[A]_I = [A]_{100} - (10 \text{ s} \times \text{rate}) = 0.37 \text{ M} - (10 \text{ s} \times 0.0047 \text{ M s}^{-1}) = 0.32 \text{ M}$
- (c)  $[A]_{III} = [A]_{100} - (10 \text{ s} \times \text{rate}) = 0.50 \text{ M} - (10 \text{ s} \times 0.0032 \text{ M s}^{-1}) = 0.47 \text{ M}$

- 24. (a)** We can demonstrate consistency with the stoichiometry by adding the two reactions. Sum of the reactions:  $A + B + I + B \longrightarrow I + C + D$  We then cancel the I that appears on both sides of the resultant equation:  $A + 2B \longrightarrow C + D$  We determine the rate of the reaction from the mechanism by assuming that the rate of the elementary slow step equals the reaction rate: Reaction rate =  $k_{slow}[A][B]$ . This is equivalent to the observed rate law.

- (b) Again, we demonstrate consistency with the stoichiometry by adding the two reactions to obtain:  $2B + A + B_2 \longrightarrow B_2 + C + D$  We then cancel the “ $B_2$ ” that appears on both sides of the resultant equation, and finally have:  $2B + A \longrightarrow C + D$  The reaction rate is the rate of the elementary slow step: Reaction rate =  $k_{slow}[A][B_2]$  But  $B_2$  is a reaction intermediate whose concentration is difficult to determine. We can determine that concentration by assuming that the fast initial step goes equally rapidly in the forward and reverse directions.  $k_f[B]^2 = k_r[B_2]$   $[B_2] = (k_f/k_r)[B]^2$  The resulting expression for  $[B_2]$  is substituted into the expression for reaction rate, and we see that the experimentally determined rate law is not recovered.

$$\text{Reaction rate} = k_{slow}[A][B_2] = k_{slow}[A](k_f/k_r)[B]^2 = k'[A][B]^2$$

## EXERCISES

### Rates of Reactions

**25.** Rate =  $-\frac{\Delta[A]}{\Delta t} = -\frac{(0.474 \text{ M} - 0.485 \text{ M})}{82.4 \text{ s} - 71.5 \text{ s}} = 1.0 \times 10^{-3} \text{ M s}^{-1}$

**27. (a)**  $[A] = [A]_i + \Delta[A] = 0.588 \text{ M} - 0.013 \text{ M} = 0.575 \text{ M}$

(b)  $\Delta[A] = 0.565 \text{ M} - 0.588 \text{ M} = -0.023 \text{ M}$

$$\Delta t = \Delta[A] \frac{\Delta t}{\Delta[A]} = \frac{-0.023 \text{ M}}{-2.2 \times 10^{-2} \text{ M/min}} = 1.0 \text{ min}$$

$$\text{time} = t + \Delta t = (4.40 + 1.0) \text{ min} = 5.4 \text{ min}$$

29. (a)  $\text{Rate} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[C]}{2\Delta t} = 1.76 \times 10^{-5} \text{ M s}^{-1}$

$$\frac{\Delta[C]}{\Delta t} = 2 \times 1.76 \times 10^{-5} \text{ M s}^{-1} = 3.52 \times 10^{-5} \text{ M/s}$$

(b)  $\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[C]}{2\Delta t} = -1.76 \times 10^{-5} \text{ M s}^{-1}$  Assume this rate is constant.

$$[A] = 0.3580 \text{ M} + \left( -1.76 \times 10^{-5} \text{ M s}^{-1} \times 1.00 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) = 0.357 \text{ M}$$

(c)  $\frac{\Delta[A]}{\Delta t} = -1.76 \times 10^{-5} \text{ M s}^{-1}$

$$\Delta t = \frac{\Delta[A]}{-1.76 \times 10^{-5} \text{ M/s}} = \frac{0.3500 \text{ M} - 0.3580 \text{ M}}{-1.76 \times 10^{-5} \text{ M/s}} = 4.5 \times 10^2 \text{ s}$$

31. Notice that, for every 1000 mmHg drop in the pressure of A(g), there will be a corresponding 2000 mmHg rise in the pressure of B(g) plus a 1000 mmHg rise in the pressure of C(g).

- (a) We set up the calculation with three lines of information below the balanced equation: (1) the initial conditions, (2) the changes that occur, which are related to each other by reaction stoichiometry, and (3) the final conditions, which simply are initial conditions + changes.

	A(g)	$\rightarrow$	2B(g)	+	C(g)
Initial	1000. mmHg		0. mmHg		0. mmHg
Changes	-1000. mmHg		+2000. mmHg		+1000. mmHg
Final	0. mmHg		2000. mmHg		1000. mmHg

$$\text{Total final pressure} = 0. \text{ mmHg} + 2000. \text{ mmHg} + 1000. \text{ mmHg} = 3000. \text{ mmHg}$$

(b)

	A(g)	$\rightarrow$	2B(g)	+	C(g)
Initial	1000. mmHg		0. mmHg		0. mmHg
Changes	-200. mmHg		+400. mmHg		+200. mmHg
Final	800 mmHg		400. mmHg		200. mmHg

$$\text{Total pressure} = 800. \text{ mmHg} + 400. \text{ mmHg} + 200. \text{ mmHg} = 1400. \text{ mmHg}$$

## Method of Initial Rates

- 33.** From Expt. 1 and Expt. 2 we see that [B] remains fixed while [A] triples. As a result, the initial rate increases from  $4.2 \times 10^{-3}$  M/min to  $1.3 \times 10^{-2}$  M/min, that is, the initial reaction rate triples. Therefore, the reaction is first-order in [A]. Between Expt. 2 and Expt. 3, we see that [A] doubles, which would double the rate, and [B] doubles. As a consequence, the initial rate goes from  $1.3 \times 10^{-2}$  M/min to  $5.2 \times 10^{-2}$  M/min, that is, the rate quadruples. Since an additional doubling of the rate is due to the change in [B], the reaction is first-order in [B]. Now we determine the value of the rate constant.

$$\text{Rate} = k[A]^1[B]^1 \quad k = \frac{\text{Rate}}{[A][B]} = \frac{5.2 \times 10^{-2} \text{ M/min}}{3.00 \text{ M} \times 3.00 \text{ M}} = 5.8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$$

The rate law is  $\text{Rate} = (5.8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1})[A]^1[B]^1$

- 35. (a)** From Expt. 1 to Expt. 2, [B] remains constant at 1.40 M and [C] remains constant at 1.00 M, but [A] is halved ( $\times 0.50$ ). At the same time the rate is halved ( $\times 0.50$ ). Thus, the reaction is first-order with respect to A, since  $0.50^x = 0.50$  when  $x = 1$ . From Expt. 2 to Expt. 3, [A] remains constant at 0.70 M and [C] remains constant at 1.00 M, but [B] is halved ( $\times 0.50$ ), from 1.40 M to 0.70 M. At the same time, the rate is quartered ( $\times 0.25$ ). Thus, the reaction is second-order with respect to B, since  $0.50^y = 0.25$  when  $y = 2$ . From Expt. 1 to Expt. 4, [A] remains constant at 1.40 M and [B] remains constant at 1.40 M, but [C] is halved ( $\times 0.50$ ), from 1.00 M to 0.50 M. At the same time, the rate is increased by a factor of 2.0.

$$\left[ \text{rate}_4 = 16 \text{ rate}_3 = 16 \times \frac{1}{4} \text{ rate}_2 = 4 \text{ rate}_2 = 4 \times \frac{1}{2} \text{ rate}_1 = 2 \times \text{rate}_1. \right]$$

Thus, the order of the reaction with respect to C is  $-1$ , since  $0.5^z = 2.0$  when  $z = -1$ .

$$\begin{aligned} \text{(b)} \quad \text{rate}_5 &= k(0.70 \text{ M})^1(0.70 \text{ M})^2(0.50 \text{ M})^{-1} = k \left( \frac{1.40 \text{ M}}{2} \right)^1 \left( \frac{1.40 \text{ M}}{2} \right)^2 \left( \frac{1.00 \text{ M}}{2} \right)^{-1} \\ &= k \frac{1}{2} (1.40 \text{ M})^1 \frac{1}{2}^2 (1.40 \text{ M})^2 \frac{1}{2}^{-1} (1.00 \text{ M})^{-1} = \text{rate}_1 \left( \frac{1}{2} \right)^{1+2-1} = \text{rate}_1 \left( \frac{1}{2} \right)^2 = \frac{1}{4} \text{rate}_1 \end{aligned}$$

This is based on  $\text{rate}_1 = k(1.40 \text{ M})^1(1.40 \text{ M})^2(1.00 \text{ M})^{-1}$

## First-Order Reactions

37. (a) TRUE The rate of the reaction does decrease as more and more of B and C are formed, but not because more and more of B and C are formed. Rather the rate decreases because the concentration of A must decrease to form more and more of B and C.

(b) FALSE The time required for one half of substance A to react—the half-life—is independent of the quantity of “A” present.

39. (a) Since the half-life is 180 s, after 900 s five half-lives have elapsed, and the original quantity of A has been cut in half five times.

final quantity of A =  $(0.5)^5 \times$  initial quantity of A =  $0.03125 \times$  initial quantity of A  
About 3.13% of the original quantity of A remains unreacted after 900 s.

(b) For a first-order reaction  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{180 \text{ s}} = 0.00385 \text{ s}^{-1}$

$$\text{Rate} = k[A] = 0.00385 \text{ s}^{-1} \times 0.50 \text{ M} = 0.00193 \text{ M/s}$$

41. We determine the value of the first-order rate constant and from that we determine the half-life. If the reactant is 99% decomposed in 137 min, then only 1% (0.010) of the initial concentration remains.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.010}{1.000} = -4.61 = -k \times 137 \text{ min} \quad k = \frac{4.61}{137 \text{ min}} = 0.0336 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0336 \text{ min}^{-1}} = 20.6 \text{ min}$$

43. (a)  $\ln \left( \frac{\frac{35}{100} [A]_0}{[A]_0} \right) = \ln(0.35) = -kt = (-4.81 \times 10^{-3} \text{ min}^{-1})t \quad t = 218 \text{ min.}$

Note: We did not need to know the initial concentration of acetoacetic acid to answer the question.

(b) Assume the reaction takes place in a 1.00 L container.

$$10.0 \text{ g acetoacetic acid} \times \frac{1 \text{ mol acetoacetic acid}}{102.090 \text{ g acetoacetic acid}} = 0.09795 \text{ mol acetoacetic acid.}$$

After 575 min. (~ 4 half-lives, hence, we expect ~ 6.25% remains), use integrated form of the rate law:

$$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt = (-4.81 \times 10^{-3} \text{ min}^{-1})(575 \text{ min}) = -2.766$$

$$\frac{[A]_t}{[A]_0} = e^{-2.766} = 0.06293 \text{ (~ 6.3% remains)} \quad \frac{[A]_t}{0.09795 \text{ M}} = 0.063$$

$$[A]_t = 6.2 \times 10^{-3} \text{ moles.}$$

$[A]_{\text{reacted}} = [A]_0 - [A]_t = (0.098 - 6.2 \times 10^{-3}) \text{ moles} = 0.092 \text{ moles acetoacetic acid.}$   
 Stoichiometry is such that for every mole of acetoacetic acid, one mole of  $\text{CO}_2$  forms. Hence, we need to determine the volume of 0.0918 moles  $\text{CO}_2$  at 24.5 °C (297.65 K) and 748 torr (0.984 atm).

$$V = \frac{nRT}{P} = \frac{0.0918 \text{ mol} \left( 0.08206 \frac{\text{L atm}}{\text{K mol}} \right) 297.65 \text{ K}}{0.984 \text{ atm}} = 2.3 \text{ L CO}_2$$

- 45. (a)** If the reaction is first-order, we will obtain the same value of the rate constant from several sets of data.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.497 \text{ M}}{0.600 \text{ M}} = -k \times 100 \text{ s} = -0.188, \quad k = \frac{0.188}{100 \text{ s}} = 1.88 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.344 \text{ M}}{0.600 \text{ M}} = -k \times 300 \text{ s} = -0.556, \quad k = \frac{0.556}{300 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.285 \text{ M}}{0.600 \text{ M}} = -k \times 400 \text{ s} = -0.744, \quad k = \frac{0.744}{400 \text{ s}} = 1.86 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.198 \text{ M}}{0.600 \text{ M}} = -k \times 600 \text{ s} = -1.109, \quad k = \frac{1.109}{600 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

The virtual constancy of the rate constant throughout the time of the reaction confirms that the reaction is first-order.

- (b)** We assume that the rate constant equals the average of the values obtained in part (a).

$$k = \frac{1.88 + 1.85 + 1.86 + 1.85}{4} \times 10^{-3} \text{ s}^{-1} = 1.86 \times 10^{-3} \text{ s}^{-1}$$

- (c)** We use the integrated first-order rate equation:

$$[A]_{750} = [A]_0 \exp(-kt) = 0.600 \text{ M} \exp(-1.86 \times 10^{-3} \text{ s}^{-1} \times 750 \text{ s})$$

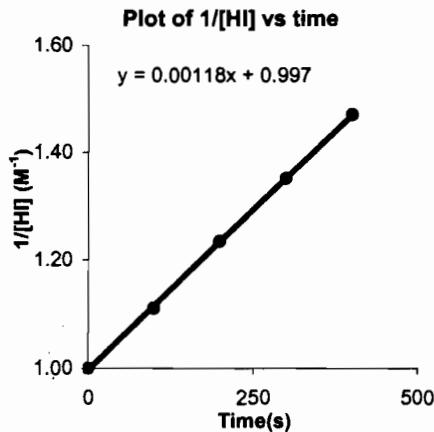
$$[A]_{750} = 0.600 \text{ M} e^{-1.40} = 0.148 \text{ M}$$

## Reactions of Various Orders

47. For reaction:  $\text{HI(g)} \rightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{g})$  (700 K)

Time (s)	[HI] (M)	$\ln[\text{HI}]$	$1/[\text{HI}] (\text{M}^{-1})$
0	1.00	0	1.00
100	0.90	-0.105	1.11
200	0.81	-0.211	1.235
300	0.74	-0.301	1.35
400	0.68	-0.386	1.47

From data above, a plot of  $1/[\text{HI}]$  vs.  $t$  yields a straight line. The reaction is second-order in  $\text{HI}$  at 700 K. Rate =  $k[\text{HI}]^2$ . The slope of the line =  $k = 0.00118 \text{ M}^{-1} \text{s}^{-1}$



49. (a) In the first 22 s,  $[\text{A}]$  decreases from 0.715 M to 0.605 M, that is,  $\Delta[\text{A}] = -0.110 \text{ M}$ .

The rate in these 22 s is then determined. Rate =  $\frac{-\Delta[\text{A}]}{\Delta t} = \frac{0.110 \text{ M}}{22 \text{ s}} = 5.0 \times 10^{-3} \text{ M/s}$

In the first 74 s,  $\Delta[\text{A}] = 0.345 \text{ M} - 0.715 \text{ M}$ , and the rate is determined.

$$\text{Rate} = \frac{-\Delta[\text{A}]}{\Delta t} = \frac{0.370 \text{ M}}{74 \text{ s}} = 5.0 \times 10^{-3} \text{ M/s}$$

Finally, in the first 132 s,  $\Delta[\text{A}] = 0.055 \text{ M} - 0.715 \text{ M}$ , and the rate is determined as

follows. Rate =  $\frac{-\Delta[\text{A}]}{\Delta t} = \frac{0.660 \text{ M}}{132 \text{ s}} = 5.0 \times 10^{-3} \text{ M/s}$ . Since the rate is constant for this reaction, it must be zero-order.

- (b) The half-life of this reaction is the time needed for one half of the initial  $[\text{A}]$  to react.

$$\text{Thus, } \Delta[\text{A}] = 0.715 \text{ M} \div 2 = 0.358 \text{ M} \text{ and } t_{1/2} = \frac{0.358 \text{ M}}{5.0 \times 10^{-3} \text{ M/s}} = 72 \text{ s.}$$

51. (a) Initial rate =  $-\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1.490 \text{ M} - 1.512 \text{ M}}{1.0 \text{ min} - 0.0 \text{ min}} = +0.022 \text{ M/min}$

$$\text{Initial rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{2.935 \text{ M} - 3.024 \text{ M}}{1.0 \text{ min} - 0.0 \text{ min}} = +0.089 \text{ M/min}$$

- (b) When the initial concentration is doubled ( $\times 2.0$ ), from 1.512 M to 3.024 M, the initial rate quadruples ( $\times 4.0$ ). Thus, the reaction is second-order in A, since  $2.0^x = 4.0$  when  $x = 2$ .

- 53.** The half-life of the reaction depends on the concentration of "A" and, thus, this reaction cannot be first-order. For a second-order reaction, the half-life varies inversely with the rate:  $t_{1/2} = 1/(k[A]_0)$  or  $k = 1/(t_{1/2}[A]_0)$ . Let us attempt to verify the second-order nature of this reaction by seeing if the rate constant is fixed.

$$k = \frac{1}{1.00 \text{ M} \times 50 \text{ min}} = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{2.00 \text{ M} \times 25 \text{ min}} = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$$

$$k = \frac{1}{0.50 \text{ M} \times 100 \text{ min}} = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$$

The constancy of the rate constant demonstrates that this reaction indeed is second-order. The rate equation is  $\text{Rate} = k[A]^2$  and  $k = 0.020 \text{ L mol}^{-1} \text{ min}^{-1}$ .

- 55.** Zeroth-order:  $t_{1/2} = \frac{[A]_0}{2k}$       Second-order:  $t_{1/2} = \frac{1}{k[A]_0}$

A zero-order reaction has a half life that varies proportionally to  $[A]_0$ , therefore, increasing  $[A]_0$  increases the half-life for the reaction. A second-order reaction's half-life varies inversely proportional to  $[A]_0$ , that is, as  $[A]_0$  increases, the half-life decreases. The reason for the difference is that a zero-order reaction has a constant rate of reaction (independent of  $[A]_0$ ). The larger the value of  $[A]_0$ , the longer it will take to react. In a second-order reaction, the rate of reaction increases as the square of the  $[A]_0$ , hence, for high  $[A]_0$ , the rate of reaction is large and for very low  $[A]_0$ , the rate of reaction is very slow. If we consider a bimolecular elementary reaction, we can easily see that a reaction will not take place unless two molecules of reactants collide. This is more likely when the  $[A]_0$  is large than when it is small.

## Collision Theory; Activation Energy

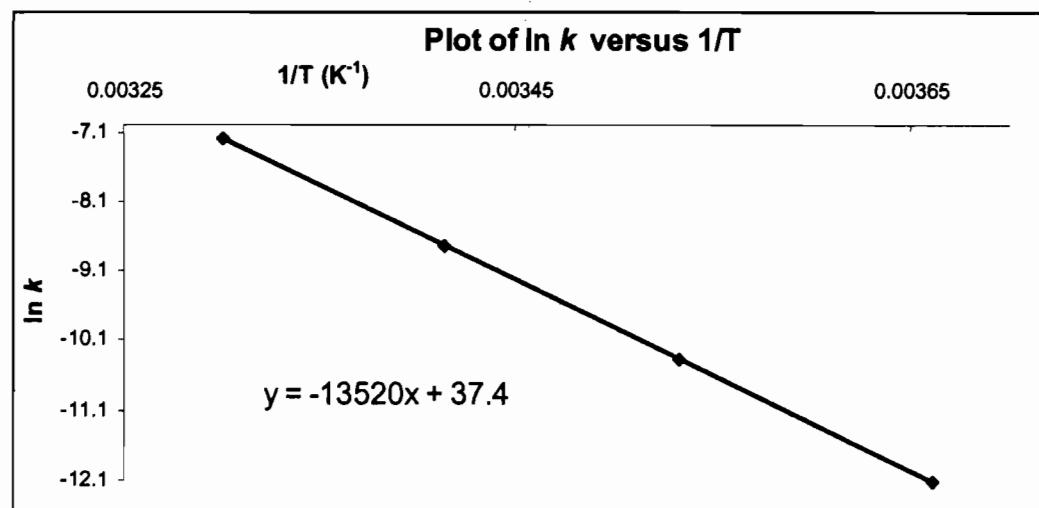
- 57. (a)** The rate of a reaction depends on at least two factors other than the frequency of collisions. The first of these is whether each collision possesses sufficient energy to get over the energy barrier to products. This depends on the activation energy of the reaction; the higher it is, the smaller will be the fraction of successful collisions. The second factor is whether the molecules in a given collision are properly oriented for a successful reaction. The more complex the molecules are, the smaller will be the fraction of collisions that are correctly oriented.

- (b) Although the collision frequency increases relatively slowly with temperature, the fraction of those collisions that have sufficient energy to overcome the activation energy increases much more rapidly. Therefore, the rate of reaction will increase dramatically with temperature.
- (c) The addition of a catalyst has the net effect of decreasing the activation energy of the overall reaction, by enabling an alternate mechanism. The lower activation energy of the alternate mechanism, (compared to the uncatalyzed mechanism), means that a larger fraction of molecules have sufficient energy to react. Thus the rate increases, even though the temperature does not.
59. (a) The products are 21 kJ/mol closer in energy to the constant energy activated complex than are the reactants. Thus, the activation energy for the reverse reaction is  $84 \text{ kJ/mol} - 21 \text{ kJ/mol} = 63 \text{ kJ/mol}$ .
- (b) The reaction profile for this reaction is sketched at below.
- 
61. (a) There are two intermediates (B and C).
- (b) There are three transition states (peaks/maxima) in the energy diagram.
- (c) Fastest step has the smallest  $E_a$ , hence, step 3 is the fastest step in the reaction with step 2 a close second.
- (d) Reactant A (step 1) is the reactant in the rate-limiting step
- (e) endothermic, need energy to go from A → B
- (f) exothermic, energy released when going from A → D.

## Effect of Temperature on Rates of Reaction

63. (a) First we need to compute values of  $\ln k$  and  $1/T$ . Then we plot the graph of  $\ln k$  versus  $1/T$ .

$T, ^\circ\text{C}$	0 $^\circ\text{C}$	10 $^\circ\text{C}$	20 $^\circ\text{C}$	30 $^\circ\text{C}$
$T, \text{K}$	273 K	283 K	293 K	303 K
$1/T, \text{K}^{-1}$	0.00366	0.00353	0.00341	0.00330
$k, \text{s}^{-1}$	$5.6 \times 10^{-6}$	$3.2 \times 10^{-5}$	$1.6 \times 10^{-4}$	$7.6 \times 10^{-4}$
$\ln k$	-12.09	-10.35	-8.74	-7.18



(b) The slope  $= -E_a / R$ .  $E_a = -R \times \text{slope} = -8.3145 \frac{\text{J}}{\text{mol K}} \times -1.35 \times 10^4 \text{ K} = 112 \text{ kJ/mol}$

- (c) We apply the Arrhenius equation, with  $k = 5.6 \times 10^{-6} \text{ s}^{-1}$  at  $0^\circ\text{C}$  (273 K),  $k = ?$  at  $40^\circ\text{C}$  (313 K), and  $E_a = 113 \times 10^3 \text{ J/mol}$ .

$$\ln \frac{k}{5.6 \times 10^{-6} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{113 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{273 \text{ K}} - \frac{1}{313 \text{ K}} \right) = 6.36$$

$$e^{6.36} = 578 = \frac{k}{5.6 \times 10^{-6} \text{ s}^{-1}} \quad k = 578 \times 5.6 \times 10^{-6} \text{ s}^{-1} = 3.2 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.2 \times 10^{-3} \text{ s}^{-1}} = 2.2 \times 10^2 \text{ s}$$

- 65.** The half-life of a first-order reaction is inversely proportional to its rate constant:  $k = 0.693 / t_{1/2}$ . Thus we can apply a modified version of the Arrhenius equation.

$$(a) \ln \frac{k_2}{k_1} = \ln \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \ln \frac{46.2 \text{ min}}{2.6 \text{ min}} = \frac{E_a}{R} \left( \frac{1}{298 \text{ K}} - \frac{1}{(102+273) \text{ K}} \right)$$

$$2.88 = \frac{E_a}{R} 6.89 \times 10^{-4} \quad E_a = \frac{2.88 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{6.89 \times 10^{-4} \text{ K}^{-1}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 34.8 \text{ kJ/mol}$$

$$(b) \ln \frac{10.0 \text{ min}}{46.2 \text{ min}} = \frac{34.8 \times 10^3 \text{ J / mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{T} - \frac{1}{298} \right) = -1.53 = 4.19 \times 10^3 \left( \frac{1}{T} - \frac{1}{298} \right)$$

$$\left( \frac{1}{T} - \frac{1}{298} \right) = \frac{-1.53}{4.19 \times 10^3} = -3.65 \times 10^{-4} \quad \frac{1}{T} = 2.99 \times 10^{-3} \quad T = 334 \text{ K} = 61 \text{ }^\circ\text{C}$$

- 67. (a)** It is the change in the value of the rate constant that causes the reaction to go faster. Let  $k_1$  be the rate constant at room temperature,  $20^\circ \text{ C}$  or  $293 \text{ K}$ . Then  $k_2 = 2k_1$  is the rate constant ten degrees higher, at  $30^\circ \text{ C}$  or  $303 \text{ K}$ .

$$\ln \frac{k_2}{k_1} = \ln \frac{2k_1}{k_1} = 0.693 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{R} \left( \frac{1}{293} - \frac{1}{303 \text{ K}} \right) = 1.13 \times 10^{-4} \text{ K}^{-1} \frac{E_a}{R}$$

$$E_a = \frac{0.693 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{1.13 \times 10^{-4} \text{ K}^{-1}} = 5.1 \times 10^4 \text{ J / mol} = 51 \text{ kJ / mol}$$

- (b)** Since the activation energy for the depicted reaction (i.e.,  $\text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2$ ) is 209 kJ/mol, we would not expect this reaction to follow the rule of thumb.

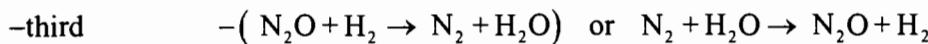
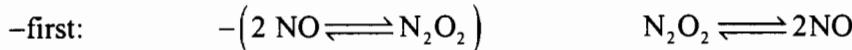
## Catalysis

- 69. (a)** Although a catalyst is *recovered unchanged from the reaction mixture*, it does “take part in the reaction.” Some catalysts actually slow down the rate of a reaction. Usually, however, these negative catalysts are called inhibitors.
- (b)** The function of a catalyst is to *change the mechanism of a reaction*. The new mechanism is one that has a different (lower) activation energy than the original reaction.
- 71.** Both platinum and an enzyme can be considered heterogeneous catalysts in the sense that the catalytic activity occurs on their surfaces or near them. Even so, some would classify an enzyme as a homogeneous catalyst. The most important difference, however, is one of specificity. Platinum is a rather nonspecific catalyst, catalyzing many different reactions. An enzyme, however, is quite specific, usually catalyzing only one reaction rather than all reactions of a given class.

- 73.** For the straight-line graph of Rate versus [Enzyme], an excess of substrate must be present.

## Reaction Mechanisms

- 75.** The molecularity of an elementary process is the number of reactant molecules in that process. This molecularity is equal to the order of the overall reaction only if the elementary process in question is the slowest and, thus, the rate-determining step of the overall reaction. In addition, the elementary process in question should be the only elementary step that influences the rate of the reaction.
- 77.** The three elementary steps must sum to the overall reaction. That is, the overall reaction is the sum of step 1 + step 2 + step 3. Hence, step 2 = overall reaction – step 1 – step 3. All species in the equations below are gases.



The rate of this rate-determining step is:  $\text{Rate} = k_2 [\text{H}_2][\text{N}_2\text{O}_2]$

Since  $\text{N}_2\text{O}_2$  does not appear in the overall reaction, we need to replace its concentration with the concentrations of species that do appear in the overall reaction. To do this, recall that the first step is rapid, with the forward reaction occurring at the same rate as the reverse reaction.  $k_1[\text{NO}]^2 = \text{forward rate} = \text{reverse rate} = k_{-1}[\text{N}_2\text{O}_2]$

This expression is solved for  $[\text{N}_2\text{O}_2]$ , which then is substituted into the rate equation for the overall reaction.

$$[\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{k_{-1}}$$

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{H}_2] [\text{NO}]^2$$

The reaction is first-order in  $[\text{H}_2]$  and second-order in  $[\text{NO}]$ . This result conforms to the experimentally determined reaction order.

- 79.** Proposed mechanism:  $\text{Cl}_2(\text{g}) \rightleftharpoons \frac{k_1}{k_{-1}} 2\text{Cl}(\text{g})$  Observed rate law:  $\text{Rate} = k[\text{Cl}_2][\text{NO}_2]^2$
- $$\frac{2\text{Cl}(\text{g}) + 2\text{NO}(\text{g}) \xrightarrow{k_2} 2\text{NOCl}(\text{g})}{\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{NOCl}(\text{g})}$$

The first step is a fast equilibrium reaction and step 2 is slow. Thus, the predicted rate law is  $\text{Rate} = k_2[\text{Cl}]^2[\text{NO}]^2$

In the first step, set the rate in the forward direction for the equilibrium equal to the rate in the reverse direction. Then solve for  $[Cl]^2$ .

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}} \quad \text{Use: Rate}_{\text{forward}} = k_1[Cl_2] \text{ and Rate}_{\text{reverse}} = k_{-1}[Cl]^2$$

From this we see:  $k_1[Cl_2] = k_{-1}[Cl]^2$ . Rearranging (solving for  $[Cl]^2$ )

$$[Cl]^2 = \frac{k_1[Cl_2]}{k_{-1}} \quad \text{Substitute into Rate} = k_2[Cl]^2[NO]^2 = k_2 \frac{k_1[Cl_2]}{k_{-1}} [NO]^2 = k_{\text{obs}}[Cl_2][NO_2]^2$$

Since the predicted rate law is the same as the experimental rate law, this mechanism is plausible..

## FEATURE PROBLEMS

- 104. (a)** To determine the order of the reaction, we need  $[C_6H_5N_2Cl]$  at each time. To determine this value, note that 58.3 mL  $N_2(g)$  evolved corresponds to total depletion of  $C_6H_5N_2Cl$ , to  $[C_6H_5N_2Cl] = 0.000\text{ M}$ . Thus, at any point in time,

$$[C_6H_5N_2Cl] = 0.071\text{ M} - \left( \text{volume } N_2(g) \times \frac{0.071\text{ M } C_6H_5N_2Cl}{58.3\text{ mL } N_2(g)} \right)$$

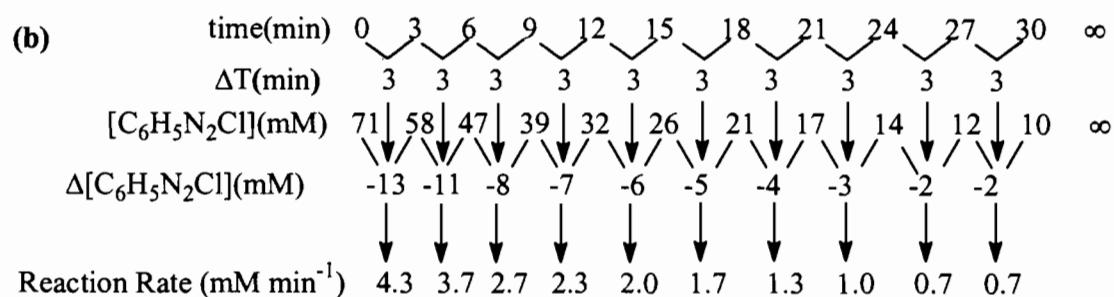
Consider 21 min:

$$[C_6H_5N_2Cl] = 0.071\text{ M} - \left( 44.3\text{ mL } N_2 \times \frac{0.071\text{ M } C_6H_5N_2Cl}{58.3\text{ mL } N_2(g)} \right) = 0.017\text{ M}$$

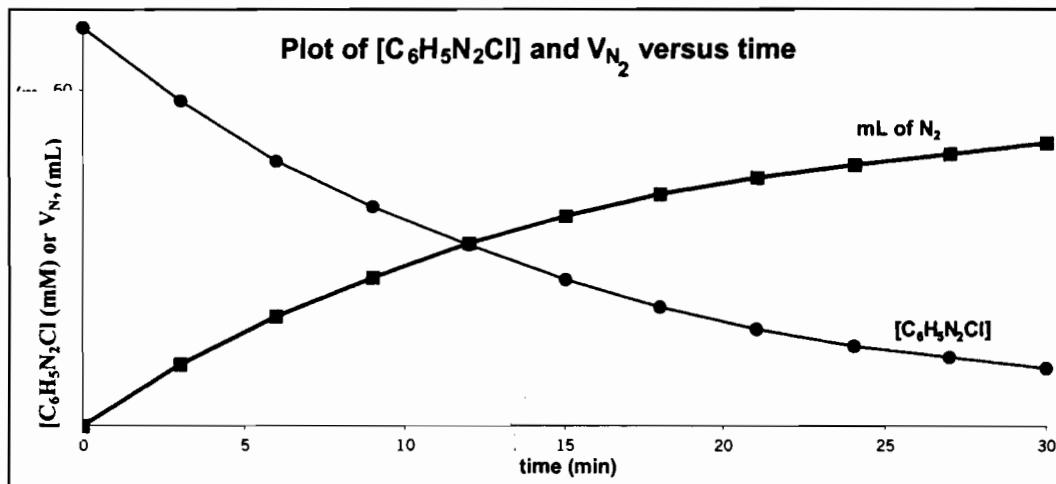
The numbers in the following table are determined with this method.

time, min	0	3	6	9	12	15	18	21	24	27	30	$\infty$
$V_{N_2}$ , mL	0	10.8	19.3	26.3	32.4	37.3	41.3	44.3	46.5	48.4	50.4	58.3
$[C_6H_5N_2Cl]$ , mM	71	58	47	39	32	26	21	17	14	12	10	0

[The concentration is given in thousandths of a mole per liter (mM).]



- (c) The two graphs are drawn on the same axes.



- (b) The rate of the reaction at  $t = 21$  min is the slope of the tangent line to the  $[C_6H_5N_2Cl]$  curve. The tangent line intercepts the vertical axis at about  $[C_6H_5N_2Cl] = 39$  mM and the horizontal axis at about 37 min

$$\text{Rate} = \frac{39 \times 10^{-3} \text{ M}}{37 \text{ min}} = 1.05 \times 10^{-3} \text{ M min}^{-1} = 1.1 \times 10^{-3} \text{ M min}^{-1}$$

The agreement with the reported value is very good.

- (e) The initial rate is the slope of the tangent line to the  $[C_6H_5N_2Cl]$  curve at  $t = 0$ . The intercept with the vertical axis is 71 mM, of course. That with the horizontal axis is about 13 min.

$$\text{Rate} = \frac{71 \times 10^{-3} \text{ M}}{13 \text{ min}} = 5.5 \times 10^{-3} \text{ M min}^{-1}$$

- (f) The first-order rate law is  $\text{Rate} = k[C_6H_5N_2Cl]$ , which we solve for  $k$ :

$$k = \frac{\text{Rate}}{[C_6H_5N_2Cl]}$$

$$k_0 = \frac{5.5 \times 10^{-3} \text{ M min}^{-1}}{71 \times 10^{-3} \text{ M}} = 0.077 \text{ min}^{-1}$$

$$k_{21} = \frac{1.1 \times 10^{-3} \text{ M min}^{-1}}{17 \times 10^{-3} \text{ M}} = 0.065 \text{ min}^{-1}$$

An average value would be a good estimate:  $k_{\text{avg}} = 0.071 \text{ min}^{-1}$

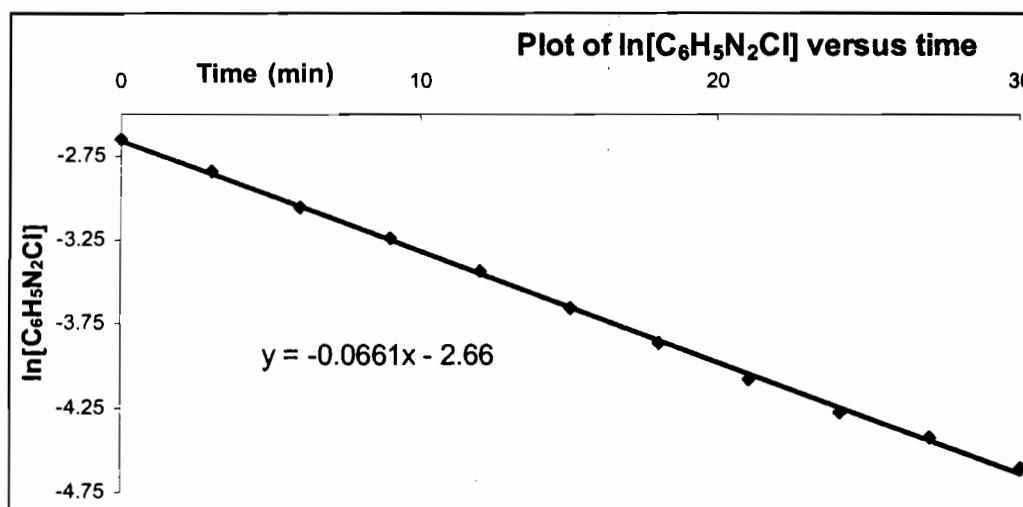
- (g) The estimated rate constant gives one value of the half-life:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.071 \text{ min}^{-1}} = 9.8 \text{ min}$$

The first half-life occurs when  $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  drops from 0.071 M to 0.0355 M. This seems to occur at about 10.5 min.

- (h) The reaction should be three-fourths complete in two half-lives, about 20 minutes.

- (i) The graph plots  $\ln[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]$  (in millimoles/L) vs. time in minutes.



The linearity of the graph demonstrates that the reaction is first-order.

(j)  $k = -\text{slope} = -(-6.61 \times 10^{-2}) \text{ min}^{-1} = 0.0661 \text{ min}^{-1}$

$$t_{1/2} = \frac{0.693}{0.0661 \text{ min}^{-1}} = 10.5 \text{ min},$$

in good agreement with our previously determined values.

- 105. (a)** In Experiments 1 & 2,  $[\text{KI}]$  is the same (0.20 M), while  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  is halved, from 0.20 M to 0.10 M. As a consequence, the time to produce a color change doubles, that is, the rate is halved. This indicates that reaction (a) is first-order in  $\text{S}_2\text{O}_8^{2-}$ . Experiments 2 and 3 produce a similar conclusion. In Experiments 4 and 5,  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  is the same (0.20 M) while  $[\text{KI}]$  is halved, from 0.10 to 0.050 M. As a consequence, the time to produce a color change nearly doubles, that is, the rate is halved. This indicates that reaction (a) is also first-order in  $\text{I}^-$ . Reaction (a) is (1 + 1) second-order overall.

- (b) The blue color appears when all the  $\text{S}_2\text{O}_3^{2-}$  has been consumed, for only then does reaction (b) cease. The same amount of  $\text{S}_2\text{O}_3^{2-}$  is placed in each reaction mixture.

$$\begin{aligned}\text{amount } \text{S}_2\text{O}_3^{2-} &= 10.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.010 \text{ mol } \text{Na}_2\text{S}_2\text{O}_3}{1 \text{ L}} \times \frac{1 \text{ mol } \text{S}_2\text{O}_3^{2-}}{1 \text{ mol } \text{Na}_2\text{S}_2\text{O}_3} \\ &= 1.0 \times 10^{-4} \text{ mol}\end{aligned}$$

Through stoichiometry, we determine the amount of each reactant that reacts before this amount of  $\text{S}_2\text{O}_3^{2-}$  will be consumed.

$$\begin{aligned}\text{amount } \text{S}_2\text{O}_8^{2-} &= 1.0 \times 10^{-4} \text{ mol } \text{S}_2\text{O}_3^{2-} \times \frac{1 \text{ mol } \text{I}_3^-}{2 \text{ mol } \text{S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mol } \text{S}_2\text{O}_8^{2-}}{1 \text{ mol } \text{I}_3^-} \\ &= 5.0 \times 10^{-5} \text{ mol } \text{S}_2\text{O}_8^{2-}\end{aligned}$$

$$\text{amount } \text{I}^- = 5.0 \times 10^{-5} \text{ mol } \text{S}_2\text{O}_8^{2-} \times \frac{2 \text{ mol } \text{I}^-}{1 \text{ mol } \text{S}_2\text{O}_8^{2-}} = 1.0 \times 10^{-4} \text{ mol } \text{I}^-$$

Note that we do not use “3 mol  $\text{I}^-$ ” from equation (a) since one mole has not been oxidized; it simply complexes with the product  $\text{I}_2$ . The total volume of each solution is  $(25.0 \text{ mL} + 25.0 \text{ mL} + 10.0 \text{ mL} + 5.0 \text{ mL}) = 65.0 \text{ mL}$ , or  $0.0650 \text{ L}$ .

The amount of  $\text{S}_2\text{O}_8^{2-}$  that reacts in each case is  $5.0 \times 10^{-5} \text{ mol}$  and thus

$$\Delta[\text{S}_2\text{O}_8^{2-}] = \frac{-5.0 \times 10^{-5} \text{ mol}}{0.0650 \text{ L}} = -7.7 \times 10^{-4} \text{ M}$$

$$\text{Thus, Rate}_1 = \frac{-\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{+7.7 \times 10^{-4} \text{ M}}{21 \text{ s}} = 3.7 \times 10^{-5} \text{ M s}^{-1}$$

$$(c) \text{ For Experiment 2, Rate}_2 = \frac{-\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = \frac{+7.7 \times 10^{-4} \text{ M}}{42 \text{ s}} = 1.8 \times 10^{-5} \text{ M s}^{-1}$$

To determine the value of  $k$ , we need initial concentrations, as altered by dilution.

$$[\text{S}_2\text{O}_8^{2-}]_1 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL total}} = 0.077 \text{ M} \quad [\text{I}^-]_1 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL}} = 0.077 \text{ M}$$

$$\text{Rate}_1 = 3.7 \times 10^{-5} \text{ M s}^{-1} = k[\text{S}_2\text{O}_8^{2-}]^1[\text{I}^-]^1 = k(0.077 \text{ M})^1(0.077 \text{ M})^1$$

$$k = \frac{3.7 \times 10^{-5} \text{ M s}^{-1}}{0.077 \text{ M} \times 0.077 \text{ M}} = 6.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$[\text{S}_2\text{O}_8^{2-}]_2 = 0.10 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL total}} = 0.038 \text{ M} \quad [\text{I}^-]_2 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL}} = 0.077 \text{ M}$$

$$\text{Rate}_2 = 1.8 \times 10^{-5} \text{ M s}^{-1} = k \left[ \text{S}_2\text{O}_8^{2-} \right]^1 \left[ \text{I}^- \right]^1 = k (0.038 \text{ M})^1 (0.077 \text{ M})^1$$

$$k = \frac{1.8 \times 10^{-5} \text{ M s}^{-1}}{0.038 \text{ M} \times 0.077 \text{ M}} = 6.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

- (d) First we determine concentrations for Experiment 4.

$$\left[ \text{S}_2\text{O}_8^{2-} \right]_4 = 0.20 \text{ M} \times \frac{25.0 \text{ mL}}{65.0 \text{ mL total}} = 0.077 \text{ M} \quad \left[ \text{I}^- \right]_4 = 0.10 \times \frac{25.0 \text{ mL}}{65.0 \text{ mL}} = 0.038 \text{ M}$$

We have two expressions for Rate; let us equate them and solve for the rate constant.

$$\text{Rate}_4 = \frac{-\Delta \left[ \text{S}_2\text{O}_8^{2-} \right]}{\Delta t} = \frac{+7.7 \times 10^{-4} \text{ M}}{\Delta t} = k \left[ \text{S}_2\text{O}_8^{2-} \right]_4^1 \left[ \text{I}^- \right]_4^1 = k (0.077 \text{ M})(0.038 \text{ M})$$

$$k = \frac{7.7 \times 10^{-4} \text{ M}}{\Delta t \times 0.077 \text{ M} \times 0.038 \text{ M}} = \frac{0.26 \text{ M}^{-1}}{\Delta t}$$

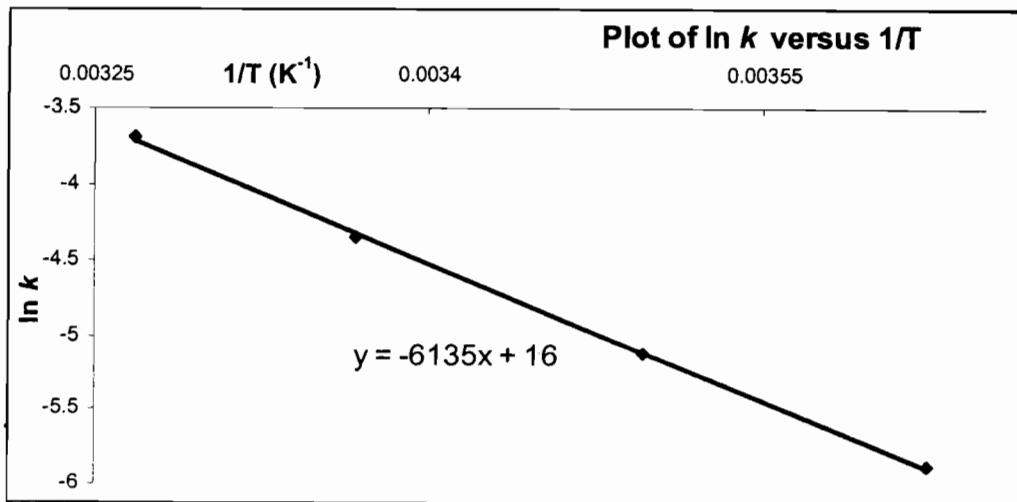
$$k_3 = \frac{0.26 \text{ M}^{-1}}{189 \text{ s}} = 0.0014 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{13} = \frac{0.26 \text{ M}^{-1}}{88 \text{ s}} = 0.0030 \text{ M}^{-1} \text{ s}^{-1}$$

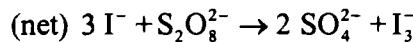
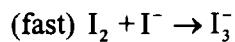
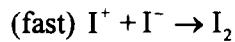
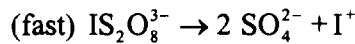
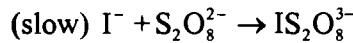
$$k_{24} = \frac{0.26 \text{ M}^{-1}}{42 \text{ s}} = 0.0062 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{33} = \frac{0.26 \text{ M}^{-1}}{21 \text{ s}} = 0.012 \text{ M}^{-1} \text{ s}^{-1}$$

- (e) We plot  $\ln k$  vs.  $1/T$ . The slope of the line  $= -E_a / R$ .



- (f) For the mechanism to agree with the reaction stoichiometry, the steps of the mechanism must sum to the overall reaction, in the manner of Hess's law.



Each of the intermediates cancels:  $\text{IS}_2\text{O}_8^{3-}$  is produced in the first step and consumed in the second,  $\text{I}^+$  is produced in the second step and consumed in the third,  $\text{I}_2$  is produced in the third step and consumed in the 4th. The mechanism is consistent with the stoichiometry. The rate of the slow step of the mechanism is

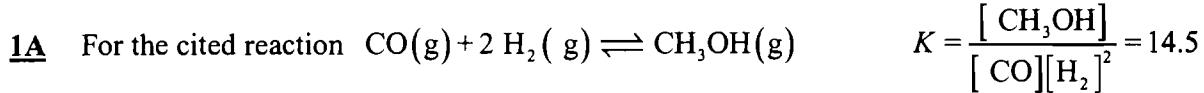
$$\text{Rate}_1 = k_1 [\text{S}_2\text{O}_8^{2-}]^1 [\text{I}^-]^1$$

This is exactly the same as the experimental rate law. It is reasonable that the first step be slow since it involves two negatively charged species coming together. We know that like charges repel, and thus this should not be an easy or rapid process.

# CHAPTER 16

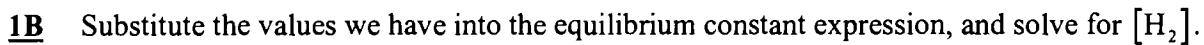
## PRINCIPLES OF CHEMICAL EQUILIBRIUM

### PRACTICE EXAMPLES

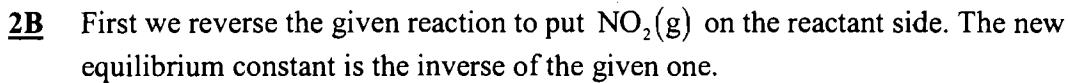
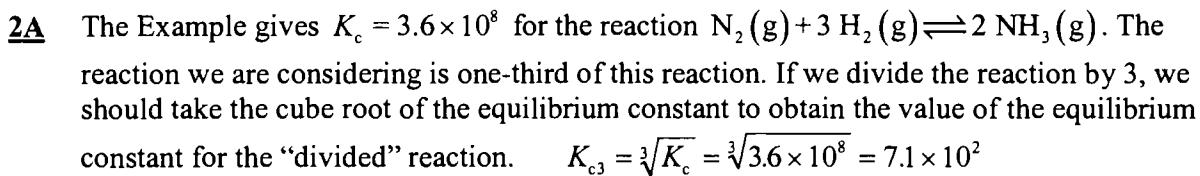


Given that  $[\text{CO}] = [\text{CH}_3\text{OH}]$ . Thus, one may be substituted for the other, and the resulting

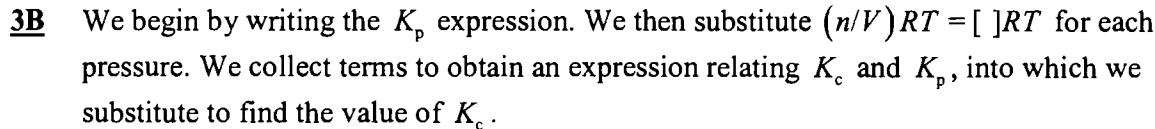
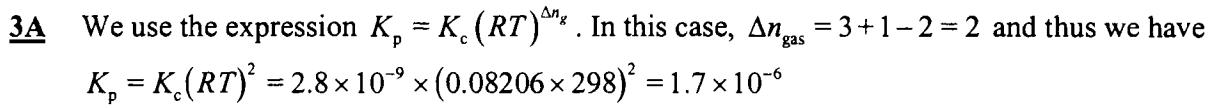
$$\text{equation solved for } [\text{H}_2]. \quad K = \frac{[\text{CO}]}{[\text{CO}][\text{H}_2]^2} = 14.5 = \frac{1}{[\text{H}_2]^2} \quad [\text{H}_2] = \sqrt{\frac{1}{14.5}} = 0.263 \text{ M}$$



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 1.8 \times 10^4 = \frac{(2.00 \text{ M})^2}{0.015 \text{ M} [\text{H}_2]^3} \quad [\text{H}_2] = \sqrt[3]{[\text{H}_2]^3} = \sqrt[3]{\frac{(2.00)^2}{1.8 \times 10^4 \times 0.015}} = 0.25 \text{ M}$$



Then we double the reaction to obtain 2 moles of  $\text{NO}_2(\text{g})$  as reactant. The equilibrium constant is then raised to the second power.



$$K_p = \frac{\{P(\text{H}_2)\}^2 \{P(\text{S}_2)\}}{\{P(\text{H}_2\text{S})\}^2} = \frac{([\text{H}_2]RT)^2 ([\text{S}_2]RT)}{([\text{H}_2\text{S}]RT)^2} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} RT = K_c RT$$

Same result can be obtained by using  $K_p = K_c (RT)^{\Delta n_{\text{gas}}}$ , since  $\Delta n_{\text{gas}} = 2 + 1 - 2 = +1$ .

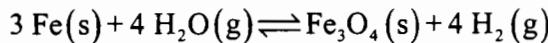
$$K_c = \frac{K_p}{RT} = \frac{1.2 \times 10^{-2}}{0.0806 \times (1065 + 273)} = 1.1 \times 10^{-4}$$

But the reaction has been reversed and halved. Thus

$$K_{\text{final}} = \sqrt{\frac{1}{K_c}} = \sqrt{\frac{1}{1.1 \times 10^{-4}}} = \sqrt{9090} = 95.3$$

- 4A** We remember that neither solids, such as  $\text{Ca}_5(\text{PO}_4)_3\text{OH(s)}$ , nor liquids, such as  $\text{H}_2\text{O(l)}$ , appear in the equilibrium constant expression. Concentrations of products appear in the numerator, those of reactants in the denominator.  $K_c = \frac{[\text{Ca}^{2+}]^5 [\text{HPO}_4^{2-}]^3}{[\text{H}^+]^4}$

- 4B** First we write the balanced chemical equation for the reaction. Then we write the equilibrium constant expressions, remembering that gases and solutes in aqueous solution appear in the  $K_c$  expression, but pure liquids and pure solids do not.



$$K_p = \frac{\{P(\text{H}_2)\}^4}{\{P(\text{H}_2\text{O})\}^4} \quad K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} \quad \text{Because } \Delta n_{\text{gas}} = 4 - 4 = 0, K_p = K_c$$

- 5A** We compare the value of the reaction quotient,  $Q_c$ , with that of  $K_c$ .

$$Q_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.50 \text{ M} \times 0.20 \text{ M}}{4.50 \text{ M}} = 0.022 < 0.0454 = K_c$$

Because  $Q_c < K_c$ , the net reaction will proceed to the right, forming products.

- 5B** We compute the value of  $Q_c$ . Each concentration equals the mass ( $m$ ) of the substance divided by its molar mass (which quotient is the amount of the substance in moles) and further divided by the volume of the container.

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{\frac{m \times \frac{1 \text{ mol CO}_2}{44.0 \text{ g CO}_2}}{V} \times \frac{m \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2}}{V}}{\frac{m \times \frac{1 \text{ mol CO}}{28.0 \text{ g CO}}}{V} \times \frac{m \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}}}{V}} = \frac{\frac{1}{44.0 \times 2.0}}{\frac{1}{28.0 \times 18.0}} = \frac{28.0 \times 18.0}{44.0 \times 2.0} = 5.7 > 1.00 = K_c$$

(In evaluating the expression above, we cancelled the equal values of  $V$ , and we also cancelled the equal values of  $m$ .) Because the value of  $Q_c$  is larger than the value of  $K_c$ , reaction will proceed to the left to reach a state of equilibrium. Thus, at equilibrium there will be larger amounts of reactants, and smaller amounts of products than there are initially.

- 6A**  $O_2(g)$  is a reactant. The equilibrium system will shift right forming product in an attempt to consume some of the added reactant. Looked at in another way,  $[O_2]$  is increased above its equilibrium value by the addition of oxygen. This makes  $Q_c$  smaller than  $K_c$ . (The  $[O_2]$  is in the denominator of the expression.) And the system shifts right to compensate.
- 6B** (a) The position of an equilibrium mixture is affected only by changing the concentration of substances that appear in the equilibrium constant expression,  $K_c = [CO_2]$ . Since  $CaO(s)$  is a pure solid, its concentration does not appear in the equilibrium constant expression and thus its addition will have no direct effect on the position of equilibrium.
- (b) The addition of  $CO_2(g)$  will increase  $[CO_2]$  above its equilibrium value. The reaction will shift left to alleviate this increase; some  $CaCO_3(s)$  will form.
- (c) Since  $CaCO_3(s)$  is a pure solid like  $CaO(s)$ , its concentration does not appear in the equilibrium constant expression and thus the addition of any solid  $CaCO_3$  to an equilibrium mixture will not have an effect upon the position of equilibrium
- 7A** We know that a decrease in volume or an increase in pressure of an equilibrium mixture of gases causes a net reaction in the direction producing the smaller number of moles of gas. In the reaction in question, that direction is to the left: one mole of  $N_2O_4(g)$  is formed when two moles of  $NO_2(g)$  combine. Thus, decreasing the cylinder volume would have the initial effect of doubling both  $[N_2O_4]$  and  $[NO_2]$ . In order to reestablish equilibrium, some  $NO_2$  will then be converted into  $N_2O_4$ . Note, however, that the  $NO_2$  concentration will still ultimately end up being higher than it was prior to pressurization.
- 7B** In the balanced chemical equation for the chemical reaction  $\Delta n_{\text{gas}} = (1+1) - (1+1) = 0$ . As a consequence, a change in overall volume or total gas pressure will have no effect on the position of equilibrium. In the equilibrium constant expression, the two partial pressures in the numerator will be affected to exactly the same degree as the two partial pressures in the denominator, and  $Q_p$  will continue to equal  $K_p$ .
- 8A** The cited reaction is endothermic. Raising the temperature on an equilibrium mixture favors the endothermic reaction. Thus,  $N_2O_4(g)$  should decompose more completely at higher temperatures and the amount of  $NO_2(g)$  formed from a given amount of  $N_2O_4(g)$  will be greater at high temperatures than at low ones.
- 8B** The  $NH_3(g)$  formation reaction is  $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$   $\Delta H^\circ = -46.11 \text{ kJ/mol}$  This reaction is an exothermic reaction. Lowering temperature causes a shift in the direction of this exothermic reaction. The reaction will shift right at a lower temperature.  $[NH_3(g)]$  will be greater at  $-100^\circ\text{C}$ .

**9A** We write the expression for  $K_c$  and then substitute expressions for molar concentrations.

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{0.22 \text{ mol } H_2}{3.00 \text{ L}}\right)^2 \frac{0.11 \text{ mol } S_2}{3.00 \text{ L}}}{\left(\frac{2.78 \text{ mol } H_2S}{3.00 \text{ L}}\right)^2} = 2.3 \times 10^{-4}$$

**9B** We write the equilibrium constant expression and solve it for  $[N_2O_4]$ .

$$K_c = 4.61 \times 10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} \quad [N_2O_4] = \frac{[NO_2]^2}{4.61 \times 10^{-3}} = \frac{(0.0236 \text{ M})^2}{4.61 \times 10^{-3}} = 0.121 \text{ M}$$

Then we determine the mass of  $N_2O_4$  present in 2.26 L.

$$N_2O_4 \text{ mass} = 2.26 \text{ L} \times \frac{0.121 \text{ mol } N_2O_4}{1 \text{ L}} \times \frac{92.01 \text{ g } N_2O_4}{1 \text{ mol } N_2O_4} = 25.2 \text{ g } N_2O_4$$

**10A** We use the initial-change-equilibrium setup to establish the amount of each substance at equilibrium. We label each entry in the table in the order of its determination (1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>), to better illustrate the technique. We know the initial amounts of all substances (1st). (There are zero moles of each product at the start).

Because “initial”+“change”=“equilibrium”, the equilibrium amount (2nd) of  $Br_2(g)$  enables us to determine “change” (3rd) for  $Br_2(g)$ . We then use stoichiometry to write other entries (4th) on the “change” line. And finally, we determine the remaining equilibrium amounts (5th).

reaction:	2 NOBr(g)	$\rightleftharpoons$	2 NO(g)	+	Br <sub>2</sub> (g)
initial:	1.86 mol (1 <sup>st</sup> )		0.00 mol (1 <sup>st</sup> )		0.00 mol (1 <sup>st</sup> )
change:	-0.164 mol (4 <sup>th</sup> )		+0.164 mol (4 <sup>th</sup> )		+0.082 mol (3 <sup>rd</sup> )
equil.:	1.70 mol (5 <sup>th</sup> )		0.164 mol (5 <sup>th</sup> )		0.082 mol (2 <sup>nd</sup> )

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{\left(\frac{0.164 \text{ mol NO}}{5.00 \text{ L}}\right)^2 \left(\frac{0.082 \text{ mol Br}_2}{5.00 \text{ L}}\right)}{\left(\frac{1.70 \text{ mol NOBr}}{5.00 \text{ L}}\right)^2} = 1.5 \times 10^{-4}$$

In this case,

$$\Delta n_{\text{gas}} = 2 + 1 - 2 = +1. \quad K_p = K_c (RT)^{+1} = 1.5 \times 10^{-4} \times 0.08206 \times 298 = 3.7 \times 10^{-3}$$

- 10B** We use the amounts stated in the problem to determine the equilibrium amount of each substance.

reaction:	$2 \text{SO}_3(\text{g}) \rightleftharpoons 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$		
initial:	0 mol	0.100 mol	0.100 mol
changes:	+0.0916 mol	-0.0916 mol	-0.0916/2 mol
equil.:	0.0916 mol	0.0084 mol	0.0542 mol
concentrations:	$\frac{0.916 \text{ mol}}{1.52 \text{ L}}$	$\frac{0.0084 \text{ mol}}{1.52 \text{ L}}$	$\frac{0.0542 \text{ mol}}{1.52 \text{ L}}$
concentrations:	0.0603 M	0.0055 M	0.0357 M

We use these values to compute  $K_c$  for the reaction and then the relationship

$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$  (with  $\Delta n_{\text{gas}} = 2 + 1 - 2 = +1$ ) to determine the value of  $K_p$ .

$$K_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2} = \frac{(0.0055)^2 (0.0357)}{(0.0603)^2} = 3.0 \times 10^{-4} K_p = 3.0 \times 10^{-4} \times 0.08206 \times 900 \approx 0.022$$

- 11A** The equilibrium constant expression is  $K_p = P\{\text{H}_2\text{O}\} P\{\text{CO}_2\} = 0.231$  at 100 °C. From the balanced chemical equation, we see that one mole of  $\text{H}_2\text{O}(\text{g})$  is formed for each mole of  $\text{CO}_2(\text{g})$ . Consequently,  $P\{\text{H}_2\text{O}\} = P\{\text{CO}_2\}$  and  $K_p = (P\{\text{CO}_2\})^2$ . We solve this expression for  $P\{\text{CO}_2\}$ :  $P\{\text{CO}_2\} = \sqrt[2]{(P\{\text{CO}_2\})^2} = \sqrt[2]{K_p} = \sqrt[2]{0.231} = 0.481 \text{ atm}$

- 11B** The equation for the reaction is  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \quad K_p = 0.108$  at 25 °C. The two partial pressures do not have to be equal at equilibrium. The only instance in which they must be equal is when all of the two gases come from the decomposition of  $\text{NH}_4\text{HS}(\text{s})$ . In this case, some of the  $\text{NH}_3(\text{g})$  comes from another source. We can obtain the pressure of  $\text{H}_2\text{S}(\text{g})$  by substitution into the equilibrium constant expression, since we are given the equilibrium pressure of  $\text{NH}_3(\text{g})$ .

$$K_p = P\{\text{H}_2\text{S}\} P\{\text{NH}_3\} = 0.108 = P\{\text{H}_2\text{S}\} \times 0.500 \text{ atm} \quad P\{\text{H}_2\text{S}\} = \frac{0.108}{0.500} = 0.216 \text{ atm}$$

$$\text{So, } P_{\text{total}} = P_{\text{H}_2\text{S}} + P_{\text{NH}_3} = 0.216 \text{ atm} + 0.500 \text{ atm} = 0.716 \text{ atm}$$

- 12A** We set up this problem in the same manner we have previously employed, designating the equilibrium amount of  $\text{HI}$  as  $2x$ . (Note that we use the same multipliers for  $x$  as the stoichiometric coefficients.)

Equation:	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$		
Initial:	0.150 mol	0.200 mol	0 mol
Changes:	$-x$ mol	$-x$ mol	$+2x$ mol
Equil.:	$(0.150 - x)$ mol	$(0.200 - x)$ mol	$2x$ mol

$$K_c = \frac{\left(\frac{2x}{15.0}\right)^2}{\frac{0.150-x}{15.0} \times \frac{0.200-x}{15.0}} = \frac{(2x)^2}{(0.150-x)(0.200-x)} = 50.2$$

We substitute these expressions into the equilibrium constant expression and solve for  $x$

$$4x^2 = (0.150-x)(0.200-x)50.2 = 50.2(0.0300 - 0.350x + x^2) = 1.51 - 17.6x + 50.2x^2$$

$$0 = 46.2x^2 - 17.6x + 1.51 \quad \text{Now we use the quadratic formula to obtain a value of } x.$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{17.6 \pm \sqrt{(17.6)^2 - 4 \times 46.2 \times 1.51}}{2 \times 46.2} = \frac{17.6 \pm 5.54}{92.4} = 0.250 \text{ or } 0.131$$

The first root cannot be used because we cannot have  $(0.150 - 0.250 = -0.100)$  a negative amount of  $\text{H}_2$ . Thus, we have  $2 \times 0.131 = 0.262$  mol HI at equilibrium. We check by substituting the amounts into the  $K_c$  expression. (Notice that the volumes cancel.) The slight disagreement in the two values (52 compared to 50.2) is the result of rounding error.

$$K_c = \frac{(0.262)^2}{(0.150 - 0.131)(0.200 - 0.131)} = \frac{0.0686}{0.019 \times 0.069} = 52$$

- 12B (a)** The equation for the reaction is  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$   $K_c = 4.61 \times 10^{-3}$  at  $25^\circ\text{C}$ . In the example, this reaction is conducted in a 0.372 L flask. The effect of moving the mixture to the larger, 10.0 L container is that the reaction will shift to produce a greater number of moles of gas;  $\text{NO}_2(\text{g})$  will be produced and  $\text{N}_2\text{O}_4(\text{g})$  will dissociate. Consequently, the amount of  $\text{N}_2\text{O}_4$  will decrease.

- (b)** The equilibrium constant expression substituting 10.0 L for 0.372 L, follows.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{\left(\frac{2x}{10.0}\right)^2}{\frac{0.0240-x}{10.0}} = \frac{4x^2}{10.0(0.0240-x)} = 4.61 \times 10^{-3}$$

This can be solved with the quadratic equation, and the result is  $x = 0.0118$  moles. We can attempt the method of successive approximations. *First*, assume that  $x \ll 0.0240$ . We obtain:

$$x = \frac{\sqrt{4.61 \times 10^{-3} \times 10.0 (0.0240 - 0)}}{4} = \sqrt{4.61 \times 10^{-3} \times 2.50 (0.0240 - 0)} = 0.0166$$

Clearly  $x$  is not much smaller than 0.0240. So, *second*, assume  $x \approx 0.0166$ . We obtain:

$$x = \sqrt{4.61 \times 10^{-3} \times 2.50 (0.0240 - 0.0166)} = 0.00925$$

This assumption is not valid either. So, *third*, assume  $x \approx 0.00925$ . We obtain:

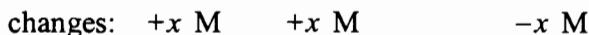
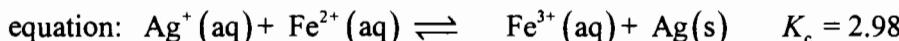
$$x = \sqrt{4.61 \times 10^{-3} \times 2.50 (0.0240 - 0.00925)} = 0.0130$$

Notice that after each cycle the value we obtain for  $x$  gets closer to the value obtained from the quadratic equation. The values from the next several cycles follow.

cycle	4 <sup>th</sup>	5 <sup>th</sup>	6 <sup>th</sup>	7 <sup>th</sup>	8 <sup>th</sup>	9th	10th	11 <sup>th</sup>
$x$ value	0.0112	0.0121	0.0117	0.0119	0.0118 <sub>1</sub>	0.0118 <sub>6</sub>	0.0118 <sub>3</sub>	0.0118 <sub>4</sub>

The amount of  $\text{N}_2\text{O}_4$  at equilibrium is 0.0118 mol, less than the 0.0210 mol  $\text{N}_2\text{O}_4$  at equilibrium in the 0.372 L flask, as predicted.

**13A** Again we organize our solution on the balanced chemical equation.



$$K_c = \frac{[\text{Fe}^{3+}]}{[\text{Ag}^+][\text{Fe}^{2+}]} = 2.98 = \frac{1.20 - x}{x^2} \quad 2.98x^2 = 1.20 - x \quad 0 = 2.98x^2 + x - 1.20$$

We use the quadratic formula to obtain a solution.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.00 \pm \sqrt{(1.00)^2 + 4 \times 2.98 \times 1.20}}{2 \times 2.98} = \frac{-1.00 \pm 3.91}{5.96} = 0.488 \text{ or } -0.824$$

A negative root makes no physical sense. We obtain the equilibrium concentrations from  $x$ .

$$[\text{Ag}^+] = [\text{Fe}^{2+}] = 0.488 \text{ M} \quad [\text{Fe}^{3+}] = 1.20 - 0.488 = 0.71 \text{ M}$$

**13B** We first calculate the value of  $Q_c$  to determine the direction of the reaction.

$$Q_c = \frac{[\text{V}^{2+}][\text{Cr}^{3+}]}{[\text{V}^{3+}][\text{Cr}^{2+}]} = \frac{0.150 \times 0.150}{0.0100 \times 0.0100} = 225 < 7.2 \times 10^2 = K_c$$

Because the reaction quotient has a smaller value than the equilibrium constant, a net reaction will occur to the right. We now set up this solution as we have others, based on the balanced chemical equation.

	$\text{V}^{3+}(\text{aq})$	$+$	$\text{Cr}^{2+}(\text{aq})$	$\rightleftharpoons$	$\text{V}^{2+}(\text{aq})$	$+$	$\text{Cr}^{3+}(\text{aq})$
initial	0.0100 M		0.0100 M		0.150 M		0.150 M
changes	$-x$ M		$-x$ M		$+x$ M		$+x$ M
equil	$(0.0100 - x)$ M		$(0.0100 - x)$ M		$(0.150 + x)$ M		$(0.150 + x)$ M

$$K_c = \frac{[\text{V}^{2+}][\text{Cr}^{3+}]}{[\text{V}^{3+}][\text{Cr}^{2+}]} = \frac{(0.150 + x)(0.150 + x)}{(0.0100 - x)(0.0100 - x)} = 7.2 \times 10^2 = \left( \frac{0.150 + x}{0.0100 - x} \right)^2$$

If we take the square root of both sides of this expression, we have

$$\sqrt{7.2 \times 10^2} = \frac{0.150 + x}{0.0100 - x} = 27$$

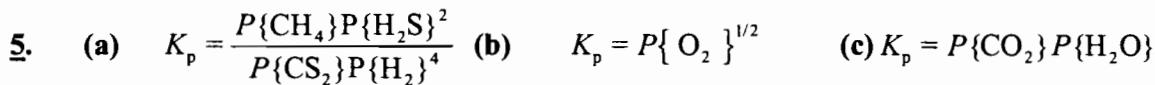
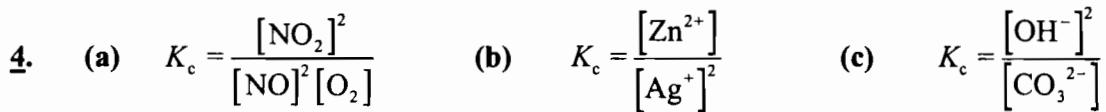
$0.150 + x = 0.27 - 27x$  which becomes  $28x = 0.12$  and yields  $x = 0.0043$  M. Then the equilibrium concentrations are:  $[V^{3+}] = [Cr^{2+}] = 0.0100$  M  $- 0.0043$  M  $= 0.0057$  M  
 $[V^{2+}] = [Cr^{3+}] = 0.150$  M  $+ 0.0043$  M  $= 0.154$  M

## REVIEW QUESTIONS

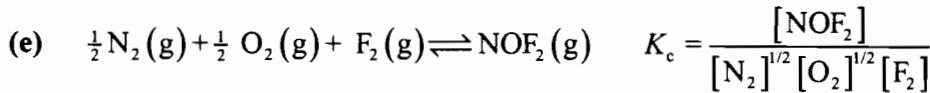
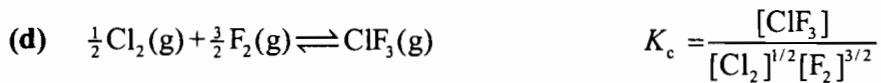
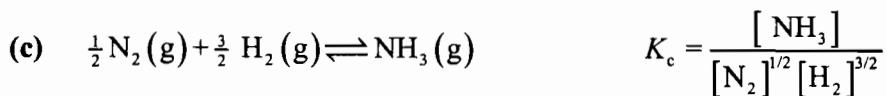
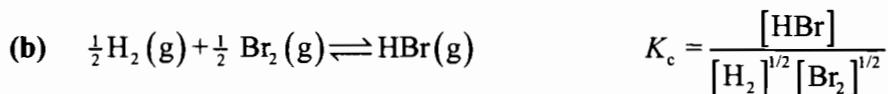
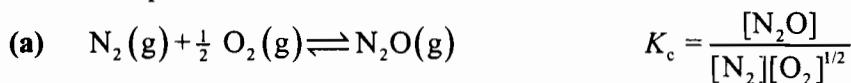
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1. (a)  $K_p$  is the symbol for the equilibrium constant in terms of partial pressures: the quotient of the equilibrium partial pressures of the products divided by those of the reactants, with each reactant or product partial pressure (in atmospheres) raised to a power equal to its stoichiometric coefficient in the balanced equation.  
(b)  $Q_c$  is the symbol for the reaction quotient in terms of molarities: the quotient of the molarities of the products divided by those of the reactants, each concentration raised to a power equal to its stoichiometric coefficient. These concentrations need not be those at equilibrium.  
(c)  $\Delta n_{gas}$  is the difference between the sum of the stoichiometric coefficients of the gaseous products and the similar sum for gaseous reactants, using the coefficients from the balanced chemical equation.
2. (a) A dynamic equilibrium is a balanced situation that is created by opposing processes proceeding at such rates that the net result is no apparent change, although individual molecules may indeed be undergoing change, and probably are.  
(b) The direction of net reaction describes whether a chemical reaction produces more product (to the right) or forms more reactant (to the left), generally as the result of the alteration of reaction conditions.  
(c) Le Châtelier's principle states that if a stress is applied to a system that is at equilibrium, the system will react in such a way as to relieve the stress and attain a new equilibrium position.  
(d) The effect of a catalyst on the position of equilibrium is nonexistent. A catalyst does, however, speed up the rate at which equilibrium is established.
3. (a) A reaction that goes to completion is one that reacts until the amount of one of the reactants is gone. A reversible reaction is one that comes to a point of balance before all reactants are depleted.

- (b) The equilibrium constant  $K_c$  contains the equilibrium concentrations of products and reactants, while the  $K_p$  expression contains their partial pressures. The values of these two numbers are related by the expression  $K_p = K_c (RT)^{\Delta n_g}$ .
- (c) The reaction quotient,  $Q_c$ , and the equilibrium constant expression,  $K_c$ , have the same functional form, with the concentrations of products over those of reactants, each raised to a power equal to the stoichiometric coefficient of that species. However, the concentrations that are used differ. In the  $K_c$  expression, these concentrations are equilibrium concentrations, while in the  $Q_c$  expression they are not necessarily the concentrations at equilibrium—often they are the initial concentrations. Similar statements can be made concerning  $Q_p$  and  $K_p$ , except that partial pressures replace concentrations.
- (d) A homogeneous equilibrium is one that takes place in a solution, either entirely gas or entirely liquid. A heterogeneous equilibrium is one that is established when two phases of matter are present, generally a solid with either a liquid or a gaseous solution.



6. In each case we write the equation for the formation reaction and then the equilibrium constant expression for that reaction.



7. (a) This is the reverse of the first reaction;  $K_c$  is the inverse value.

$$K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{1}{23.2} = 0.0431$$

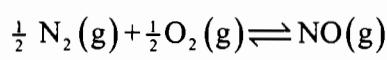
- (b) This is twice the second reaction;  $K_c$  is its square.

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = (56)^2 = 3.1 \times 10^3$$

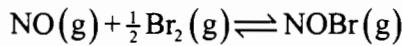
- (c) This is half of the reverse of the third reaction;  $K_c$  is the the inverse of the square

$$\text{root. } K_c = \frac{[\text{H}_2\text{S}]}{[\text{H}_2][\text{S}_2]^{1/2}} = \frac{1}{\sqrt{2.3 \times 10^{-4}}} = 66$$

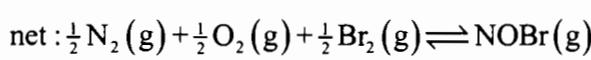
8. We combine one-half of the reversed first reaction with the second reaction to obtain the desired reaction.



$$K_c = \frac{1}{\sqrt{2.1 \times 10^{30}}}$$



$$K_c = 1.4$$



$$K_c = \frac{1.4}{\sqrt{2.1 \times 10^{30}}} = 9.7 \times 10^{-16}$$

9. Answer (d) is correct.  $\text{I}_2$  ( 1 mol) is the limiting reagent in this reaction. If the reaction were to go to completion, 2 mol HI would be produced. Thus, the only way that 2 mol HI could be produced (answer b) would be if  $K_c$  were infinite. 1 mol HI could be produced (answer a), but without knowing the value of  $K_c$  for this reaction, we cannot be sure. The only certain answer is that something less than 2 mol HI are produced, answer (d).

10. Simply substitute into the  $K_c$  expression.  $K_c = \frac{[\text{C}]^2}{[\text{A}]^2[\text{B}]} = \frac{(0.43 \text{ M})^2}{(0.55 \text{ M})^2 \times 0.33 \text{ M}} = 1.9$

11. The formation of  $2.0 \times 10^{-11}$  mol  $\text{S}(\text{g})$  does not significantly change the amount of  $\text{S}_2(\text{g})$

$$\text{from its original 0.0040 mol. Thus, } K_c = \frac{[\text{S}]^2}{[\text{S}_2]} = \frac{\left( \frac{2.0 \times 10^{-11} \text{ mol}}{0.500 \text{ L}} \right)^2}{\frac{0.0040 \text{ mol}}{0.500 \text{ L}}} = 2.0 \times 10^{-19}$$

12. (a) If the amounts of  $\text{SO}_2$  and  $\text{SO}_3$  are equal, then  $[\text{SO}_2] = [\text{SO}_3]$ .

$$K_c = 35.5 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{1}{[\text{O}_2]} \quad [\text{O}_2] = \frac{1}{35.5} = 0.0282 \text{ M}$$

$$\text{mol O}_2 = 0.0282 \text{ M} \times 2.05 \text{ L} = 0.0578 \text{ mol O}_2$$

(b) If there are twice as many moles of  $\text{SO}_3$  in the flask as  $\text{SO}_2$ , then  $[\text{SO}_3] = 2 \times [\text{SO}_2]$

$$K_c = 35.5 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{2^2 [\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{4}{[\text{O}_2]} \quad [\text{O}_2] = \frac{4}{35.5} = 0.113 \text{ M}$$

$$\text{mol O}_2 = 0.113 \text{ M} \times 2.05 \text{ L} = 0.232 \text{ mol O}_2$$

13. In each case we use the relationship  $K_p = K_c (RT)^{\Delta n_{\text{gas}}}$

(a) For  $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$   $K_p = K_c = 0.0431$

(b) For  $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$   $K_p = K_c (RT)^{-1} = \frac{3.1 \times 10^3}{0.0821 \times 900} = 42$

(c) For  $\text{H}_2(g) + \frac{1}{2} \text{S}_2(g) \rightleftharpoons \text{H}_2\text{S}(g)$   $K_p = K_c (RT)^{-1/2} = \frac{66}{\sqrt{0.0821 \times 1405}} = 6.1$

14. We first find the value of  $K_p$  for the reaction

$$2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{O}_2(g), \quad K_c = 1.8 \times 10^{-6} \text{ at } 184^\circ\text{C} = 457 \text{ K}.$$

For this reaction  $\Delta n_{\text{gas}} = 2 + 1 - 2 = +1$ .

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}} = 1.8 \times 10^{-6} (0.08206 \times 457)^{+1} = 6.8 \times 10^{-5}$$

To obtain the final reaction  $\text{NO}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{NO}_2(g)$  from the initial reaction, that initial reaction must be reversed and then divided by two. Thus, in order to determine the value of the equilibrium constant for the final reaction, the value of  $K_p$  for the initial reaction must be inverted, and the square root taken of the result.

$$K_{p, \text{final}} = \sqrt{\frac{1}{6.8 \times 10^{-5}}} = 1.2 \times 10^2$$

15. (a)  $K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{\frac{n\{\text{CO}\}}{V} \times \frac{n\{\text{H}_2\text{O}\}}{V}}{\frac{n\{\text{CO}_2\}}{V} \times \frac{n\{\text{H}_2\}}{V}}$

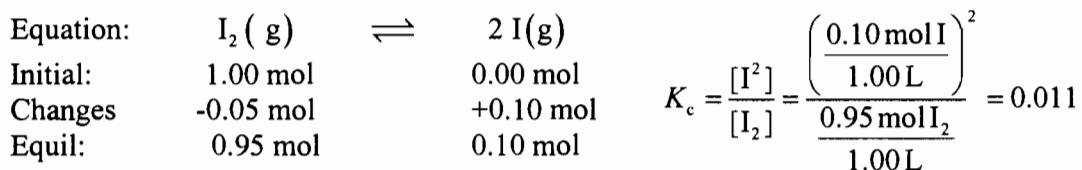
(b) Note that  $K_p = K_c$  for this reaction, since  $\Delta n_{\text{gas}} = 0$ .

$$K_c = K_p = \frac{0.224 \text{ mol CO} \times 0.224 \text{ mol H}_2\text{O}}{0.276 \text{ mol CO}_2 \times 0.276 \text{ mol H}_2} = 0.659$$

16. (a)  $K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{\frac{0.105 \text{ g PCl}_5}{2.50 \text{ L}} \times \frac{1 \text{ mol PCl}_5}{208.2 \text{ g}}}{\left( \frac{0.220 \text{ g PCl}_3}{2.50 \text{ L}} \times \frac{1 \text{ mol PCl}_3}{137.3 \text{ g}} \right) \times \left( \frac{2.12 \text{ g Cl}_2}{2.50 \text{ L}} \times \frac{1 \text{ mol Cl}_2}{70.9 \text{ g}} \right)} = 26.3$

(b)  $K_p = K_c (RT)^{\Delta n} = 26.3 (0.08206 \times 523)^{-1} = 0.613$

17. (a) If 5% of the 1.00 mol  $I_2$  is dissociated into atoms, then 0.05 mol  $I_2$  has dissociated.



(b)  $K_p = K_c (RT)^{+1} = 0.011 (0.0821 \times 1473) = 1.3$

18. (a) We determine the concentration of each species in the gaseous mixture, use these concentrations to determine the value of the reaction quotient, and compare this value of  $Q_c$  with the value of  $K_c$ .

$$[\text{SO}_2] = \frac{0.455 \text{ mol } \text{SO}_2}{1.90 \text{ L}} = 0.239 \text{ M} \quad [\text{O}_2] = \frac{0.183 \text{ mol } \text{O}_2}{1.90 \text{ L}} = 0.0963 \text{ M}$$

$$[\text{SO}_3] = \frac{0.568 \text{ mol } \text{SO}_3}{1.90 \text{ L}} = 0.299 \text{ M} \quad Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(0.299)^2}{(0.239)^2 0.0963} = 16.3$$

Since  $Q_c = 16.3 \neq 2.8 \times 10^2 = K_c$ , this mixture is not at equilibrium.

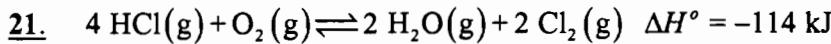
- (b) Since the value of  $Q_c$  is smaller than that of  $K_c$ , the reaction will proceed to the right, forming products to reach equilibrium.

19. Increasing the volume of an equilibrium mixture causes that mixture to shift toward the side (reactants or products) where the sum of the stoichiometric coefficients of the gaseous species is the larger. That is: shifts to the right if  $\Delta n_{\text{gas}} > 0$ , shifts to the left if  $\Delta n_{\text{gas}} < 0$ , and does not shift if  $\Delta n_{\text{gas}} = 0$

- (a)  $\text{C(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{(g)}$ ,  $\Delta n_{\text{gas}} > 0$ , shift right, toward products
- (b)  $\text{Ca(OH)}_2\text{(s)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{CaCO}_3\text{(s)} + \text{H}_2\text{O(g)}$ ,  $\Delta n_{\text{gas}} = 0$ , no shift, no change in equilibrium position.
- (c)  $4 \text{NH}_3\text{(g)} + 5 \text{O}_2\text{(g)} \rightleftharpoons 4 \text{NO(g)} + 6 \text{H}_2\text{O(g)}$ ,  $\Delta n_{\text{gas}} > 0$ , shift right, form products

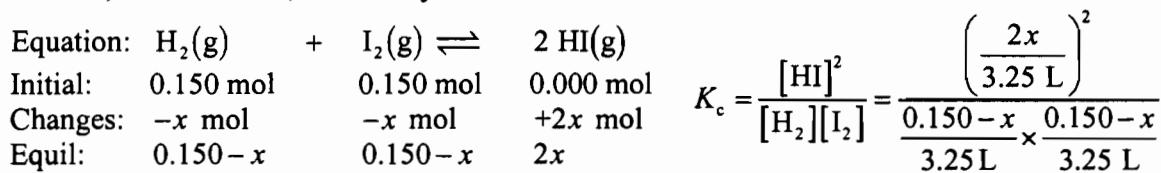
20. The equilibrium position for a reaction that is exothermic shifts to the left (favors reactants) when temperature is raised. For one that is endothermic, it shifts right (favors products) when temperature is raised.

- (a)  $\text{NO(g)} \rightleftharpoons \frac{1}{2} \text{N}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)}$   $\Delta H^\circ = -90.2 \text{ kJ}$  shifts left, % dissociation  $\downarrow$
- (b)  $\text{SO}_3\text{(g)} \rightleftharpoons \text{SO}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)}$   $\Delta H^\circ = +98.9 \text{ kJ}$  shifts right, % dissociation  $\uparrow$
- (c)  $\text{N}_2\text{H}_4\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + 2 \text{H}_2\text{(g)}$   $\Delta H^\circ = -95.4 \text{ kJ}$  shifts left, % dissociation  $\downarrow$
- (d)  $\text{COCl}_2\text{(g)} \rightleftharpoons \text{CO(g)} + \text{Cl}_2\text{(g)}$   $\Delta H^\circ = +108.3 \text{ kJ}$  shifts right, % dissociation  $\uparrow$



- (a) Adding  $\text{O}_2(\text{g})$  to the equilibrium mixture at constant volume will cause the position of equilibrium to shift to the right, increasing the equilibrium amount of  $\text{Cl}_2(\text{g})$ .
- (b) Removing  $\text{HCl(g)}$  from the equilibrium mixture at constant volume will cause the position of equilibrium to shift to the left, decreasing the amount of  $\text{Cl}_2(\text{g})$ .
- (c) Because  $\Delta n_{\text{gas}} < 0$ , transferring the equilibrium mixture to a container of twice the volume will cause the position of equilibrium to shift to the left, decreasing the amount of  $\text{Cl}_2(\text{g})$ .
- (d) Adding a catalyst to a mixture at equilibrium has no effect on the equilibrium position.
- (e) Raising the temperature of this exothermic reaction will cause the equilibrium position to shift to the left, decreasing the amount of  $\text{Cl}_2(\text{g})$ .

22. The information for the calculation is organized around the chemical equation. Let  $x = \text{mol H}_2$  (or  $\text{I}_2$ ) that reacts. Then use stoichiometry to determine the amount of  $\text{HI}$  formed, in terms of  $x$ , and finally solve for  $x$ .

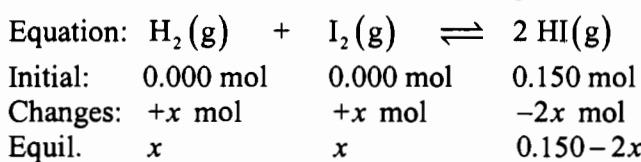


Then take the square root of both sides:  $\sqrt{K_c} = \sqrt{50.2} = \frac{2x}{0.150 - x} = 7.09$

$$2x = 1.06 - 7.09x \quad x = \frac{1.06}{9.09} = 0.117 \text{ mol, amount HI} = 2x = 2 \times 0.117 \text{ mol} = 0.234 \text{ mol HI}$$

amount  $\text{H}_2 = \text{amount I}_2 = (0.150 - x) \text{ mol} = (0.150 - 0.117) \text{ mol} = 0.033 \text{ mol H}_2$  or  $\text{I}_2$

23. This calculation is set up in a manner similar to the calculation of Review Question 22. In this case, we let  $x$  equal the amount of  $\text{I}_2$  that is formed.



$$K_c = 50.2 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{0.150 - 2x}{3.25 \text{ L}}\right)^2}{\frac{x}{3.25 \text{ L}} \times \frac{x}{3.25 \text{ L}}} = \frac{(0.150 - 2x)^2}{x^2} \quad \sqrt{50.2} = \frac{0.150 - 2x}{x} = 7.09$$

$$0.150 - 2x = 7.09x \quad x = \frac{0.150}{2 + 7.09} = 0.0165 \quad \text{amount I}_2 = x = 0.0165 \text{ mol I}_2$$

24. We first determine the initial pressure of  $\text{NH}_3$ .

$$P\{\text{NH}_3\} = \frac{nRT}{V} = \frac{0.100 \text{ mol } \text{NH}_3 \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{2.58 \text{ L}} = 0.948 \text{ atm}$$

Equation:	$\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
Initial:	0.948 atm
Changes:	+x atm
Equil:	(0.948 + x) atm

$$K_p = P\{\text{NH}_3\} P\{\text{H}_2\text{S}\} = 0.108 = (0.948 + x)x = 0.948x + x^2 \quad 0 = x^2 + 0.948x - 0.108$$

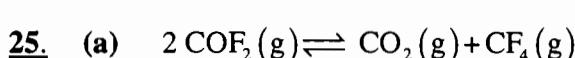
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.948 \pm \sqrt{0.899 + 0.432}}{2} = 0.103 \text{ atm}, -1.05 \text{ atm}$$

The negative root makes no physical sense. The total gas pressure is obtained as follows.

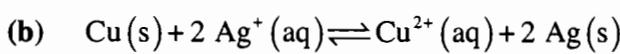
$$P_{\text{tot}} = P\{\text{NH}_3\} + P\{\text{H}_2\text{S}\} = (0.948 + x) + x = 0.948 + 2x = 0.948 + 2 \times 0.103 = 1.154 \text{ atm}$$

## EXERCISES

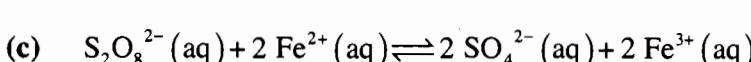
### Writing Equilibrium Constant Expressions



$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$



$$K_c = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$



$$K_c = \frac{[\text{SO}_4^{2-}]^2 [\text{Fe}^{3+}]^2}{[\text{S}_2\text{O}_8^{2-}] [\text{Fe}^{2+}]^2}$$

27. Since  $K_p = K_c (RT)^{\Delta n_g}$ , it is also true that  $K_c = K_p (RT)^{-\Delta n_g}$ .

$$(a) K_c = \frac{[\text{SO}_2(\text{g})][\text{Cl}_2(\text{g})]}{[\text{SO}_2\text{Cl}_2(\text{g})]} = K_p (RT)^{-(+1)} = 2.9 \times 10^{-2} (0.0821 \times 303)^{-1} = 0.0012$$

$$(b) K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} = K_p (RT)^{-(+1)} = (1.48 \times 10^4) (0.0821 \times 457) = 5.55 \times 10^5$$

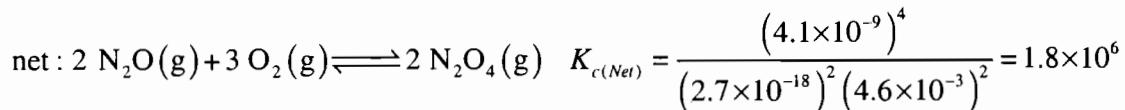
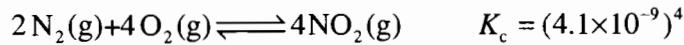
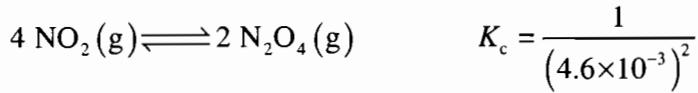
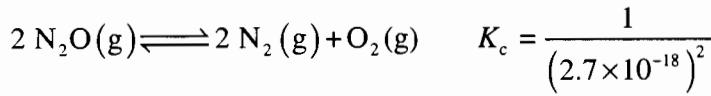
$$(c) K_c = \frac{[\text{H}_2\text{S}]^3}{[\text{H}_2]^3} = K_p (RT)^0 = K_p = 0.429$$

29. The equilibrium reaction is  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$  with  $\Delta n_{\text{gas}} = +1$ .  $K_p = K_c (RT)^{\Delta n_g}$  gives  $K_c = K_p (RT)^{-\Delta n_g}$ .

$$K_p = P\{\text{H}_2\text{O}\} = 23.8 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.0313$$

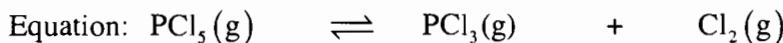
$$K_c = K_p (RT)^{-+1} = \frac{K_p}{RT} = \frac{0.0313}{0.0821 \times 298} = 1.28 \times 10^{-3}$$

31. We combine the several given reactions to obtain the net reaction.

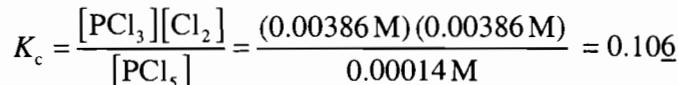


## Experimental Determination of Equilibrium Constants

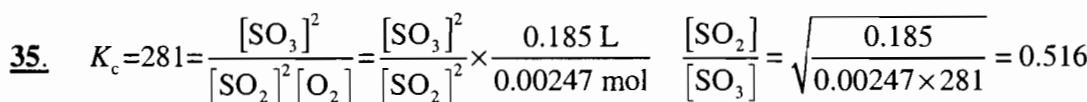
33. First, we determine the concentration of  $\text{PCl}_5$  and of  $\text{Cl}_2$  present initially and at equilibrium, respectively. Then we use the balanced equation to help us determine the concentration of each species present at equilibrium.



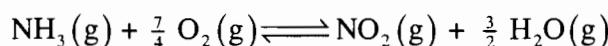
At equilibrium,  $[\text{Cl}_2] = [\text{PCl}_3] = 0.00386 \text{ M}$  and  $[\text{PCl}_5] = 0.00400 \text{ M} - x \text{ M} = 0.00014 \text{ M}$



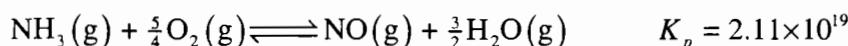
## Equilibrium Relationships

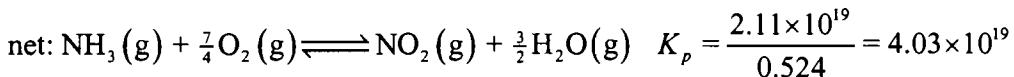
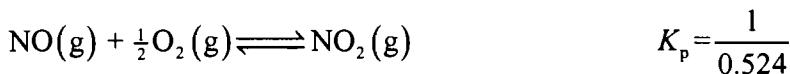


37. (a) A possible equation for the oxidation of  $\text{NH}_3(g)$  to  $\text{NO}_2(g)$  follows.



- (b)  $K_p$  is obtained by appropriately combining values of  $K_c$  given in the problem.





## Direction and Extent of Chemical Change

**39.** We compute the value of  $Q_c$  for the given amounts of product and reactants.

$$Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{\left(\frac{1.8 \text{ mol SO}_3}{7.2 \text{ L}}\right)^2}{\left(\frac{3.6 \text{ mol SO}_2}{7.2 \text{ L}}\right)^2 \frac{2.2 \text{ mol O}_2}{7.2 \text{ L}}} = 0.82 < K_c = 100$$

The mixture described cannot be maintained indefinitely. In fact, because  $Q_c < K_c$ , the reaction will proceed to the right, that is, toward products, until equilibrium is established.

**41.** We use the balanced chemical equation as a basis to organize the information we have about the reaction.

Equation:	$\text{SbCl}_5\text{(g)} \rightleftharpoons \text{SbCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$		
Initial:	0.00 mol	0.280 mol	0.160 mol
	2.50 L	2.50 L	2.50 L
Initial:	0.000 M	0.112 M	0.0640 M
Changes:	$+x$ M	$-x$ M	$-x$ M
Equil:	$x$ M	$(0.112 - x)$ M	$(0.0640 - x)$ M

$$K_c = 0.025 = \frac{[\text{SbCl}_3][\text{Cl}_2]}{[\text{SbCl}_5]} = \frac{(0.112 - x)(0.0640 - x)}{x} = \frac{0.00717 - 0.176x + x^2}{x}$$

$$0.025x = 0.00717 - 0.176x + x^2 \quad x^2 - 0.201x + 0.00717 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{0.201 \pm \sqrt{0.0404 - 0.0287}}{2} = 0.0464 \text{ or } 0.155$$

The second of the two values for  $x$  gives a negative value of  $[\text{Cl}_2] (= -0.091 \text{ M})$ , and thus is physically meaningless. Thus, concentrations and amounts follow.

$$[\text{SbCl}_5] = x = 0.0464 \text{ M} \quad \text{amount SbCl}_5 = 2.50 \text{ L} \times 0.0464 \text{ M} = 0.116 \text{ mol SbCl}_5$$

$$[\text{SbCl}_3] = 0.112 - x = 0.066 \text{ M} \quad \text{amount SbCl}_3 = 2.50 \text{ L} \times 0.066 \text{ M} = 0.17 \text{ mol SbCl}_3$$

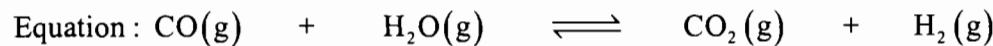
$$[\text{Cl}_2] = 0.0640 - x = 0.0176 \text{ M} \quad \text{amount Cl}_2 = 2.50 \text{ L} \times 0.0176 \text{ M} = 0.0440 \text{ mol Cl}_2$$

Or, in the first line labeled "Initial," we could have set  $y = \text{number of moles of SbCl}_5$  produced. Then our final answer would be  $y = 0.116 \text{ mol SbCl}_5$ . That is, we would have obtained the answer more directly.

43. We first compute the initial concentration of each species present. Then we determine the equilibrium concentrations of all species. Finally, we compute the mass of  $\text{CO}_2$  present at equilibrium.

$$[\text{CO}]_{\text{int}} = \frac{1.00 \text{ g}}{1.41 \text{ L}} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} = 0.0253 \text{ M} \quad [\text{H}_2\text{O}]_{\text{int}} = \frac{1.00 \text{ g}}{1.41 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 0.0394 \text{ M}$$

$$[\text{H}_2]_{\text{int}} = \frac{1.00 \text{ g}}{1.41 \text{ L}} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 0.352 \text{ M}$$



$$\text{Initial: } 0.0253 \text{ M} \quad 0.0394 \text{ M} \quad 0.0000 \text{ M} \quad 0.352 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (0.0253 - x) \text{ M} \quad (0.0394 - x) \text{ M} \quad x \text{ M} \quad (0.352 + x) \text{ M}$$

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 23.2 = \frac{x(0.352 + x)}{(0.0253 - x)(0.0394 - x)} = \frac{0.352x + x^2}{0.000997 - 0.0647x + x^2}$$

$$0.0231 - 1.50x + 23.2x^2 = 0.352x + x^2 \quad 22.2x^2 - 1.852x + 0.0231 = 0$$

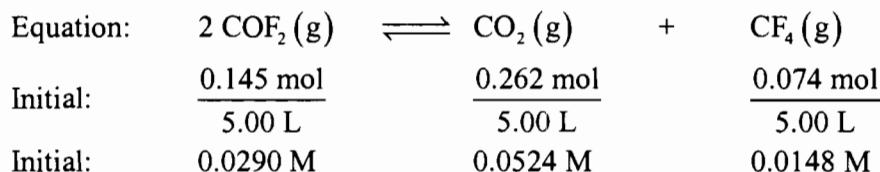
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{1.852 \pm \sqrt{3.430 - 2.051}}{44.4} = 0.0682 \text{ M}, \quad 0.0153 \text{ M}$$

The first value of  $x$  gives a negative  $[\text{CO}] (= -0.0429 \text{ M})$  and a negative

$[\text{H}_2\text{O}] (= -0.0288 \text{ M})$ . Thus,  $x = 0.0153 \text{ M} = [\text{CO}_2]$ . Now we find the mass of  $\text{CO}_2$ .

$$1.41 \text{ L} \times \frac{0.0153 \text{ mol CO}_2}{1 \text{ L mixture}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} = 0.949 \text{ g CO}_2$$

45. (a) We use the balanced chemical equation as a basis to organize the information we have about the reactants and products.



And we now compute a value of  $Q_c$  to compare with the given value of  $K_c$ .

$$Q_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} = \frac{(0.0524)(0.0148)}{(0.0290)^2} = 0.922 < 2.00 = K_c$$

Because  $Q_c$  is not equal to  $K_c$ , the mixture is not at equilibrium.

- (b) Because  $Q_c$  is smaller than  $K_c$ , the reaction will shift right, that is, products will be formed, in reaching a state of equilibrium.

(c) We continue the organization of information about reactants and products.

Equation:	$2 \text{COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$		
Initial:	0.0290 M	0.0524 M	0.0148 M
Changes:	$-2x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil:	$(0.0290 - 2x) \text{ M}$	$(0.0524 + x) \text{ M}$	$(0.0148 + x) \text{ M}$

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} = \frac{(0.0524 + x)(0.0148 + x)}{(0.0290 - 2x)^2} = 2.00 = \frac{0.000776 + 0.0672x + x^2}{0.000841 - 0.1160x + 4x^2}$$

$$0.00168 - 0.232x + 8x^2 = 0.000776 + 0.0672x + x^2 \quad 7x^2 - 0.299x + 0.000904 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{0.299 \pm \sqrt{0.0894 - 0.0253}}{14} = 0.0033 \text{ M}, 0.0394 \text{ M}$$

The second of these values for  $x$  (0.0394) gives a negative  $[\text{COF}_2]$  ( $= -0.0498 \text{ M}$ ), clearly a nonsensical result. We now compute the concentration of each species at equilibrium, and check to ensure that the equilibrium constant is satisfied.

$$[\text{COF}_2] = 0.0290 - 2x = 0.0290 - 2(0.0033) = 0.0224 \text{ M}$$

$$[\text{CO}_2] = 0.0524 + x = 0.0524 + 0.0033 = 0.0557 \text{ M}$$

$$[\text{CF}_4] = 0.0148 + x = 0.0148 + 0.0033 = 0.0181 \text{ M}$$

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} = \frac{0.0557 \text{ M} \times 0.0181 \text{ M}}{(0.0224 \text{ M})^2} = 2.01$$

The agreement of this value of  $K_c$  with the cited value (2.00) indicates that this solution is correct. Now we determine the number of moles of each species at equilibrium.

$$\text{mol COF}_2 = 5.00 \text{ L} \times 0.0224 \text{ M} = 0.112 \text{ mol COF}_2$$

$$\text{mol CO}_2 = 5.00 \text{ L} \times 0.0557 \text{ M} = 0.279 \text{ mol CO}_2$$

$$\text{mol CF}_4 = 5.00 \text{ L} \times 0.0181 \text{ M} = 0.0905 \text{ mol CF}_4$$

But suppose we had incorrectly concluded, in part (b), that reactants would be formed in reaching equilibrium. What result would we obtain? The set up follows.

Equation :	$2 \text{COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$		
Initial :	0.0290 M	0.0524 M	0.0148 M
Changes :	$+2y \text{ M}$	$-y \text{ M}$	$-y \text{ M}$
Equil :	$(0.0290 + 2y) \text{ M}$	$(0.0524 - y) \text{ M}$	$(0.0148 - y) \text{ M}$

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} = \frac{(0.0524 - y)(0.0148 - y)}{(0.0290 + 2y)^2} = 2.00 = \frac{0.000776 - 0.0672y + y^2}{0.000841 + 0.1160y + 4y^2}$$

$$0.00168 + 0.232y + 8y^2 = 0.000776 - 0.0672y + y^2 - 7y^2 + 0.299y + 0.000904 = 0$$

$$y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.299 \pm \sqrt{0.0894 - 0.0253}}{14} = -0.0033 \text{ M}, -0.0394 \text{ M}$$

The second of these values for  $x$  ( $-0.0394$ ) gives a negative  $[\text{COF}_2]$  ( $= -0.0498 \text{ M}$ ), clearly a nonsensical result. We now compute the concentration of each species at equilibrium, and check to ensure that the equilibrium constant is satisfied.

$$[\text{COF}_2] = 0.0290 + 2y = 0.0290 + 2(-0.0033) = 0.0224 \text{ M}$$

$$[\text{CO}_2] = 0.0524 - y = 0.0524 + 0.0033 = 0.0557 \text{ M}$$

$$[\text{CF}_4] = 0.0148 - y = 0.0148 + 0.0033 = 0.0181 \text{ M}$$

These are the same equilibrium concentrations that we obtained by making the correct decision regarding the direction that the reaction would take. Thus, you can be assured that, if you perform the algebra correctly, it will guide you even if you make the incorrect decision about the direction of the reaction.

47. We organize the known data around the balanced chemical equation.

Equation:	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HI}(\text{g})$
Initial:	0.125 mol		0.125 mol		0.000 mol
Changes:	$-x \text{ mol}$		$-x \text{ mol}$		$+2x \text{ mol}$
Equil:	$(0.125 - x) \text{ mol}$		$(0.125 - x) \text{ mol}$		$2x \text{ mol}$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x \text{ mol}}{6.14 \text{ L}}\right)^2}{\frac{(0.125 - x) \text{ mol}}{6.14 \text{ L}} \times \frac{(0.125 - x) \text{ mol}}{6.14 \text{ L}}} = \left(\frac{2x}{0.125 - x}\right)^2 = 50.2$$

$$\sqrt{50.2} = \frac{2x}{0.125 - x} = 7.09 \quad 2x = 0.886 - 7.09x \quad 9.09x = 0.886 \quad x = \frac{0.886}{9.09} = 0.0975 \text{ mol}$$

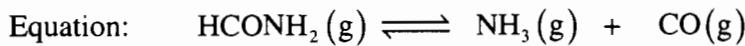
$$\text{amount HI} = 2x = 2 \times 0.0975 \text{ mol} = 0.195 \text{ mol}$$

$$\text{amount H}_2 = \text{amount I}_2 = 0.125 - x = 0.125 - 0.0975 = 0.0275 \text{ mol}$$

$$\text{Total amount} = 0.195 \text{ mol HI} + 0.0275 \text{ mol H}_2 + 0.0275 \text{ mol I}_2 = 0.250 \text{ mol}$$

$$\text{mol\% HI} = \frac{0.195 \text{ mol HI}}{0.250 \text{ mol total}} \times 100\% = 78.0\% \text{ HI}$$

**49.**  $[\text{HCONH}_2]_{\text{init}} = \frac{0.186 \text{ mol}}{2.16 \text{ L}} = 0.0861 \text{ M}$



Initial:  $0.0861 \text{ M}$   $0 \text{ M}$   $0 \text{ M}$

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.0861-x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_c = \frac{[\text{NH}_3][\text{CO}]}{[\text{HCONH}_2]} = \frac{x \cdot x}{0.0861-x} = 4.84 \quad x^2 = 0.417 - 4.84x \quad 0 = x^2 + 4.84x - 0.417$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.84 \pm \sqrt{23.4 + 1.67}}{2} = 0.084 \text{ M}, -4.92 \text{ M}$$

The negative concentration obviously is physically meaningless. We determine the total concentration of all species, and then the total pressure.

$$[\text{total}] = [\text{NH}_3] + [\text{CO}] + [\text{HCONH}_2] = x + x + 0.0861 - x = 0.0861 + 0.084 = 0.170 \text{ M}$$

$$P_{\text{tot}} = 0.170 \text{ mol L}^{-1} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 400 \text{ K} = 5.58 \text{ atm}$$

- 51. (a)** We organize the solution around the balanced chemical equation.



Initial:  $1.00 \text{ M}$   $0 \text{ M}$   $0 \text{ M}$

Changes:  $-2x \text{ M}$   $+2x$   $+x$

Equil:  $(1.00 - 2x) \text{ M}$   $2x$   $x$

$$K_c = \frac{[\text{Cr}^{2+}]^2 [\text{Cd}^{2+}]}{[\text{Cr}^{3+}]^2} = \frac{(2x)^2 (x)}{(1.00 - 2x)^2} = 0.288$$

*Via successive approximations, one obtains*  
 $x = 0.257 \text{ M}$

Therefore, at equilibrium,  $[\text{Cd}^{2+}] = 0.257 \text{ M}$ ,  $[\text{Cr}^{2+}] = 0.514 \text{ M}$  and  $[\text{Cr}^{3+}] = 0.486 \text{ M}$

- (b)** Minimum mass of  $\text{Cd}(\text{s}) = 0.350 \text{ L} \times 0.257 \text{ M} \times 112.41 \text{ g/mol} = 10.1 \text{ g}$  of Cd metal

- 53.** We are told in this question that the reaction  $\text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2\text{Cl}_2(\text{g})$  has  $K_c = 4.0$  at a certain temperature  $T$ . This means that at the temperature  $T$ ,  $[\text{SO}_2\text{Cl}_2] = 4.0 \times [\text{Cl}_2] \times [\text{SO}_2]$ . Careful scrutiny of the three diagrams reveals that sketch (b) is the best representation because it contains numbers of  $\text{SO}_2\text{Cl}_2$ ,  $\text{SO}_2$  and  $\text{Cl}_2$  molecules that are consistent with the  $K_c$  for the reaction. In other words, sketch (b) is the best choice because it contains 12  $\text{SO}_2\text{Cl}_2$  molecules (per unit volume), 1  $\text{Cl}_2$  molecule (per unit volume) and 3  $\text{SO}_2$  molecules (per unit volume) which, is the requisite number of each type of molecule needed to generate the expected  $K_c$  value for the reaction at temperature  $T$ .

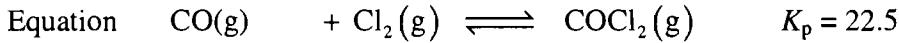
## Partial Pressure Equilibrium Constant, $K_p$

- 55.** We substitute the given equilibrium pressure into the equilibrium constant expression and solve for the other equilibrium pressure.  $K_p = \frac{P\{O_2\}^3}{P\{CO_2\}^2} = 28.5 = \frac{P\{O_2\}^3}{(0.0721 \text{ atm } CO_2)^2}$
- $$P\{O_2\} = \sqrt[3]{P\{O_2\}^3} = \sqrt[3]{28.5(0.0721 \text{ atm})^2} = 0.529 \text{ atm } O_2$$
- $$P_{\text{total}} = P\{CO_2\} + P\{O_2\} = 0.0721 \text{ atm } CO_2 + 0.529 \text{ atm } O_2 = 0.601 \text{ atm total}$$

- 57. (a)** We first determine the initial pressure of each gas.

$$P\{CO\} = P\{Cl_2\} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 668 \text{ K}}{1.75 \text{ L}} = 31.3 \text{ atm}$$

Then we calculate equilibrium partial pressures, organizing our calculation around the balanced chemical equation. We see that the equilibrium constant is not very large, meaning that we must solve the equation exactly (or by using successive approximations).



$$\text{Initial: } 31.3 \text{ atm} \quad 31.3 \text{ atm} \quad 0 \text{ atm}$$

$$\text{Changes: } -x \text{ atm} \quad -x \text{ atm} \quad +x \text{ atm}$$

$$\text{Equil: } 31.3 - x \text{ atm} \quad 31.3 - x \text{ atm} \quad x \text{ atm}$$

$$K_p = \frac{P\{COCl_2\}}{P\{CO\} P\{Cl_2\}} = 22.5 = \frac{x}{(31.3 - x)^2} = \frac{x}{(979.7 - 62.6x + x^2)}$$

$$22.5(979.7 - 62.6x + x^2) = x = 22043 - 1408.5x + 22.5x^2 = x$$

$$22043 - 1409.5x + 22.5x^2 = 0 \quad (\text{Solve using the quadratic equation})$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-1409.5) \pm \sqrt{(-1409.5)^2 - 4(22.5)(22043)}}{2(22.5)}$$

$$x = \frac{1409.5 \pm \sqrt{2818}}{45} = 30.14, 32.5 \text{ (too large)}$$

$$P\{CO\} = P\{Cl_2\} = 31.3 \text{ atm} - 30.14 \text{ atm} = 1.15 \text{ atm} \quad P\{COCl_2\} = 30.14 \text{ atm}$$

$$\text{(b)} \quad P_{\text{total}} = P\{CO\} + P\{Cl_2\} + P\{COCl_2\} = 1.15 \text{ atm} + 1.15 \text{ atm} + 30.14 \text{ atm} = 32.4 \text{ atm}$$

## Le Châtelier's Principle

- 59.** Continuous removal of the product, of course, has the effect of decreasing the concentration of the products below their equilibrium values. Thus, the equilibrium system is disturbed by removing the products and the system will attempt (in vain, as it turns out) to re-establish the equilibrium by shifting toward the right, that is, by producing more products.

- 61.** (a) This reaction is exothermic with  $\Delta H^\circ = -150 \text{ kJ}$ . Thus, high temperatures favor the reverse reaction. The amount of  $\text{H}_2(\text{g})$  present at high temperatures will be less than that present at low temperatures.
- (b)  $\text{H}_2\text{O}(\text{g})$  is one of the reactants involved. Introducing more will cause the equilibrium position to shift to the right, favoring products. The amount of  $\text{H}_2(\text{g})$  will increase.
- (c) Doubling the volume of the container will favor the side of the reaction with the largest sum of gaseous stoichiometric coefficients. The sum of the stoichiometric coefficients of gaseous species is the same (4) on both sides of this reaction. Therefore, increasing the volume of the container will have no effect on the amount of  $\text{H}_2(\text{g})$  present at equilibrium.
- (d) A catalyst merely speeds up the rate at which a reaction reaches the equilibrium position. The addition of a catalyst has no effect on the amount of  $\text{H}_2(\text{g})$  present at equilibrium.
- 63.** (a) The formation of  $\text{NO}(\text{g})$  from the elements is an endothermic reaction ( $\Delta H^\circ = +181 \text{ kJ/mol}$ ). Since the equilibrium position of endothermic reactions is shifted toward products at higher temperatures, we expect the formation of  $\text{NO}(\text{g})$  from the elements to be enhanced at higher temperatures.
- (b) Reaction rates always are enhanced by higher temperatures, since a larger fraction of the collisions will have an energy which surmounts the activation energy. This enhancement of rates affects both the forward and the reverse reactions. Thus, the position of equilibrium is reached more rapidly at higher temperatures than at lower temperatures.
- 65.** If the total pressure of a mixture of gases at equilibrium is doubled by compression, the equilibrium will shift to the side with fewer moles of gas to counteract the increase in pressure. Thus, if the pressure of an equilibrium mixture of  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  and  $\text{NH}_3(\text{g})$  is doubled, the reaction involving these three gases, i.e.  $\text{N}_2(\text{g}) + 3 \text{ H}_2(\text{g}) \rightleftharpoons 2 \text{ NH}_3(\text{g})$  will proceed in the forward direction to produce a new equilibrium mixture that contains additional ammonia and less molecular nitrogen and molecular hydrogen. In other words, the partial pressure of  $\text{N}_2(\text{g})$  will have decreased when equilibrium is re-established. It is important to note, however, that the final equilibrium partial pressure for the  $\text{N}_2$  will, nevertheless, be higher than its original partial pressure prior to the doubling of the total pressure.

## FEATURE PROBLEMS

- 88.** We first determine the amount in moles of acetic acid in the equilibrium mixture.

$$\text{amount CH}_3\text{CO}_2\text{H} = 28.85 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1000 \text{ mol Ba(OH)}_2}{1 \text{ L}} \times \frac{2 \text{ mol CH}_3\text{CO}_2\text{H}}{1 \text{ mol Ba(OH)}_2}$$

$$\times \frac{\text{complete equilibrium mixture}}{0.01 \text{ of equilibrium mixture}} = 0.5770 \text{ mol CH}_3\text{CO}_2\text{H}$$

Equation:	$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}$		
Initial:	0.500 mol	1.000 mol	0.000 mol
Changes:	-0.423 mol	-0.423 mol	+0.423 mol
Equil:	0.077 mol	0.577 mol	0.423 mol

$$K_c = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{CO}_2\text{H}]} = \frac{\frac{0.423 \text{ mol}}{V} \times \frac{0.423 \text{ mol}}{V}}{\frac{0.077 \text{ mol}}{V} \times \frac{0.577 \text{ mol}}{V}} = \frac{0.423 \times 0.423}{0.077 \times 0.577} = 4.0$$

- 89.** In order to determine whether or not equilibrium has been established in each bulb, we need to calculate the concentrations for all three species at the time of opening. The results from these calculations are tabulated below and a typical calculation is given beneath this table.

Bulb #	Time Bulb opened (hours)	initial amount HI(g) (in mmol)	amount of I <sub>2</sub> (g) and H <sub>2</sub> (g) at time of opening (in mmol)	amount HI(g) at time of opening (in mmol)	[HI] (mM)	[I <sub>2</sub> ] & [H <sub>2</sub> ] (mM)	$\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$
1	2	2.345	0.1572	2.03	5.08	0.393	0.00599
2	4	2.518	0.2093	2.10	5.25	0.523	0.00992
3	12	2.463	0.2423	1.98	4.95	0.606	0.0150
4	20	3.174	0.3113	2.55	6.38	0.778	0.0149
5	40	2.189	0.2151	1.76	4.40	0.538	0.0150

Consider for instance bulb #4 (opened after 20 hours)

$$\text{Initial moles of HI(g)} = 0.406 \text{ g HI(g)} \times \frac{1 \text{ mole HI}}{127.9 \text{ g HI}} = 0.003174 \text{ mol HI(g)} \text{ or } 3.174 \text{ mmol}$$

moles of I<sub>2</sub>(g) present in bulb when opened.

$$= 0.04150 \text{ L Na}_2\text{S}_2\text{O}_3 \times \frac{0.0150 \text{ mol Na}_2\text{S}_2\text{O}_3}{1 \text{ L Na}_2\text{S}_2\text{O}_3} \times \frac{1 \text{ mol I}_2}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} = 3.113 \times 10^{-4} \text{ mol I}_2$$

millimoles of  $I_2(g)$  present in bulb when opened =  $3.113 \times 10^{-4}$  mol  $I_2$

moles of  $H_2$  present in bulb when opened = moles of  $I_2(g)$  present in bulb when opened.

$$HI \text{ reacted} = 3.113 \times 10^{-4} \text{ mol } I_2 \times \frac{2 \text{ mole HI}}{1 \text{ mol } I_2} = 6.226 \times 10^{-4} \text{ mol HI (0.6226 mmol HI)}$$

moles of  $HI(g)$  in bulb when opened =  $3.174$  mmol  $HI$  -  $0.6226$  mmol  $HI$  =  $2.55$  mmol  $HI$

Concentrations of  $HI$ ,  $I_2$  and  $H_2$

$$[HI] = 2.55 \text{ mmol HI} \div 400. \text{ mL} = 6.38 \text{ mM}$$

$$[I_2] = [H_2] = 0.3113 \text{ mmol} \div 400 \text{ mL} = 0.778 \text{ mM}$$

$$\text{Ratio: } \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.778 \text{ mM})(0.778 \text{ mM})}{(6.38 \text{ mM})^2} = 0.0149$$

As the time increases, the ratio  $\frac{[H_2][I_2]}{[HI]^2}$  initially climbs sharply, but then plateaus at

$0.0150$  somewhere between  $4$  and  $12$  hours. Consequently, it seems quite reasonable to conclude that the reaction  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$  has a  $K_c \sim 0.015$  at  $623 \text{ K}$

- 90.** We first need to determine the number of moles of ammonia that were present in the sample of gas that left the reactor. This will be accomplished by using the data from the titrations involving  $HCl(aq)$ .

Original number of moles of  $HCl(aq)$  in the  $20.00 \text{ mL}$  sample

$$= 0.01872 \text{ L of KOH} \times \frac{0.0523 \text{ mol KOH}}{1 \text{ L KOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol KOH}} \\ = 9.7906 \times 10^{-4} \text{ moles of HCl}_{(\text{initially})}$$

Moles of unreacted  $HCl(aq)$

$$= 0.01542 \text{ L of KOH} \times \frac{0.0523 \text{ mol KOH}}{1 \text{ L KOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol KOH}} = \\ 8.0647 \times 10^{-4} \text{ moles of HCl}_{(\text{unreacted})}$$

Moles of  $HCl$  that reacted and /or moles of  $NH_3$  present in the sample of reactor gas  
 $= 9.7906 \times 10^{-4} \text{ moles} - 8.0647 \times 10^{-4} \text{ moles} = 1.73 \times 10^{-4} \text{ mole of } NH_3 \text{ (or HCl)}$

The remaining gas, which is a mixture of  $N_2$  and  $H_2$  gases, was found to occupy  $1.82 \text{ L}$  at  $273.2 \text{ K}$  and  $1.00 \text{ atm}$ . Thus, the total number of moles of  $N_2$  and  $H_2$  can be found via the

$$\text{ideal gas law: } n_{H_2 + N_2} = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.82 \text{ L})}{(0.08206 \frac{\text{L atm}}{\text{K mol}})(273.2 \text{ K})} = 0.08118 \text{ moles of } (N_2 + H_2)$$

According to the stoichiometry for the reaction, 2 parts  $\text{NH}_3$  decompose to give 3 parts  $\text{H}_2$  and 1 part  $\text{N}_2$ . Thus the non-reacting mixture must be 75%  $\text{H}_2$  and 25%  $\text{N}_2$ .

So, the number of moles of  $\text{N}_2 = 0.25 \times 0.08118$  moles = 0.0203 moles  $\text{N}_2$  and the number of moles of  $\text{H}_2 = 0.75 \times 0.08118$  moles = 0.0609 moles  $\text{H}_2$

Before we can calculate  $K_c$ , we need to determine the volume that the  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$  molecules occupied in the reactor. Once again, the ideal gas law ( $PV = nRT$ ) will be employed.  $n_{\text{gas}} = 0.08118$  moles  $(\text{N}_2 + \text{H}_2) + 1.73 \times 10^{-4}$  moles  $\text{NH}_3 = 0.08135$  moles

$$V_{\text{gases}} = \frac{nRT}{P} = \frac{(0.08135 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{K mol}})(1174.2 \text{ K})}{30.0 \text{ atm}} = 0.2613 \text{ L}$$

$$\text{So, } K_c = \frac{\left[ \frac{1.73 \times 10^{-4} \text{ moles}}{0.2613 \text{ L}} \right]^2}{\left[ \frac{0.0609 \text{ moles}}{0.2613 \text{ L}} \right]^3 \left[ \frac{0.0203 \text{ moles}}{0.2613 \text{ L}} \right]^1} = 4.46 \times 10^{-4}$$

To calculate  $K_p$  at 901 °C, we need to employ the equation  $K_p = K_c(RT)^{\Delta n_{\text{gas}}}$ ,  $\Delta n_{\text{gas}} = -2$

$$K_p = 4.46 \times 10^{-4} [(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})] \times (1174.2 \text{ K})^{-2} = 4.80 \times 10^{-8} \text{ at } 901^\circ\text{C} \text{ for the reaction } \text{N}_2(\text{g}) + 3 \text{ H}_2(\text{g}) \rightleftharpoons 2 \text{ NH}_3(\text{g})$$

91. For step 1, rate of the forward reaction = rate of the reverse reaction, so,

$$k_1[\text{I}_2] = k_{-1}[\text{I}]^2 \text{ or } \frac{k_1}{k_{-1}} = \frac{[\text{I}]^2}{[\text{I}_2]} = K_c \text{ (step 1)}$$

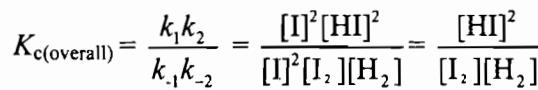
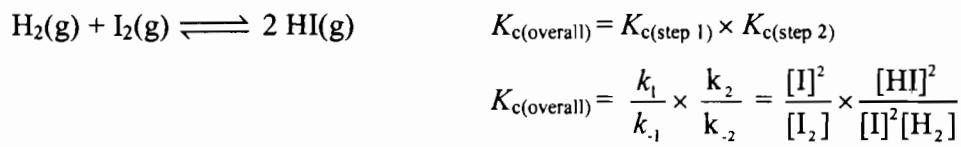
Like the first step, the rates for the forward and reverse reactions are equal in the second step and thus,

$$k_2[\text{I}]^2[\text{H}_2] = k_{-2}[\text{HI}]^2 \text{ or } \frac{k_2}{k_{-2}} = \frac{[\text{HI}]^2}{[\text{I}]^2[\text{H}_2]} = K_c \text{ (step 2)}$$

Now we combine the two elementary steps to obtain the overall equation and its associated equilibrium constant.



and



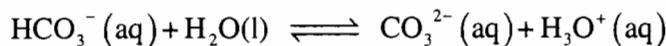
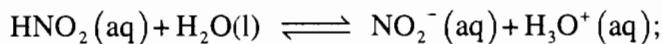
# CHAPTER 17

## ACIDS AND BASES

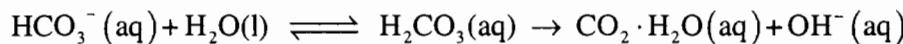
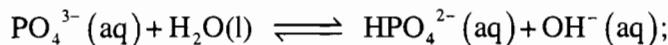
### PRACTICE EXAMPLES

- 1A** (a) In the forward direction, HF is the acid, (proton donor; forms  $\text{F}^-$ ), and  $\text{H}_2\text{O}$  is the base (proton acceptor; forms  $\text{H}_3\text{O}^+$ ). In the reverse direction  $\text{F}^-$  is the base (forms HF), accepting a proton from  $\text{H}_3\text{O}^+$ , which is the acid, (forms  $\text{H}_2\text{O}$ ).
- (b) In the forward direction,  $\text{HSO}_4^-$  is the acid, (proton donor; forms  $\text{SO}_4^{2-}$ ), and  $\text{NH}_3$  is the base (proton acceptor; forms  $\text{NH}_4^+$ ). In the reverse direction  $\text{SO}_4^{2-}$  is the base (forms  $\text{HSO}_4^-$ ), accepting a proton from  $\text{NH}_4^+$ , which is the acid, (forms  $\text{NH}_3$ ).
- (c) In the forward direction,  $\text{HCl}$  is the acid, (proton donor; forms  $\text{Cl}^-$ ), and  $\text{C}_2\text{H}_3\text{O}_2^-$  is the base (proton acceptor; forms  $\text{HC}_2\text{H}_3\text{O}_2$ ). In the reverse direction  $\text{Cl}^-$  is the base (forms  $\text{HCl}$ ), accepting a proton from  $\text{HC}_2\text{H}_3\text{O}_2$ , which is the acid, (forms  $\text{C}_2\text{H}_3\text{O}_2^-$ ).

- 1B** We know that the formulas of most acids begin with H. Thus, we identify  $\text{HNO}_2$  and  $\text{HCO}_3^-$  as acids.



A negatively charged species will attract a positively charged proton and act as a base. Thus  $\text{PO}_4^{3-}$  and  $\text{HCO}_3^-$  can act as bases. We also know that  $\text{PO}_4^{3-}$  is a base because it cannot act as an acid—it has no protons to donate—and we know that all three species have acid-base properties.



Notice that  $\text{HCO}_3^-$  is the amphiprotic species, acting as both an acid and as a base.

- 2A**  $[\text{H}_3\text{O}^+]$  is readily computed from pH:  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.85} = 1.4 \times 10^{-3} \text{ M}$ .

$[\text{OH}^-]$  can be found in two ways: (1) from  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ , giving

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12} \text{ M}, \text{ or (2) from } \text{pH} + \text{pOH} = 14.00, \text{ giving}$$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 2.85 = 11.15, \text{ and then } [\text{OH}] = 10^{-\text{pOH}} = 10^{-11.15} = 7.1 \times 10^{-12} \text{ M}.$$

**2B**  $[\text{H}_3\text{O}^+]$  is computed from pH in each case:  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

$$[\text{H}_3\text{O}^+]_{\text{conc.}} = 10^{-2.50} = 3.2 \times 10^{-3} \text{ M} \quad [\text{H}_3\text{O}^+]_{\text{dil.}} = 10^{-3.10} = 7.9 \times 10^{-4} \text{ M}$$

All of the  $\text{H}_3\text{O}^+$  in the dilute solution comes from the concentrated solution.

$$\text{amount H}_3\text{O}^+ = 1.00 \text{ L conc. soln} \times \frac{3.2 \times 10^{-3} \text{ mol H}_3\text{O}^+}{1 \text{ L conc. soln}} = 3.2 \times 10^{-3} \text{ mol H}_3\text{O}^+$$

Next we calculate the volume of the dilute solution.

$$\text{volume of dilute solution} = 3.2 \times 10^{-3} \text{ mol H}_3\text{O}^+ \times \frac{1 \text{ L dilute soln}}{7.9 \times 10^{-4} \text{ mol H}_3\text{O}^+} = 4.1 \text{ L dilute soln}$$

Thus, the volume of water to be added = 3.1 L

Infinite dilution does not lead to infinitely small hydrogen ion concentrations. Since dilution is done with water, the pH of an infinitely dilute solution will approach that of pure water, approximately pH = 7.

**3A** pH is computed directly from the  $[\text{H}_3\text{O}^+]$ ,  $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0025) = 2.60$ .

We know that HI is a strong acid and, thus, is completely dissociated into  $\text{H}_3\text{O}^+$  and  $\text{I}^-$ .

The consequence is that  $[\text{I}^-] = [\text{H}_3\text{O}^+] = 0.0025 \text{ M}$ .  $[\text{OH}^-]$  is most readily computed from pH:  $\text{pOH} = 14.00 - \text{pH} = 14.00 - 2.60 = 11.40$ ;  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.40} = 4.0 \times 10^{-12} \text{ M}$

**3B** The number of moles of  $\text{HCl(g)}$  is calculated from the ideal gas law. Then  $[\text{H}_3\text{O}^+]$  is calculated, based on the fact that  $\text{HCl(aq)}$  is a strong acid (1 mol  $\text{H}_3\text{O}^+$  is produced from each mol of  $\text{HCl}$ ).

$$\text{moles HCl(g)} = \frac{\left(747 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times 0.535 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times (26.5 + 273.2) \text{ K}} = 0.0214 \text{ mol HCl(g)}$$

$$[\text{H}_3\text{O}^+] = \frac{0.0214 \text{ mol HCl}}{0.625 \text{ L soln}} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HCl}} = 0.0342 \text{ M} \quad \text{pH} = -\log(0.0342) = 1.466$$

**4A** pH is most readily determined from  $\text{pOH} = -\log[\text{OH}^-]$ . Assume  $\text{Mg(OH)}_2$  is a strong base.

$$[\text{OH}^-] = \frac{9.63 \text{ mg Mg(OH)}_2}{100.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Mg(OH)}_2}{58.32 \text{ g Mg(OH)}_2} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Mg(OH)}_2}$$

$$[\text{OH}^-] = 0.00330 \text{ M}; \text{pOH} = -\log(0.00330) = 2.481$$

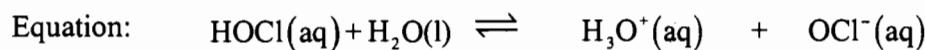
$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 2.481 = 11.519$$

- 4B** Notice that KOH is a strong base, which means that each mole of KOH produces one mole of  $\text{OH}^-$  (aq). First we calculate  $[\text{OH}^-]$  and the pOH. We then use  $\text{pH} + \text{pOH} = 14.00$  to determine pH.

$$[\text{OH}^-] = \frac{3.00 \text{ g KOH}}{100.00 \text{ g soln}} \times \frac{1 \text{ mol KOH}}{56.11 \text{ g KOH}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol KOH}} \times \frac{1.0242 \text{ g soln}}{1 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.548 \text{ M}$$

$$\text{pOH} = -\log(0.548) = 0.261 \quad \text{pH} = 14.000 - \text{pOH} = 14.000 - 0.261 = 13.739$$

- 5A** First we determine  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.18} = 6.6 \times 10^{-5}$  M. Then we organize the solution around the balanced chemical equation.



Initial:	0.150 M	$\approx 0$ M	0 M
Changes:	$-6.6 \times 10^{-5}$ M	$+6.6 \times 10^{-5}$ M	$+6.6 \times 10^{-5}$ M
Equil:	0.150 M	$6.6 \times 10^{-5}$ M	$6.6 \times 10^{-5}$ M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(6.6 \times 10^{-5})(6.6 \times 10^{-5})}{0.150} = 2.9 \times 10^{-8}$$

- 5B** First, we use pH to determine  $[\text{OH}^-]$ .  $\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.08 = 3.92$ .

$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-3.92} = 1.2 \times 10^{-4}$  M. We determine the initial concentration of cocaine and then organize the solution around the balanced equation in the manner we have used before.

$$[\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}] = \frac{0.17 \text{ g C}_{17}\text{H}_{21}\text{O}_4\text{N}}{100 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol C}_{17}\text{H}_{21}\text{O}_4\text{N}}{303.36 \text{ g C}_{17}\text{H}_{21}\text{O}_4\text{N}} = 0.0056 \text{ M}$$

Equation:	$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{C}_{17}\text{H}_{21}\text{O}_4\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq})$
Initial:	0.0056 M
Changes:	$-1.2 \times 10^{-4}$ M
Equil:	0.0055 M

$$K_b = \frac{[\text{C}_{17}\text{H}_{21}\text{O}_4\text{NH}^+][\text{OH}^-]}{[\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}]} = \frac{(1.2 \times 10^{-4})(1.2 \times 10^{-4})}{0.0055} = 2.6 \times 10^{-6}$$

- 6A** Again we organize our solution around the balanced chemical equation.

Equation:	$\text{HC}_2\text{H}_2\text{FO}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_2\text{FO}_2^-(\text{aq})$
Initial:	0.100 M
Changes:	$-x$ M
Equil:	$(0.100 - x)$ M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_2\text{FO}_2^-]}{[\text{HC}_2\text{H}_2\text{FO}_2]} \quad K_a = 2.6 \times 10^{-3}$$

With simplifying assumption  $[\text{H}_3\text{O}^+] = 0.016 \text{ M}$ ,  $\text{pH} = 1.80$

With the quadratic formula  $[\text{H}_3\text{O}^+] = 0.0149 \text{ M}$ ,  $\text{pH} = 1.83$

Thus, the calculated pH is considerably lower than 2.89. (Example 17-6).

**6B** We first determine the concentration of undissociated acid. We then use this value in a set up that is based on the balanced chemical equation.

Equation:	$\text{HC}_9\text{H}_7\text{O}_4 \text{ (aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{C}_9\text{H}_7\text{O}_4^- \text{ (aq)}$
Initial:	0.0171 M
Changes:	$-x \text{ M}$
Equil:	$(0.0171 - x) \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]} = 3.3 \times 10^{-4} = \frac{x \cdot x}{0.0171 - x}$$

$x^2 + 3.3 \times 10^{-4} - 5.6 \times 10^{-6} = 0$  (Solve quadratic for the positive root)

$$x = \frac{-3.3 \times 10^{-4} \pm \sqrt{1.1 \times 10^{-7} + 2.3 \times 10^{-5}}}{2} = 0.0022 \text{ M}; \quad \text{pH} = -\log(0.0022) = 2.66$$

**7A** Again we organize our solution around the balanced chemical equation.

Equation:	$\text{HC}_2\text{H}_2\text{FO}_2 \text{ (aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{C}_2\text{H}_2\text{FO}_2^- \text{ (aq)}$
Initial:	0.015 M
Changes:	$-x \text{ M}$
Equil:	$(0.015 - x) \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_2\text{FO}_2^-]}{[\text{HC}_2\text{H}_2\text{FO}_2]} = 2.6 \times 10^{-3} = \frac{(x)(x)}{0.015 - x} \approx \frac{x^2}{0.015}$$

$$x = \sqrt{x^2} = \sqrt{0.015 \times 2.6 \times 10^{-3}} = 0.0062 \text{ M} = [\text{H}_3\text{O}^+] \quad \text{Our assumption is invalid:}$$

0.0062 is not quite small compared to 0.015. Thus we use another cycle of successive approximations.

$$K_a = \frac{(x)(x)}{0.015 - 0.0062} = 2.6 \times 10^{-3} \quad x = \sqrt{(0.015 - 0.0062) \times 2.6 \times 10^{-3}} = 0.0048 \text{ M} = [\text{H}_3\text{O}^+]$$

$$K_a = \frac{(x)(x)}{0.015 - 0.0048} = 2.6 \times 10^{-3} \quad x = \sqrt{(0.015 - 0.0048) \times 2.6 \times 10^{-3}} = 0.0051 \text{ M} = [\text{H}_3\text{O}^+]$$

$$K_a = \frac{(x)(x)}{0.015 - 0.0051} = 2.6 \times 10^{-3} \quad x = \sqrt{(0.015 - 0.0051) \times 2.6 \times 10^{-3}} = 0.0051 \text{ M} = [\text{H}_3\text{O}^+]$$

Two successive identical results is a signal that we have the solution.

$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0051) = 2.29$ . The quadratic equation gives the same result (0.0051 M) as this method of successive approximations.

**7B** We first determine the concentration of undissociated piperidine. We then use that value in a set up based on the balanced chemical equation.

$$[\text{C}_5\text{H}_{11}\text{N}] = \frac{114 \text{ mg C}_5\text{H}_{11}\text{N}}{315 \text{ mL soln}} \times \frac{1 \text{ mmol C}_5\text{H}_{11}\text{N}}{85.15 \text{ mg C}_5\text{H}_{11}\text{N}} = 0.00425 \text{ M}$$

Equation:	$\text{C}_5\text{H}_{11}\text{N}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_5\text{H}_{11}\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq})$		
Initial:	0.00425 M	0 M	$\approx 0 \text{ M}$
Changes:	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil:	$(0.00425 - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$K_b = \frac{[\text{C}_5\text{H}_{11}\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_{11}\text{N}]} = 1.6 \times 10^{-3} = \frac{x \cdot x}{0.00425 - x} \approx \frac{x \cdot x}{0.00425}$$

We assumed that  $x \ll 0.00425$

$$x = \sqrt{0.0016 \times 0.00425} = 0.0026 \text{ M} \quad \text{The assumption is not valid. Let's assume}$$

$$x \approx 0.0026$$

$$x = \sqrt{0.0016(0.00425 - 0.0026)} = 0.0016 \quad \text{Let's try again, with } x \approx 0.0016$$

$$x = \sqrt{0.0016(0.00425 - 0.0016)} = 0.0021 \quad \text{Yet another try, with } x \approx 0.0021$$

$$x = \sqrt{0.0016(0.00425 - 0.0021)} = 0.0019 \quad \text{The last time, with } x \approx 0.0019$$

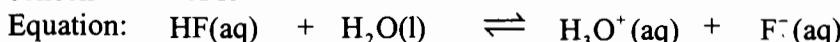
$$x = \sqrt{0.0016(0.00425 - 0.0019)} = 0.0019 \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0019) = 2.72$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.72 = 11.28$$

We could have solved the problem with the quadratic equation rather than by successive approximations. The same answer is obtained. In fact, if we substitute  $x = 0.0019$  into the  $K_b$  expression, we obtain  $(0.0019)^2 / (0.00425 - 0.0019) = 1.5 \times 10^{-3}$  compared to  $K_b = 1.6 \times 10^{-3}$ . The error is due to rounding, not to an incorrect value. Using  $x = 0.0020$  gives a value of  $1.8 \times 10^{-3}$ , while using  $x = 0.0018$  gives  $1.3 \times 10^{-3}$ .

**8A** We organize the solution around the balanced chemical equation;  $a$  M is the initial concentration of HF.



Initial:  $a$  M  $\approx 0$  M 0 M

Changes:  $-x$  M  $+x$  M  $+x$  M

Equil:  $(a-x)$  M  $x$  M  $x$  M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{a-x} \approx \frac{x^2}{a} = 6.6 \times 10^{-4}$$

$$x = \sqrt{a \times 6.6 \times 10^{-4}}$$

$$\text{For } 0.20 \text{ M HF, } x = \sqrt{0.20 \times 6.6 \times 10^{-4}} = 0.011 \text{ M} \quad \% \text{dissoc} = \frac{0.011 \text{ M}}{0.20 \text{ M}} \times 100\% = 5.5\%$$

$$\text{For } 0.020 \text{ M HF, } x = \sqrt{0.020 \times 6.6 \times 10^{-4}} = 0.0036 \text{ M}$$

$$\text{We need another cycle of approximation: } x = \sqrt{(0.020 - 0.0036) \times 6.6 \times 10^{-4}} = 0.0033 \text{ M}$$

$$\text{Yet another cycle with } x \approx 0.0033 \text{ M: } x = \sqrt{(0.020 - 0.0033) \times 6.6 \times 10^{-4}} = 0.0033 \text{ M}$$

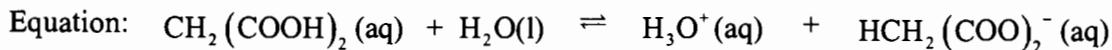
$$\% \text{dissoc} = \frac{0.0033 \text{ M}}{0.020 \text{ M}} \times 100\% = 17\%$$

As expected, the weak acid is more dissociated when diluted.

**8B** Since both  $\text{H}_3\text{O}^+$  and  $\text{C}_3\text{H}_5\text{O}_3^-$  come from the same source in equimolar amounts, their concentrations are equal.  $[\text{H}_3\text{O}^+] = [\text{C}_3\text{H}_5\text{O}_3^-] = 0.067 \times 0.0284 \text{ M} = 0.0019 \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{(0.0019)(0.0019)}{0.0284 - 0.0019} = 1.4 \times 10^{-4}$$

**9A** For an aqueous solution of a diprotic acid, the concentration of the divalent anion equals the second ionization constant:  $[\text{OOCCH}_2\text{COO}^-] = K_{a_2} = 2.0 \times 10^{-6} \text{ M}$ . We organize around the chemical equation.



Initial: 1.0 M  $\approx 0$  M 0 M

Changes:  $-x$  M  $+x$  M  $+x$  M

Equil:  $(1.0-x)$  M  $x$  M  $x$  M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCH}_2(\text{COO})_2^-]}{[\text{CH}_2(\text{COOH})_2]} = \frac{(x)(x)}{1.0-x} \approx \frac{x^2}{1.0} = 1.4 \times 10^{-3}$$

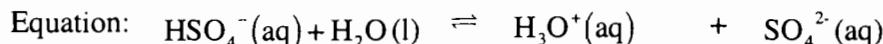
$$x = \sqrt{1.0 \times 1.4 \times 10^{-3}} = 3.7 \times 10^{-2} \text{ M} = [\text{H}_3\text{O}^+] = [\text{HOOCH}_2\text{COO}^-]$$

The assumption that  $x \ll 1.0 \text{ M}$  is valid.

**9B** We know  $K_{a_2} = [\text{doubly charged anion}]$  for a polyprotic acid. Thus  $K_{a_2} = 5.3 \times 10^{-5} = [\text{C}_2\text{O}_4^{2-}]$ . From the pH,  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-0.67} = 0.21 \text{ M}$ . We also recognize that  $[\text{HC}_2\text{O}_4^-] = [\text{H}_3\text{O}^+]$ , since the second ionization occurs to only a very small extent. We realize that  $\text{HC}_2\text{O}_4^-$  is produced by the ionization of  $\text{H}_2\text{C}_2\text{O}_4$ . Each mole of  $\text{HC}_2\text{O}_4^-$  present results from the ionization of 1 mole of  $\text{H}_2\text{C}_2\text{O}_4$ . Now we have sufficient information to determine the  $K_{a_1}$ .

$$K_{a_1} = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = \frac{0.21 \times 0.21}{1.05 - 0.21} = 5.3 \times 10^{-2}$$

**10A**  $\text{H}_2\text{SO}_4$  is a strong acid in its first ionization, and somewhat weak in its second, with  $K_{a_2} = 1.1 \times 10^{-2} = 0.011$ . Because of the strong first ionization step, this problem is one of determining concentrations in a solution that initially is 0.20 M  $\text{H}_3\text{O}^+$  and 0.20 M  $\text{HSO}_4^-$ . We base the setup on the balanced chemical equation.



Initial:	0.20 M	0.20 M	0 M
Changes:	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil:	$(0.20 - x) \text{ M}$	$(0.20 + x) \text{ M}$	$x \text{ M}$

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.20 + x)x}{0.20 - x} = 0.011 \approx \frac{0.20 \times x}{0.20}, \text{ assuming that } x \ll 0.20 \text{ M.}$$

$x = 0.011 \text{ M}$  Try one cycle of approximation:

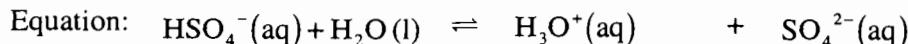
Try one cycle of approximation:

$$0.011 \approx \frac{(0.20 + 0.011)x}{(0.20 - 0.011)} = \frac{0.21x}{0.19} \quad x = \frac{0.19 \times 0.011}{0.21} = 0.010 \text{ M}$$

The next cycle of approximation produces the same answer  $0.010 \text{ M} = [\text{SO}_4^{2-}]$ ,

$$[\text{H}_3\text{O}^+] = 0.010 + 0.20 \text{ M} = 0.21 \text{ M}, \quad [\text{HSO}_4^-] = 0.20 - 0.010 \text{ M} = 0.19 \text{ M}$$

**10B** We know that  $\text{H}_2\text{SO}_4$  is a strong acid in its first ionization, and a somewhat weak acid in its second, with  $K_{a_2} = 1.1 \times 10^{-2} = 0.011$ . Because of the strong first ionization step, the problem essentially reduces to determining concentrations in a solution that initially is 0.020 M  $\text{H}_3\text{O}^+$  and 0.020 M  $\text{HSO}_4^-$ . We base the setup on the balanced chemical equation. The result is solved with the quadratic equation.



Initial:	0.020 M	0.020 M	0 M
Changes:	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil:	$(0.020 - x) \text{ M}$	$(0.020 + x) \text{ M}$	$x \text{ M}$

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.020+x)x}{0.020-x} = 0.011$$

$$0.020x + x^2 = 2.2 \times 10^{-4} - 0.011x$$

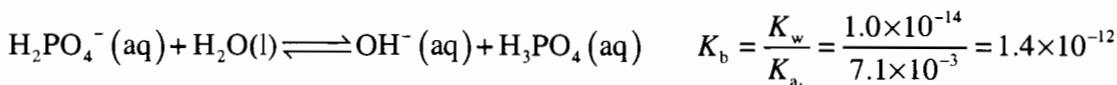
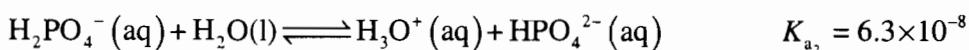
$$x^2 + 0.031x - 0.00022 = 0 \quad x = \frac{-0.031 \pm \sqrt{0.00096 + 0.00088}}{2} = 0.0060 \text{ M} = [\text{SO}_4^{2-}]$$

$$[\text{HSO}_4^-] = 0.020 - 0.0060 = 0.014 \text{ M} \quad [\text{H}_3\text{O}^+] = 0.020 + 0.0060 = 0.026 \text{ M}$$

(The method of successive approximations converges to  $x = 0.006 \text{ M}$  in 8 cycles.)

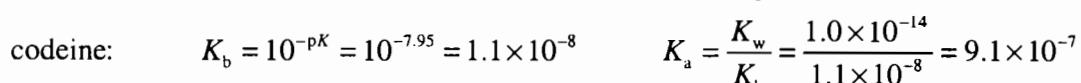
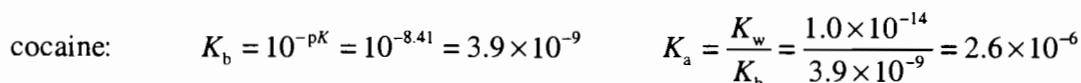
- 11A** (a)  $\text{CH}_3\text{NH}_3^+\text{NO}_3^-$  is the salt of the cation of a weak base that will hydrolyze to form an acidic solution ( $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$ ), and the anion of a strong acid that will not hydrolyze. The aqueous solutions of this compound will be acidic.
- (b) NaI is the salt of the cation of a strong base and the anion of a strong acid, neither of which hydrolyzes in water. Solutions of this compound will be pH neutral.
- (c)  $\text{NaNO}_2$  is the salt of the cation of a strong base that will not hydrolyze in water and the cation of a weak acid that will hydrolyze to form an alkaline solution ( $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$ ). Aqueous solutions of this compound will be basic (alkaline).

- 11B** Without comparing values of  $K$  we can predict that the reaction that produces  $\text{H}_3\text{O}^+$  occurs to the greater extent. The reason, of course, is that the solution produced is acidic, since its pH is less than 7.00. We write the two reactions of  $\text{H}_2\text{PO}_4^-$  with water, along with the values of their equilibrium constants.



As predicted, the acid ionization occurs to the greater extent.

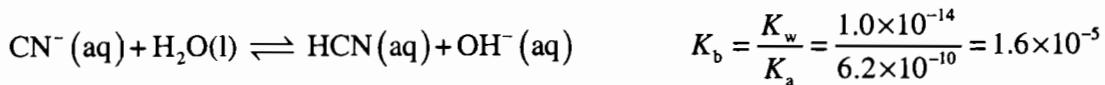
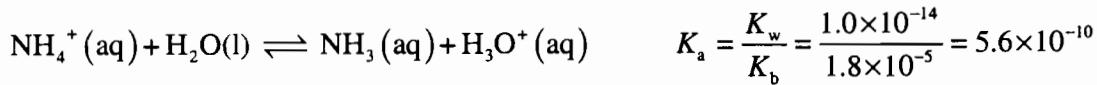
- 12A** From the value of  $\text{p}K_b$  we determine the value of  $K_b$  and then  $K_a$  for the cation.



(This method may be a bit easier:

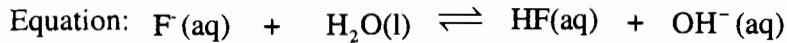
$\text{p}K_a = 14.00 - \text{p}K_b = 14.00 - 8.41 = 5.59$ ,  $K_a = 10^{-5.59} = 2.6 \times 10^{-6}$ ) The acid with the larger  $K_a$  will produce the higher  $[\text{H}^+]$ , and that solution will have the lower pH. Thus, the solution of codeine hydrochloride will have the higher pH.

**12B** Both of the ions of  $\text{NH}_4\text{CN}(\text{aq})$  react with water in hydrolysis reactions.



Since the value of the equilibrium constant for the hydrolysis reaction of cyanide ion is larger than that for the hydrolysis of ammonium ion, the cyanide ion hydrolysis reaction will proceed to a greater extent. The solution of  $\text{NH}_4\text{CN}(\text{aq})$  will be basic (alkaline).

**13A**  $\text{NaF}$  dissociates completely into sodium ions and fluoride ions. Fluoride ion hydrolyzes in aqueous solution to form hydroxide ion. The solution is organized around the balanced equation.



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-4}} = 1.5 \times 10^{-11} = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{(x)(x)}{(0.10 - x)} = \frac{x^2}{0.10}$$

$$x = \sqrt{0.10 \times 1.5 \times 10^{-11}} = 1.2 \times 10^{-6} \text{ M} = [\text{OH}^-]; \text{pOH} = -\log(1.2 \times 10^{-6}) = 5.92$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.92 = 8.08$$

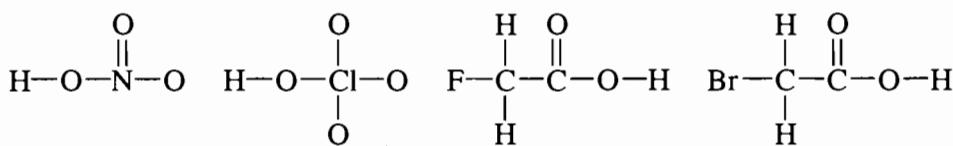
**13B** The cyanide ion hydrolyzes in solution, as shown in the solution to Practice Example 17-12B. As a consequence of that hydrolysis,  $[\text{OH}^-] = [\text{HCN}]$ .  $[\text{OH}^-]$  can be found from the pH of the solution and then values are substituted into the  $K_b$  expression for  $\text{CN}^-$ , which is solved for  $[\text{CN}^-]$ .

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.38 = 3.62$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-3.62} = 2.4 \times 10^{-4} \text{ M} = [\text{HCN}]$$

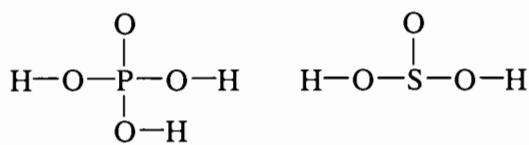
$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = 1.6 \times 10^{-5} = \frac{(2.4 \times 10^{-4})^2}{[\text{CN}^-]} \quad [\text{CN}^-] = \frac{(2.4 \times 10^{-4})^2}{1.6 \times 10^{-5}} = 3.6 \times 10^{-3} \text{ M}$$

- 14A** First we draw the Lewis structures of the four acids. Lone pairs are not depicted since we are interested only in the arrangements of atoms.



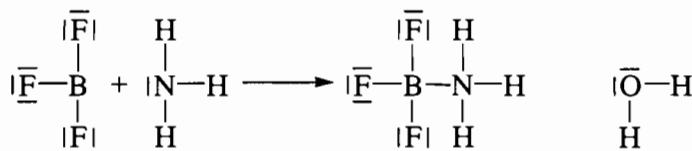
$\text{HClO}_4$  should be stronger than  $\text{HNO}_3$ . Although Cl and N have similar electronegativities, there are more terminal oxygen atoms attached to the chlorine in perchloric acid than to the nitrogen in nitric acid. By virtue of having more terminal oxygens, perchloric acid, when ionized, affords a more stable conjugate base. The more stable the anion, the more easily it is formed and hence the stronger is the conjugate acid from which it is derived.  $\text{CH}_2\text{FCOOH}$  will be a stronger acid than  $\text{CH}_2\text{BrCOOH}$  because F is a more electronegative atom than Br. The F atom withdraws additional electron density from the O—H bond, making that bond more easily broken.

- 14B** First we draw the Lewis structures of the first two acids. Lone pairs are not depicted since we are interested in the arrangements of atoms.



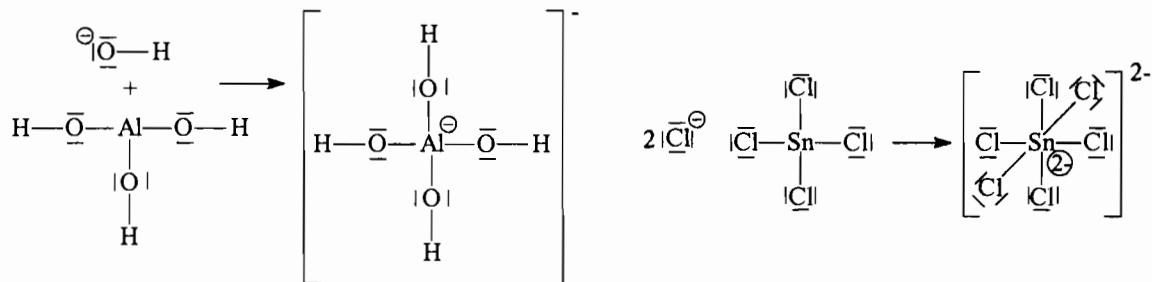
$\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_3$  both have one terminal oxygen atom, but S is more electronegative than P. This indicates that  $\text{H}_2\text{SO}_3$  ( $K_{a_1} = 1.3 \times 10^{-2}$ ) should be a stronger acid than  $\text{H}_3\text{PO}_4$  ( $K_{a_1} = 7.1 \times 10^{-3}$ ), and it is. The only difference between  $\text{CCl}_3\text{CH}_2\text{COOH}$  and  $\text{CCl}_2\text{FCH}_2\text{COOH}$  is the replacement of Cl by F. Since F is more electronegative than Cl,  $\text{CCl}_3\text{CH}_2\text{COOH}$  should be a weaker acid than  $\text{CCl}_2\text{FCH}_2\text{COOH}$ .

- 15A** We draw Lewis structures to help us decide.



- Clearly,  $\text{BF}_3$  is an electron pair acceptor, a Lewis acid, and  $\text{NH}_3$  is an electron pair donor, a Lewis base.
- $\text{H}_2\text{O}$  certainly has electron pairs (lone pairs) to donate and thus it can be a Lewis base. It is unlikely that the cation  $\text{Cr}^{3+}$  has any accessible valence electrons that can be donated to another atom; it is the Lewis acid.

**15B** The Lewis structures of the six species follow.



Both hydroxide ion and chloride ion have extra lone pairs of electrons; these two are the electron pair donors, the Lewis bases.  $\text{Al}(\text{OH})_3$  and  $\text{SnCl}_4$  have additional spaces in their structures to accept pairs of electrons, which is what occurs when they form complex anions.  $\text{Al}(\text{OH})_3$  and  $\text{SnCl}_4$  are the Lewis acids in these reactions.

## REVIEW QUESTIONS

- $K_w$  is the symbol for the ion product of water:  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  (25°C).
  - pH symbolizes the negative of the (base 10) logarithm of the hydrogen ion (actually hydronium ion,  $\text{H}_3\text{O}^+$ ) concentration:  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ . High pH indicates an alkaline solution; low pH indicates an acidic one.
  - $\text{p}K_a$  symbolizes the negative of the logarithm of the ionization constant of an acid:  $\text{p}K_a = -\log K_a$ .
  - Hydrolysis refers to the process where an ion reacts (as an acid or a base) with water to produce either hydrogen ion or hydroxide ion.
  - Lewis acids are electron pair acceptors (i.e., the recipient's pairs of  $e^-$  from Lewis bases)
- A conjugate base is the species produced when another species (molecule or ion) donates, and thus loses a proton,  $\text{H}^+$ .
  - Percent ionization is the ratio of the concentration of the ion formed by a species divided by the original concentration of that species prior to ionization multiplied by 100%.
  - Self-ionization: The process in which pure solvents partially dissociate into cations and anions. (e.g.  $2\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ )
  - Amphiprotic behavior refers to the ability of some substances, often oxides, to behave as acids in the presence of strong bases, and behave as bases in the presence of strong acids.

3. (a) A Brønsted-Lowry acid is a proton ( $H^+$ ) donor; a Brønsted-Lowry base is a proton acceptor.
- (b)  $pH = -\log[H_3O^+]$ ; the one is a logarithmic expression of the other, necessary because of the wide range of  $[H_3O^+]$  values commonly encountered.
- (c)  $K_a$  for  $NH_4^+$  and  $K_b$  for  $NH_3$  are inversely related to each other:  $K_a \times K_b = K_w$ .

The leveling effect refers to the inability of a moderately basic solvent to distinguish between the strengths of two strong acids; they both donate protons equally well to the solvent. The electron-withdrawing effect refers to the attraction of electrons to an electronegative atom or group within a molecule. If the electrons are drawn away from an O—H bond, that bond will become more polar and hence, more easily broken, thereby producing a stronger acid.

4. (a)  $HNO_2$  is an acid, a proton donor. Its conjugate base is  $NO_2^-$ .
- (b)  $OCl^-$  is a base, a proton acceptor. Its conjugate acid is  $HOCl$ .
- (c)  $NH_2^-$  is a base, a proton acceptor. Its conjugate acid is  $NH_3$ .
- (d)  $NH_4^+$  is an acid, a proton donor. Its conjugate base is  $NH_3$ .
- (e)  $CH_3NH_3^+$  is an acid, a proton donor. Its conjugate base is  $CH_3NH_2$ .

5. We write the conjugate base as the first product of the equilibrium in which the acid is the first reactant.

- (a)  $HIO_3(aq) + H_2O(l) \rightleftharpoons IO_3^-(aq) + H_3O^+(aq)$
- (b)  $C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$
- (c)  $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$
- (d)  $C_2H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_2(aq) + H_3O^+(aq)$

6. All of the solutes are strong acids or strong bases.

(a)  $[H_3O^+] = 0.00165 \text{ M } HNO_3 \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol } HNO_3} = 0.00165 \text{ M}$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.00165 \text{ M}} = 6.1 \times 10^{-12} \text{ M}$$

(b)  $[OH^-] = 0.0087 \text{ M } KOH \times \frac{1 \text{ mol } OH^-}{1 \text{ mol } KOH} = 0.0087 \text{ M}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0087 \text{ M}} = 1.1 \times 10^{-12} \text{ M}$$

$$(c) [\text{OH}^-] = 0.00213 \text{ M Sr(OH)}_2 \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Sr(OH)}_2} = 0.00426 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.00426 \text{ M}} = 2.3 \times 10^{-12} \text{ M}$$

$$(d) [\text{H}_3\text{O}^+] = 5.8 \times 10^{-4} \text{ M HI} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HI}} = 5.8 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{5.8 \times 10^{-4} \text{ M}} = 1.7 \times 10^{-11} \text{ M}$$

7. Again, all of the solutes are strong acids or strong bases.

$$(a) [\text{H}_3\text{O}^+] = 0.0045 \text{ M HCl} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HCl}} = 0.0045 \text{ M}$$

$$\text{pH} = -\log(0.0045) = 2.35$$

$$(b) [\text{H}_3\text{O}^+] = 6.14 \times 10^{-4} \text{ M HNO}_3 \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HNO}_3} = 6.14 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(6.14 \times 10^{-4}) = 3.212$$

$$(c) [\text{OH}^-] = 0.00683 \text{ M NaOH} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.00683 \text{ M}$$

$$\text{pOH} = -\log(0.00683) = 2.166 \text{ and } \text{pH} = 14.000 - \text{pOH} = 14.000 - 2.166 = 11.834$$

$$(d) [\text{OH}^-] = 4.8 \times 10^{-3} \text{ M Ba(OH)}_2 \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba(OH)}_2} = 9.6 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(9.6 \times 10^{-3}) = 2.02 \quad \text{pH} = 14.00 - 2.02 = 11.98$$

8. Most probably,  $0.11 \text{ M} = [\text{H}_3\text{O}^+]$  in  $0.10 \text{ M H}_2\text{SO}_4$ . Although  $\text{H}_2\text{SO}_4$  is completely ionized in dilute solution, this solution is not sufficiently dilute. (Recall the paragraph before Example 17-10 in the text.) Thus,  $0.20 \text{ M}$  is incorrect. However, the first ionization of  $\text{H}_2\text{SO}_4$  is complete;  $0.05 \text{ M}$  cannot be correct. And the second ionization of  $\text{H}_2\text{SO}_4$  is at least partially complete;  $0.10 \text{ M}$  incorrectly assumes that the only source of  $\text{H}_3\text{O}^+$  is the first ionization.

9. We determine the amounts of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  and then the amount of the one that is in excess. We express molar concentration in millimoles/milliliter, equivalent to mol/L.

$$24.80 \text{ mL} \times \frac{0.248 \text{ mmol HNO}_3}{1 \text{ mL soln}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HNO}_3} = 6.15 \text{ mmol H}_3\text{O}^+$$

$$15.40 \text{ mL} \times \frac{0.394 \text{ mmol KOH}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 6.07 \text{ mmol OH}^-$$

The net reaction is  $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ . There is an excess amount of  $\text{H}_3\text{O}^+$  of  $(6.15 - 6.07 \text{ mmol}) = 0.08 \text{ mmol H}_3\text{O}^+$ . This is an acidic solution. The total solution volume is  $(24.80 + 15.40 \text{ mL}) = 40.20 \text{ mL}$ .

$$[\text{H}_3\text{O}^+] = \frac{0.08 \text{ mmol H}_3\text{O}^+}{40.20 \text{ mL}} = 0.002 \text{ M} \quad \text{pH} = -\log(0.002) = 2.7$$

- 10.** Answer (4) is correct,  $\text{pH} < 13$ . If this were a strong base, its  $[\text{OH}^-] = 0.10$ , giving  $\text{pOH} = 1.0$ , and  $\text{pH} = 13.0$ . But since methylamine is a weak base, its  $[\text{OH}^-] < 0.10$ , giving  $\text{pOH} > 1.0$ , and  $\text{pH} < 13.0$ .

**11.**  $[\text{HC}_3\text{H}_5\text{O}_2]_{\text{initial}} = \left( \frac{0.275 \text{ mol}}{625 \text{ mL}} \right) \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) = 0.440 \text{ M}$

$$[\text{HC}_3\text{H}_5\text{O}_2]_{\text{equilibrium}} = 0.440 \text{ M} - 0.00239 \text{ M} = 0.438 \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(0.00239)^2}{0.438} = 1.30 \times 10^{-5}$$

- 12. (a)** The set up is based on the balanced chemical equation.



$$\text{Initial: } 0.186 \text{ M} \quad \approx 0 \text{ M} \quad 0 \text{ M}$$

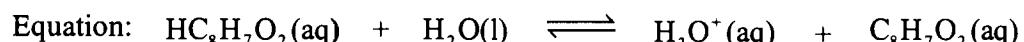
$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (0.186 - x) \text{ M} \quad x \text{ M} \quad x \text{ M}$$

$$K_a = 4.9 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_8\text{H}_7\text{O}_2^-]}{[\text{HC}_8\text{H}_7\text{O}_2]} = \frac{x \cdot x}{0.186 - x} \approx \frac{x^2}{0.186}$$

$$x = \sqrt{0.186 \times 4.9 \times 10^{-5}} = 0.0030 \text{ M} = [\text{H}_3\text{O}^+] = [\text{C}_8\text{H}_7\text{O}_2^-]$$

- (b)** The set up is based on the balanced chemical equation.



$$\text{Initial: } 0.121 \text{ M} \quad \approx 0 \text{ M} \quad 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

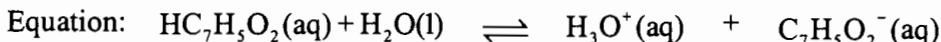
$$\text{Equil: } (0.121 - x) \text{ M} \quad x \text{ M} \quad x \text{ M}$$

$$K_a = 4.9 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_8\text{H}_7\text{O}_2^-]}{[\text{HC}_8\text{H}_7\text{O}_2]} = \frac{x^2}{0.121 - x} \approx \frac{x^2}{0.121} \quad x = 0.0024 \text{ M} = [\text{H}_3\text{O}^+]$$

We have assumed  $x \ll 0.121$ , an assumption that clearly is correct.  
 $\text{pH} = -\log(0.0024) = 2.62$

13. We need first to determine the molarity  $S$  of the acid needed.

$$[\text{H}_3\text{O}^+] = 10^{-2.85} = 1.4 \times 10^{-3} \text{ M}$$



$$\text{Initial: } \begin{matrix} S \\ 0 \text{ M} \\ 0 \text{ M} \end{matrix}$$

$$\text{Changes: } \begin{matrix} -0.0014 \text{ M} \\ +0.0014 \text{ M} \\ +0.0014 \text{ M} \end{matrix}$$

$$\text{Equil: } \begin{matrix} S - 0.0014 \text{ M} \\ 0.0014 \text{ M} \\ 0.0014 \text{ M} \end{matrix}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = \frac{(0.0014)^2}{S - 0.0014} = 6.3 \times 10^{-5} \quad S - 0.0014 = \frac{(0.0014)^2}{6.3 \times 10^{-5}} = 0.031$$

$$S = 0.031 + 0.0014 = 0.032 \text{ M} = [\text{HC}_7\text{H}_5\text{O}_2]$$

$$350.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.032 \text{ mol HC}_7\text{H}_5\text{O}_2}{1 \text{ L soln}} \times \frac{122.1 \text{ g HC}_7\text{H}_5\text{O}_2}{1 \text{ mol HC}_7\text{H}_5\text{O}_2} = 1.4 \text{ g HC}_7\text{H}_5\text{O}_2$$

14. First determine  $[\text{OH}^-]$ , and thus  $[(\text{CH}_3)_3\text{NH}^+]$ , in the solution. Then use the  $K_b$  expression to find  $[(\text{CH}_3)_3\text{N}]$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 11.12 = 2.88 \quad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-2.88} = 0.0013 \text{ M}$$

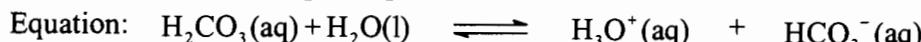
$$K_b = 6.3 \times 10^{-5} = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]_{\text{equil}}} = \frac{(0.0013)^2}{[(\text{CH}_3)_3\text{N}]_{\text{equil}}}$$

$$[(\text{CH}_3)_3\text{N}]_{\text{equil}} = \frac{(0.0013)^2}{6.3 \times 10^{-5}} = 0.027 \text{ M} (\text{CH}_3)_3\text{N}$$

Since some of the  $(\text{CH}_3)_3\text{N}$  has ionized,  $[(\text{CH}_3)_3\text{N}]_{\text{initial}} = 0.027 \text{ M} + 0.0013 \text{ M} = 0.028 \text{ M}$

15. For  $\text{H}_2\text{CO}_3$ ,  $K_1 = 4.4 \times 10^{-7}$  and  $K_2 = 4.7 \times 10^{-11}$

- (a) The first acid ionization proceeds to a far greater extent than does the second and determines the value of  $[\text{H}_3\text{O}^+]$ .



$$\text{Initial: } \begin{matrix} 0.045 \text{ M} \\ \approx 0 \text{ M} \\ 0 \text{ M} \end{matrix}$$

$$\text{Changes: } \begin{matrix} -x \text{ M} \\ +x \text{ M} \\ +x \text{ M} \end{matrix}$$

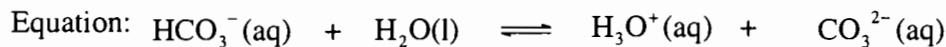
$$\text{Equil: } \begin{matrix} (0.045 - x) \text{ M} \\ x \text{ M} \\ x \text{ M} \end{matrix}$$

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.045 - x} = 4.4 \times 10^{-7} \approx \frac{x^2}{0.045} \quad x = 1.4 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]$$

- (b) Since the second ionization occurs to only a limited extent,

$$[\text{HCO}_3^-] = 1.4 \times 10^{-4} \text{ M} = 0.00014 \text{ M}$$

- (c) We use the second ionization to determine  $[\text{CO}_3^{2-}]$ .



$$\text{Initial: } 0.00014 \text{ M} \quad 0.00014 \text{ M} \quad 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (0.00014 - x) \text{ M} \quad (0.00014 + x) \text{ M} \quad x \text{ M}$$

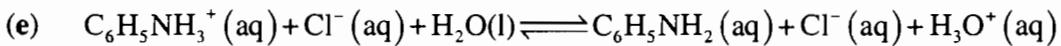
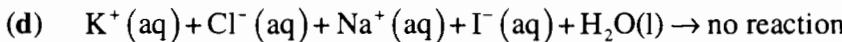
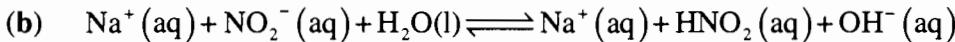
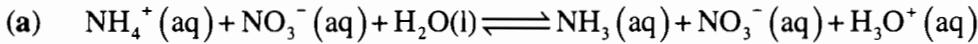
$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(0.00014 + x)x}{0.00014 - x} = 4.7 \times 10^{-11} \approx \frac{(0.00014)x}{0.00014}$$

$$x = 4.7 \times 10^{-11} \text{ M} = [\text{CO}_3^{2-}]$$

Again we assumed that  $x \ll 0.00014 \text{ M}$ , which clearly is the case. We also note that our original assumption, that the second ionization is much less significant than the first, also is a valid one. As an alternative to all of this, we could have recognized that the concentration of the divalent anion equals the second ionization constant:

$$[\text{CO}_3^{2-}] = K_2.$$

16. The species that hydrolyze are the cations of weak bases— $\text{NH}_4^+$  and  $\text{C}_6\text{H}_5\text{NH}_3^+$ —and the anions of weak acids— $\text{NO}_2^-$  and  $\text{C}_7\text{H}_5\text{O}_2^-$ .



17. Equation:  $\text{NH}_4^+ (\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{NH}_3 (\text{aq})$

$$\text{Initial: } 1.68 \text{ M} \quad \approx 0 \text{ M} \quad 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (1.68 - x) \text{ M} \quad x \text{ M} \quad x \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x^2}{1.68 - x} = 5.6 \times 10^{-10} \approx \frac{x^2}{1.68}$$

$$x = 3.07 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+] \quad \text{pH} = -\log(3.07 \times 10^{-5}) = 4.51$$

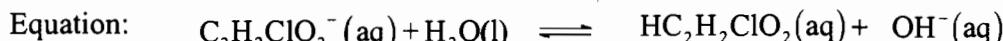
18. Recall that, for a conjugate weak acid-weak base pair,  $K_a \times K_b = K_w$

(a)  $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6}$  for  $C_5H_5NH^+$

(b)  $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$  for  $CHO_2^-$

(c)  $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-10}} = 1.0 \times 10^{-4}$  for  $C_6H_5O^-$

19. We base the calculation on the balanced chemical equation for the hydrolysis of the anion.



Initial: 2.05 M 0 M  $\approx 0$  M

Changes:  $-x$  M  $+x$  M  $+x$  M

Equil:  $(2.05 - x)$  M  $x$  M  $x$  M

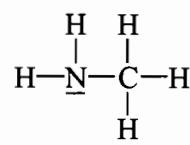
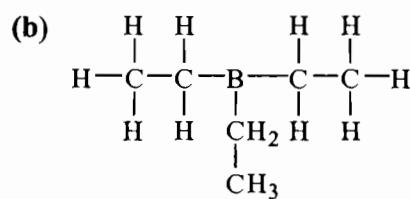
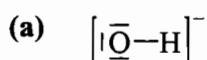
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12} = \frac{[HC_2H_2ClO_2][OH^-]}{[C_2H_2ClO_2^-]} = \frac{x \cdot x}{2.05 - x} \approx \frac{x^2}{2.05}$$

$$x = \sqrt{2.05 \times 7.1 \times 10^{-12}} = 3.8 \times 10^{-6} = [OH^-] \quad pOH = -\log(3.8 \times 10^{-6}) = 5.42$$

$$pH = 14.00 - pOH = 14.00 - 5.42 = 8.58$$

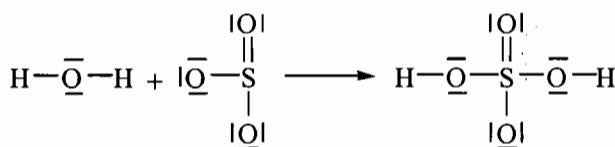
20.  $CCl_3COOH$  is a stronger acid than  $CH_3COOH$  because in  $CCl_3COOH$  there are electronegative (electron withdrawing) Cl atoms bonded to the carbon atom adjacent to the COOH group. The electron withdrawing Cl atoms further polarize the OH bond, resulting in a stronger acid.

21. (a) HI is the stronger acid because the H—I bond length is longer than the H—Br bond length and the H—I bond is weaker.  
 (b) HOClO is a stronger acid than HOBr because there is a terminal O in HOClO but not in HOBr and Cl is more electronegative than Br.  
 (c)  $H_3CCH_2CCl_2COOH$  is a stronger acid than  $I_3CCH_2CH_2COOH$  both because Cl is more electronegative than is I and also because the Cl atoms are closer to the acidic hydrogen in the COOH group and thus can exert a stronger  $e^-$  withdrawing effect on the O—H bond than can the more distant I atoms.
22. A Lewis base is an electron pair donor, while a Lewis acid is an electron pair acceptor. We draw Lewis structures to assist our interpretation.

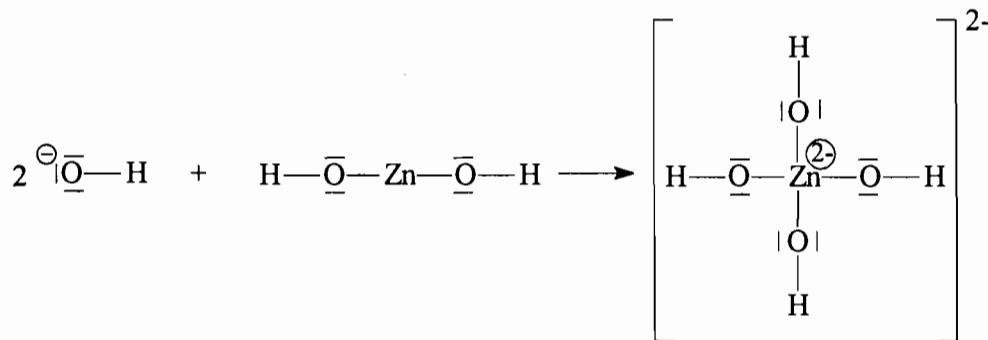


- (a) The lone pairs on oxygen can readily be donated; this is a Lewis base.  
 (b) The incomplete octet of B provides a site for acceptance of an electron pair; this is a Lewis acid.  
 (c) The lone pair on nitrogen can be donated; this is a Lewis base.
- 23.** A Lewis base is an electron pair donor, while a Lewis acid is an electron pair acceptor. We draw Lewis structures to assist our interpretation.

- (a) According to the following Lewis structures,  $\text{SO}_3$  appears to be the electron pair acceptor (the Lewis acid), and  $\text{H}_2\text{O}$  is the electron pair donor (the Lewis base). Note that an additional sulfur-to-oxygen bond is formed.



- (b) Zn in  $\text{Zn}(\text{OH})_2$  accepts a pair of electrons;  $\text{Zn}(\text{OH})_2$  is a Lewis acid.  $\text{OH}^-$  donates the pair of electrons that form the covalent bond;  $\text{OH}^-$  is a Lewis base. We have assumed that Zn has sufficient covalent character to form coordinate covalent bonds with hydroxide ions. (Lewis structure drawn below).

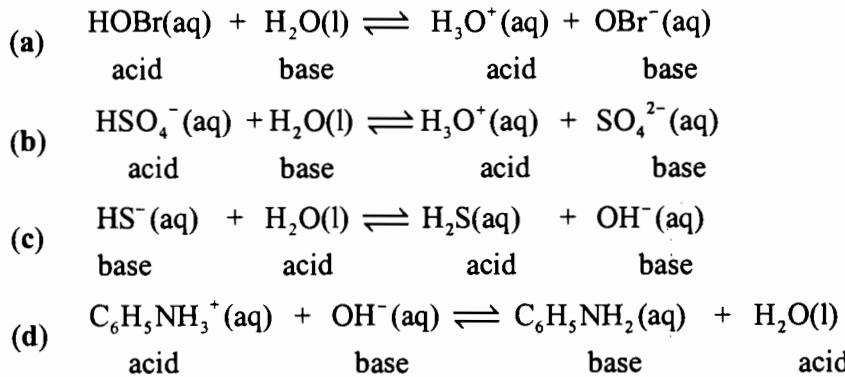


- 24.** (a)  $\text{NH}_4\text{Cl}(\text{aq})$  contains a cation,  $\text{NH}_4^+$ , that is a weak acid; it should have a pH slightly below 7.00.  
 (b)  $\text{NH}_3(\text{aq})$  is a weak base; it should have a reasonably high pH.  
 (c)  $\text{NaC}_2\text{H}_3\text{O}_2(\text{aq})$  contains an anion,  $\text{C}_2\text{H}_3\text{O}_2^-$ , that is a weak base; it should have a pH slightly above 7.00.  
 (d) Neither  $\text{K}^+(\text{aq})$  nor  $\text{Cl}^-(\text{aq})$  is an acid or a base in aqueous solution;  $\text{KCl}(\text{aq})$  should have a pH of 7.00. In order of decreasing pH:  
 $\text{NH}_3(\text{aq}) > \text{NaC}_2\text{H}_3\text{O}_2(\text{aq}) > \text{KCl}(\text{aq}) > \text{NH}_4\text{Cl}(\text{aq})$

## EXERCISES

### Brønsted-Lowry Theory of Acids and Bases

25. The acids (proton donors) and bases (proton acceptors) are labeled below their formulas. Remember that a proton, in Brønsted-Lowry acid-base theory, is  $\text{H}^+$ .



27. Answer (2),  $\text{NH}_3$ , is correct.  $\text{HC}_2\text{H}_3\text{O}_2$  will react most completely with the strongest base.  $\text{NO}_3^-$  and  $\text{Cl}^-$  are very weak bases.  $\text{H}_2\text{O}$  is a weak base, but it is amphiprotic, acting as an acid (donating protons), as in the presence of  $\text{NH}_3$ . Thus,  $\text{NH}_3$  must be the strongest base and the most effective deprotonating  $\text{HC}_2\text{H}_3\text{O}_2$ .

29. The principle here is that the weaker acid and the weaker base will predominate at equilibrium. The reason is that a strong acid will do a good job of donating its protons and, having done so, its conjugate base will be left behind. The preferred direction is:

Strong acid + strong base  $\rightarrow$  weak (conjugate) base + weak (conjugate) acid.

- (a) The reaction will favor the forward direction because  $\text{OH}^-$  (a strong base)  $>$   $\text{NH}_3$  as bases and  $\text{NH}_4^+ > \text{H}_2\text{O}$  as acids.
- (b) The reaction will favor the reverse direction because  $\text{HNO}_3 > \text{HSO}_4^-$  (a weak acid in the second ionization) as acids, and  $\text{SO}_4^{2-} > \text{NO}_3^-$  as bases.
- (c) The reaction will favor the reverse direction because  $\text{HC}_2\text{H}_3\text{O}_2 > \text{CH}_3\text{OH}$  (not usually thought of as an acid) as acids, and  $\text{CH}_3\text{O}^- > \text{C}_2\text{H}_3\text{O}_2^-$  as bases.

### Strong Acids, Strong Bases, and pH

31.  $[\text{OH}^-] = \frac{3.9 \text{ g Ba(OH)}_2 \cdot 8\text{H}_2\text{O}}{100 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol Ba(OH)}_2 \cdot 8\text{H}_2\text{O}}{315.5 \text{ g Ba(OH)}_2 \cdot 8\text{H}_2\text{O}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba(OH)}_2 \cdot 8\text{H}_2\text{O}}$   
 $= 0.25 \text{ M}$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.25 \text{ M OH}^-} = 4.0 \times 10^{-14} \text{ M} \quad \text{pH} = -\log(4.0 \times 10^{-14}) = 13.40$$

33. First determine the moles of HCl, and then its concentration.

$$\text{moles HCl} = \frac{PV}{RT} = \frac{\left(751 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times 0.205 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 296 \text{ K}} = 8.34 \times 10^{-3} \text{ mol HCl}$$

$$[\text{H}_3\text{O}^+] = \frac{8.34 \times 10^{-3} \text{ mol HCl}}{4.25 \text{ L soln}} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HCl}} = 1.96 \times 10^{-3} \text{ M}$$

35. First determine the amount of HCl, and then the volume of the concentrated solution.

$$\text{amount HCl} = 12.5 \text{ L} \times \frac{10^{-2.10} \text{ mol H}_3\text{O}^+}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol H}_3\text{O}^+} = 0.099 \text{ mol HCl}$$

$$V_{\text{solution}} = 0.099 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} \times \frac{100.0 \text{ g soln}}{36.0 \text{ g HCl}} \times \frac{1 \text{ mL soln}}{1.18 \text{ g soln}} = 8.5 \text{ mL soln}$$

37. The volume of HCl(aq) needed is determined by first finding the amount of NH<sub>3</sub>(aq) present, and then realizing that acid and base react in a 1:1 molar ratio.

$$V_{\text{HCl}} = 1.25 \text{ L base} \times \frac{0.265 \text{ mol NH}_3}{1 \text{ L base}} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol NH}_3} \times \frac{1 \text{ mol HCl}}{1 \text{ mol H}_3\text{O}^+} \times \frac{1 \text{ L acid}}{6.15 \text{ mol HCl}} \\ = 0.0539 \text{ L acid}$$

39. We determine the amounts of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> and then the amount of the one that is in excess. We express molar concentration in millimoles/milliliter, equivalent to mol/L.

$$50.00 \text{ mL} \times \frac{0.0155 \text{ mmol HI}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HI}} = 0.775 \text{ mmol H}_3\text{O}^+$$

$$75.00 \text{ mL} \times \frac{0.0106 \text{ mmol KOH}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 0.795 \text{ mmol OH}^-$$

The net reaction is  $\text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ .

There is an excess amount of OH<sup>-</sup> of  $(0.795 - 0.775) = 0.020 \text{ mmol OH}^-$ .

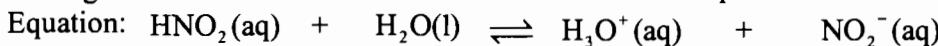
This is a basic solution. The total solution volume is  $(50.00 + 75.00) = 125.00 \text{ mL}$ .

$$[\text{OH}^-] = \frac{0.020 \text{ mmol OH}^-}{125.00 \text{ mL}} = 1.6 \times 10^{-4} \text{ M},$$

$$\text{pOH} = -\log(1.6 \times 10^{-4}) = 3.80, \quad \text{pH} = 14.00 - 3.80 = 10.20$$

## Weak Acids, Weak Bases, and pH

41. We organize the solution around the balanced chemical equation.



Initial:	0.143 M	$\approx 0 \text{ M}$	0 M
Changes:	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil:	$(0.143 - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{0.143 - x} = 7.2 \times 10^{-4} \gg \frac{x^2}{0.143} \text{ (if } x \ll 0.143\text{)}$$

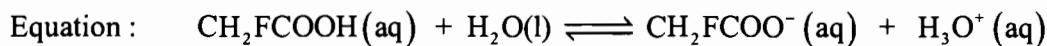
$$x = \sqrt{0.143 \times 7.2 \times 10^{-4}} = 0.010 \text{ M}$$

We have assumed that  $x \ll 0.143 \text{ M}$ , an almost-correct assumption. Another cycle of approximations yields:

$$x = \sqrt{(0.143 - 0.010) \times 7.2 \times 10^{-4}} = 0.0098 \text{ M} = [\text{H}_3\text{O}^+] \quad \text{pH} = -\log(0.0098) = 2.01$$

This is the same result as is determined with the quadratic equation.

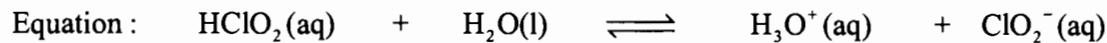
43. We base our set up on the balanced chemical equation.  $[\text{H}_3\text{O}^+] = 10^{-1.56} = 2.8 \times 10^{-2} \text{ M}$



Initial:	0.318 M	0 M	0 M
Changes:	$-0.028 \text{ M}$	$+0.028 \text{ M}$	$+0.028 \text{ M}$
Equil:	0.290 M	0.028 M	0.028 M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_2\text{FCOO}^-]}{[\text{CH}_2\text{FCOOH}]} = \frac{(0.028)(0.028)}{0.290} = 2.7 \times 10^{-3}$$

45. We use the balanced chemical equation, then solve using the quadratic formula.



Initial:	0.55 M	$\approx 0 \text{ M}$	0 M
Changes:	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil:	$(0.55 - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} = \frac{x^2}{0.55 - x} = 1.1 \times 10^{-2} = 0.011 \quad x^2 = 0.0061 - 0.011x$$

$$x^2 + 0.011x - 0.0061 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.011 \pm \sqrt{0.000121 + 0.0244}}{2} = 0.073 \text{ M} = [\text{H}_3\text{O}^+]$$

The method of successive approximations converges to the same answer in four cycles.

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.073) = 1.14 \quad \text{pOH} = 14.00 - \text{pH} = 14.00 - 1.14 = 12.86$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-12.86} = 1.4 \times 10^{-13} \text{ M}$$

47.  $[\text{C}_{10}\text{H}_7\text{NH}_2] = \frac{1 \text{ g C}_{10}\text{H}_7\text{NH}_2}{590 \text{ g H}_2\text{O}} \times \frac{1.00 \text{ g H}_2\text{O}}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol C}_{10}\text{H}_7\text{NH}_2}{143.2 \text{ g C}_{10}\text{H}_7\text{NH}_2}$   
 $= 0.012 \text{ M C}_{10}\text{H}_7\text{NH}_2$

$$K_b = 10^{-\text{pK}} = 10^{-3.92} = 1.2 \times 10^{-4}$$

Equation:	$\text{C}_{10}\text{H}_7\text{NH}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{OH}^-(\text{aq}) + \text{C}_{10}\text{H}_7\text{NH}_3^+(\text{aq})$
Initial:	0.012 M
Changes:	$-x \text{ M}$
Equil:	$(0.012 - x) \text{ M}$
$\text{OH}^-$	$\approx 0 \text{ M}$
$\text{C}_{10}\text{H}_7\text{NH}_3^+$	0 M
	$+x \text{ M}$
	$+x \text{ M}$
	$x \text{ M}$
	$x \text{ M}$

$$K_b = \frac{[\text{OH}^-][\text{C}_{10}\text{H}_7\text{NH}_3^+]}{[\text{C}_{10}\text{H}_7\text{NH}_2]} = \frac{x^2}{0.012 - x} = 1.2 \times 10^{-4} \approx \frac{x^2}{0.012} \quad \text{assuming } x \ll 0.012$$

$x = \sqrt{0.012 \times 1.2 \times 10^{-4}} = 0.0012$  This is an almost-correct assumption. Another approximation cycle gives:

$$x = \sqrt{(0.012 - 0.0012) \times 1.2 \times 10^{-4}} = 0.0011 \quad \text{Yet another cycle seems necessary.}$$

$$x = \sqrt{(0.012 - 0.0011) \times 1.2 \times 10^{-4}} = 0.0011 \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.0011) = 2.96 \quad \text{pH} = 14.00 - \text{pOH} = 11.04$$

$$\text{H}_3\text{O}^+ = 10^{-\text{pH}} = 10^{-11.04} = 9.1 \times 10^{-12} \text{ M}$$

49. We determine  $[\text{H}_3\text{O}^+]$  which, because of the stoichiometry of the reaction, equals  $[\text{C}_2\text{H}_3\text{O}_2^-]$ .

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.52} = 3.0 \times 10^{-5} \text{ M} = [\text{C}_2\text{H}_3\text{O}_2^-]$$

We solve for  $S$ , the concentration of  $\text{HC}_2\text{H}_3\text{O}_2$  in the 0.750 L solution before it dissociates.

Equation:	$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
initial:	$S \text{ M}$
changes:	$-3.0 \times 10^{-5} \text{ M}$
equil:	$(S - 3.0 \times 10^{-5}) \text{ M}$
	$0 \text{ M}$
	$\approx 0 \text{ M}$
	$+3.0 \times 10^{-5} \text{ M}$
	$+3.0 \times 10^{-5} \text{ M}$
	$3.0 \times 10^{-5} \text{ M}$
	$3.0 \times 10^{-5} \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{(3.0 \times 10^{-5})^2}{(S - 3.0 \times 10^{-5})}$$

$$(3.0 \times 10^{-5})^2 = 1.8 \times 10^{-5}(S - 3.0 \times 10^{-5}) = 9.0 \times 10^{-10} = 1.8 \times 10^{-5}S - 5.4 \times 10^{-10}$$

$$S = \frac{9.0 \times 10^{-10} + 5.4 \times 10^{-10}}{1.8 \times 10^{-5}} = 8.0 \times 10^{-5} \text{ M}$$

Now we determine the mass of vinegar needed.

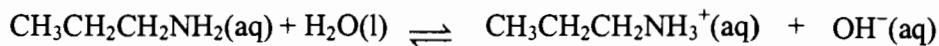
$$\text{mass vinegar} = 0.750 \text{ L} \times \frac{8.0 \times 10^{-5} \text{ mol HC}_2\text{H}_3\text{O}_2}{1 \text{ L soln}} \times \frac{60.05 \text{ g HC}_2\text{H}_3\text{O}_2}{1 \text{ mol HC}_2\text{H}_3\text{O}_2} \times \frac{100.0 \text{ g vinegar}}{5.7 \text{ g HC}_2\text{H}_3\text{O}_2}$$

$$= 0.063 \text{ g vinegar}$$

51. (a)  $n_{\text{propylamine}} = \frac{PV}{RT} = \frac{(316 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}})(0.275 \text{ L})}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})} = 4.67 \times 10^{-3} \text{ mol propylamine}$

$$[\text{propylamine}] = \frac{n}{V} = \frac{4.67 \times 10^{-3} \text{ moles}}{0.500 \text{ L}} = 9.35 \times 10^{-3} \text{ M}$$

$$K_b = 10^{-pK_b} = 10^{-3.43} = 3.7 \times 10^{-4}$$



Initial	$9.35 \times 10^{-3} \text{ M}$	$0 \text{ M}$	$\approx 0 \text{ M}$
Change	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equil.	$(9.35 \times 10^{-3} - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$K_b = 3.7 \times 10^{-4} = \frac{x^2}{9.35 \times 10^{-3} - x} \text{ or } 3.5 \times 10^{-6} - 3.7 \times 10^{-4}(x) = x^2$$

$$x^2 + 3.7 \times 10^{-4}x - 3.5 \times 10^{-6} = 0 \text{ solve quadratic:}$$

$$x = \frac{-3.7 \times 10^{-4} \pm \sqrt{(3.7 \times 10^{-4})^2 - 4(1)(-3.5 \times 10^{-6})}}{2(1)}$$

Therefore  $x = 1.695 \times 10^{-3} \text{ M} = [\text{OH}^-]$   $\text{pOH} = 2.77$  and  $\text{pH} = 11.23$

(b)  $[\text{OH}^-] = 1.7 \times 10^{-3} \text{ M} = [\text{NaOH}] \quad (\text{MM}_{\text{NaOH}} = 39.997 \text{ g mol}^{-1})$

$$n_{\text{NaOH}} = (C)(V) = 1.7 \times 10^{-3} \text{ M} \times 0.500 \text{ L} = 8.5 \times 10^{-4} \text{ moles NaOH}$$

$$\text{mass of NaOH} = (n)(\text{MM}_{\text{NaOH}}) = 8.5 \times 10^{-4} \text{ mol NaOH} \times 39.997 \text{ g NaOH/mol NaOH}$$

$$\text{mass of NaOH} = 0.034 \text{ g NaOH} (34 \text{ mg of NaOH})$$

53. If the molarity of acetic acid is doubled, we expect a lower initial pH (more  $\text{H}_3\text{O}^+(\text{aq})$  in solution) and a lower percent ionization as the concentration increases. Therefore (b) (the diagram in the center) best represents the conditions ( $\sim(2)^{1/2}$  times greater).

## Percent Ionization

55. Let us first compute the  $[\text{H}_3\text{O}^+]$  in this solution.

Equation:	$\text{HC}_3\text{H}_5\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_3\text{H}_5\text{O}_2^-(\text{aq})$
Initial:	0.45 M
Changes:	$-x \text{ M}$
Equil:	$(0.45-x) \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{x^2}{0.45-x} = 10^{-4.89} = 1.3 \times 10^{-5} \approx \frac{x^2}{0.45}$$

$x = 2.4 \times 10^{-3} \text{ M}$ ; We have assumed that  $x \ll 0.45 \text{ M}$ , an assumption that clearly is correct.

$$(a) \quad \alpha = \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HC}_3\text{H}_5\text{O}_2]_{\text{initial}}} = \frac{2.4 \times 10^{-3} \text{ M}}{0.45 \text{ M}} = 0.0053 = \text{degree of ionization}$$

$$(b) \quad \% \text{ ionization} = \alpha \times 100\% = 0.0053 \times 100\% = 0.53\%$$

57. Let  $x$  be the initial concentration of  $\text{NH}_3$  hence the amount dissociated is  $0.042x$

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\xrightleftharpoons{K_b = 1.8 \times 10^{-5}}$	$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
Initial	$x \text{ M}$	$0 \text{ M}$
Change	$-0.042x \text{ M}$	$+0.042x \text{ M}$
Equil.	$(1-0.042x) \text{ M}$ $= 0.958x$	$0.042x \text{ M}$ $0.042x \text{ M}$

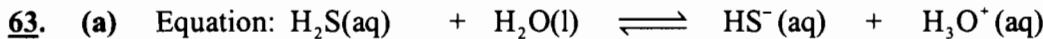
$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]_{\text{equil}}} = \frac{[0.042x]^2}{[0.958x]} = 0.00184x$$

$$[\text{NH}_3]_{\text{initial}} = x = \frac{1.8 \times 10^{-5}}{0.00184} = 0.00978 \text{ M} = 0.0098 \text{ M}$$

59. We would not expect these ionizations to be correct because the calculated degree of ionization is based on the assumption that the  $[\text{HC}_2\text{H}_3\text{O}_2]_{\text{initial}} \approx [\text{HC}_2\text{H}_3\text{O}_2]_{\text{initial}} - [\text{HC}_2\text{H}_3\text{O}_2]_{\text{equil.}}$ , which is invalid at the 13 and 42 percent levels of ionization seen here.

## Polyprotic Acids

61. Because  $\text{H}_3\text{PO}_4$  is a weak acid, there is little  $\text{HPO}_4^{2-}$  (produced in the second ionization) compared to the  $\text{H}_3\text{O}^+$  (produced in the first ionization). In turn, there is little  $\text{PO}_4^{3-}$  (produced in the third ionization) compared to the  $\text{HPO}_4^{2-}$ , and very little compared to the  $\text{H}_3\text{O}^+$ .



Initial:	0.075 M	0 M	$\approx 0$ M
Changes:	$-x$ M	$+x$ M	$+x$ M
Equil:	$(0.075 - x)$ M	$x$ M	$+x$ M

$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{0.075 - x} \approx \frac{x^2}{0.075} \quad x = 8.7 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

$$[\text{HS}^-] = 8.7 \times 10^{-5} \text{ M} \text{ and } [\text{S}^{2-}] = K_{a_2} = 1 \times 10^{-19} \text{ M}$$

- (b)** The set up for this problem is the same as for part (a), with the substitution of 0.0050 M for 0.075 M as the initial value of  $[\text{H}_2\text{S}]$ .

$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{0.0050 - x} \approx \frac{x^2}{0.0050} \quad x = 2.2 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

$$[\text{HS}^-] = 2.2 \times 10^{-5} \text{ M} \text{ and } [\text{S}^{2-}] = K_{a_2} = 1 \times 10^{-19} \text{ M}$$

- (c)** The set up for this part is the same as for part (a), with the substitution of  $1.0 \times 10^{-5}$  M for 0.075 M as the initial value of  $[\text{H}_2\text{S}]$ . The solution differs in that we cannot assume  $x \ll 1.0 \times 10^{-5}$ . Rather than solve the quadratic equation, however, we shall use the method of successive approximations.

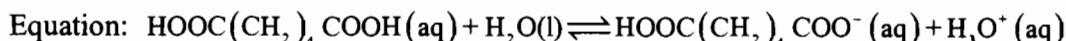
$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{1.0 \times 10^{-5} - x} \approx \frac{x^2}{1.0 \times 10^{-5}} \quad x = 1.0 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{1.0 \times 10^{-5} - 1.0 \times 10^{-6}} = \frac{x^2}{9.0 \times 10^{-6}} \quad x = 9.5 \times 10^{-7} \text{ M}$$

$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{1.0 \times 10^{-5} - 9.5 \times 10^{-7}} = \frac{x^2}{9.0 \times 10^{-6}} \quad x = 9.5 \times 10^{-7} \text{ M}$$

$$x = 9.5 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] \quad [\text{HS}^-] = 9.5 \times 10^{-7} \text{ M} \quad [\text{S}^{2-}] = K_{a_2} = 1 \times 10^{-19} \text{ M}$$

- 65.** First determine  $[\text{H}_3\text{O}^+]$ , with calculation based, on the balanced chemical equation.

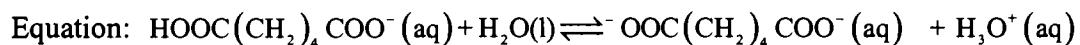


Initial:	0.10 M	0 M	$\approx 0$ M
Changes:	$-x$ M	$+x$ M	$+x$ M
Equil:	$(0.10 - x)$ M	$x$ M	$x$ M

$$K_{a_1} = \frac{[\text{H}_3\text{O}^+][\text{HOOC}(\text{CH}_2)_4\text{COO}^-]}{[\text{HOOC}(\text{CH}_2)_4\text{COOH}]} = 3.9 \times 10^{-5} = \frac{x \cdot x}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = \sqrt{0.10 \times 3.9 \times 10^{-5}} = 2.0 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$$

We see that our simplifying assumption, that  $x \ll 0.10 \text{ M}$ , is indeed valid. Now we consider the second ionization. We shall see that very little  $\text{H}_3\text{O}^+$  is produced in this ionization because of the small size of two numbers:  $K_{a_2}$  and  $[\text{HOOC}(\text{CH}_2)_4\text{COO}^-]$ . Again we base our calculation on the balanced chemical equation.



Initial:	$2.0 \times 10^{-3} \text{ M}$	$0 \text{ M}$	$2.0 \times 10^{-3} \text{ M}$
Changes:	$-y \text{ M}$	$+y \text{ M}$	$+y \text{ M}$
Equil:	$(0.0020 - y) \text{ M}$	$y \text{ M}$	$(0.0020 + y) \text{ M}$

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{OOC}(\text{CH}_2)_4\text{COO}^-]}{[\text{HOOC}(\text{CH}_2)_4\text{COO}^-]} = 3.9 \times 10^{-6} = \frac{y(0.0020 + y)}{0.0020 - y} \approx \frac{0.0020y}{0.0020}$$

$$y = 3.9 \times 10^{-6} \text{ M} = [\text{OOC}(\text{CH}_2)_4\text{COO}^-]$$

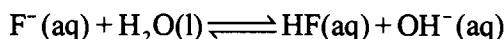
Again, we see that our assumption, that  $y \ll 0.0020 \text{ M}$ , is valid. In addition, we also see that virtually no  $\text{H}_3\text{O}^+$  is created in this second ionization. The concentrations of all species have been calculated above, with the exception of  $[\text{OH}^-]$ .

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ M}; \quad [\text{HOOC}(\text{CH}_2)_4\text{COOH}] = 0.10 \text{ M}$$

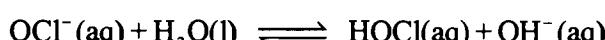
$$[\text{H}_3\text{O}^+] = [\text{HOOC}(\text{CH}_2)_4\text{COO}^-] = 2.0 \times 10^{-3} \text{ M}; \quad [\text{OOC}(\text{CH}_2)_4\text{COO}^-] = 3.9 \times 10^{-6} \text{ M}$$

## Ions as Acids and Bases (Hydrolysis)

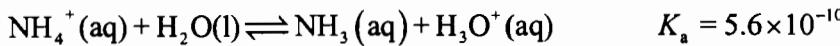
- 67.** (a) KCl forms a neutral solution, being composed of the cation of a strong base, and the anion of a strong acid; no hydrolysis occurs.
- (b) KF forms an alkaline (basic) solution, being composed of the cation of a strong base and the anion of a weak acid; the fluoride ion hydrolyzes.



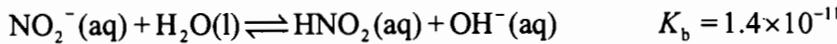
- (c)  $\text{NaNO}_3$  forms a neutral solution, being composed of the cation of a strong base and the anion of a strong acid. No hydrolysis occurs.
- (d)  $\text{Ca}(\text{OCl})_2$  forms an alkaline (basic) solution, being composed of the cation of a strong base, and the anion of a weak acid; the hypochlorite ion hydrolyzes.



- (e)  $\text{NH}_4\text{NO}_2$  forms an acidic solution. The salt is composed of the cation of a weak base and the anion of a weak acid; the ammonium ion hydrolyzes:

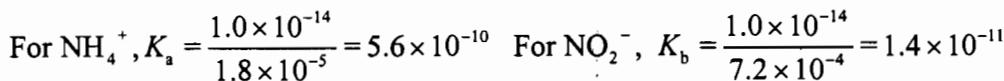


So does the nitrite ion:



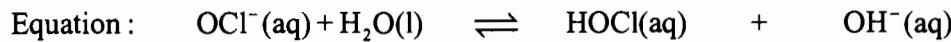
Since  $\text{NH}_4^+$  is a stronger acid than  $\text{NO}_2^-$  is a base, the solution will be acidic.

The ionization constants were computed from data in Table 17-3 and with the relationship  $K_w = K_a \times K_b$ .



Where  $1.8 \times 10^{-5} = K_b$  of  $\text{NH}_3$  and  $7.2 \times 10^{-4} = K_a$  of  $\text{HNO}_2$

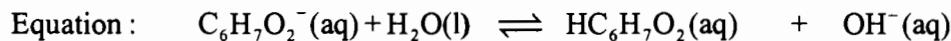
69.  $\text{NaOCl}$  dissociates completely in aqueous solution into  $\text{Na}^+(\text{aq})$ , which does not hydrolyze, and  $\text{OCl}^-(\text{aq})$ , which does hydrolyze. We determine  $[\text{OH}^-]$  in a 0.089 M solution of  $\text{OCl}^-$ , finding the value of the hydrolysis constant from the ionization constant of  $\text{HOCl}$ ,  $K_a = 2.9 \times 10^{-8}$ .



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7} = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} = \frac{x^2}{0.089 - x} \approx \frac{x^2}{0.089}$$

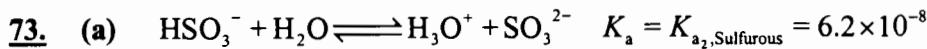
$$x = 1.7 \times 10^{-4} \text{ M} = [\text{OH}^-]; \quad \text{pOH} = -\log(1.7 \times 10^{-4}) = 3.77, \quad \text{pH} = 14.00 - 3.77 = 10.23$$

71.  $\text{KC}_6\text{H}_7\text{O}_2$  dissociates completely in aqueous solution into  $\text{K}^+(\text{aq})$ , which does not hydrolyze, and the ion  $\text{C}_6\text{H}_7\text{O}_2^-(\text{aq})$ , which does hydrolyze. We determine  $[\text{OH}^-]$  in 0.37 M  $\text{KC}_6\text{H}_7\text{O}_2$  solution. Note:  $K_a = 10^{-\text{p}K} = 10^{-4.77} = 1.7 \times 10^{-5}$



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.9 \times 10^{-10} = \frac{[\text{HC}_6\text{H}_7\text{O}_2][\text{OH}^-]}{[\text{C}_6\text{H}_7\text{O}_2^-]} = \frac{x^2}{0.37 - x} \approx \frac{x^2}{0.37}$$

$$x = 1.5 \times 10^{-5} \text{ M} = [\text{OH}^-], \quad \text{pOH} = -\log(1.5 \times 10^{-5}) = 4.82, \quad \text{pH} = 14.00 - 4.82 = 9.18$$



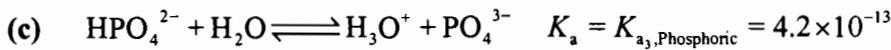
$$\text{HSO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_2\text{SO}_3 \quad K_b = \frac{K_w}{K_{a_1, \text{Sulfurous}}} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-2}} = 7.7 \times 10^{-13}$$

Since  $K_a > K_b$ , a solution of  $\text{HSO}_3^-$  is acidic.



$$\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_2\text{S} \quad K_b = \frac{K_w}{K_{a_1, \text{Hydrosulfuric}}} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$$

Since  $K_a < K_b$ , a solution of  $\text{HS}^-$  is alkaline, or basic.



$$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_2\text{PO}_4^- \quad K_b = \frac{K_w}{K_{a_2, \text{Phosphoric}}} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-8}} = 1.6 \times 10^{-7}$$

Since  $K_a < K_b$ , a solution of  $\text{HPO}_4^{2-}$  is alkaline, or basic.

75. (a)  $\text{HClO}_3$  should be a stronger acid than  $\text{HClO}_2$ . In each acid there is an  $\text{H}-\text{O}-\text{Cl}$  grouping. The remaining oxygen atoms are bonded directly to Cl as terminal O atoms. Thus, there are two terminal O atoms in  $\text{HClO}_3$  and only one in  $\text{HClO}_2$ . Of oxoacids of the same element, the one with the higher number of terminal oxygen atoms is the stronger.  $\text{HClO}_3 : K_{a_1} = 5 \times 10^2$  f and  $\text{HClO}_2 : K_a = 1.1 \times 10^{-2}$ .

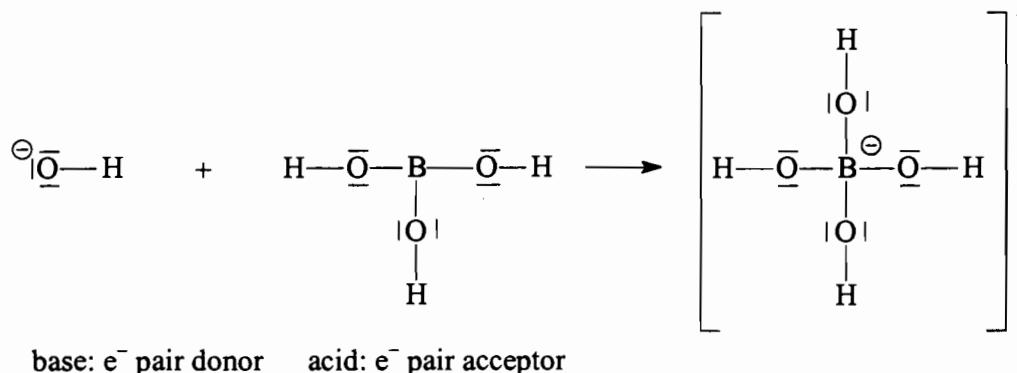
- (b)  $\text{HNO}_2$  and  $\text{H}_2\text{CO}_3$  have the same number (one) of terminal oxygen atoms. They differ in N being more electronegative than C.  $\text{HNO}_2 (K_a = 7.2 \times 10^{-4})$  is stronger than  $\text{H}_2\text{CO}_3 (K_{a_1} = 4.4 \times 10^{-7})$ .

- (c)  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SiO}_3$  have the same number (one) of terminal oxygen atoms. They differ in P being more electronegative than Si.  $\text{H}_3\text{PO}_4 (K_{a_1} = 7.1 \times 10^{-3})$  is stronger than  $\text{H}_2\text{SiO}_3 (K_{a_1} = 1.7 \times 10^{-10})$ .

77. Largest  $K_b$  (most basic) belongs to  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  (hydrocarbon chains have the lowest electronegativity). Smallest  $K_b$  (least basic) is that of o-chlorylaniline (the nitrogen lone pair is delocalized (spread out over the ring), hence, less available to accept a proton (poorer base)).

## Lewis Theory of Acids and Bases

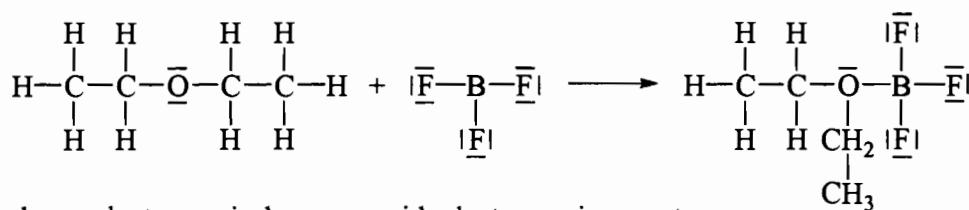
79. (a)



base:  $e^-$  pair donor      acid:  $e^-$  pair acceptor

The actual Lewis acid is  $\text{H}^+$ , which is supplied by  $\text{H}_3\text{O}^+$

(c)



base: electron pair donor      acid: electron pair acceptor

**81.**  $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

83. 

## FEATURE PROBLEMS

- 105. (a)** From the combustion analysis we can determine the empirical formula. Note that the mass of oxygen is determined by difference.

$$\text{amount C} = 1.599 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.03633 \text{ mol C}$$

$$\text{mass of C} = 0.03633 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.4364 \text{ g C}$$

$$\text{amount H} = 0.327 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.03629 \text{ mol H}$$

$$\text{mass of H} = 0.03629 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.03658 \text{ g H}$$

$$\text{amount O} = (1.054 \text{ g sample} - 0.4364 \text{ g C} - 0.03658 \text{ g H}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0364 \text{ mol O}$$

There are equal moles of the three elements. The empirical formula is CHO. The freezing-point depression data are used to determine the molar mass.

$$\Delta T_f = -K_f m \quad m = \frac{\Delta T_f}{-K_f} = \frac{-0.82 \text{ }^\circ\text{C}}{-3.90 \text{ }^\circ\text{C/mol}} = 0.21 \text{ mol}$$

$$\text{amount of solute} = 25.10 \text{ g solvent} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{0.21 \text{ mol solute}}{1 \text{ kg solvent}} = 0.0053 \text{ mol}$$

$$M = \frac{0.615 \text{ g solute}}{0.0053 \text{ mol solute}} = 1.2 \times 10^2 \text{ g/mol}$$

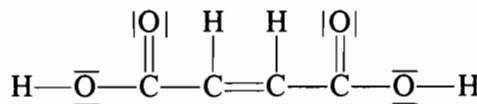
The formula mass of the empirical formula is:  $12.0 \text{ g C} + 1.0 \text{ g H} + 16.0 \text{ g O} = 29.0 \text{ g/mol}$   
Thus, there are four empirical units in a molecule, the molecular formula is  $\text{C}_4\text{H}_4\text{O}_4$ , and the molar mass is 116.1 g/mol.

- (b)** We determine the mass of maleic acid that reacts with one mol  $\text{OH}^-$ ,

$$\frac{\text{mass}}{\text{mol OH}^-} = \frac{0.4250 \text{ g maleic acid}}{34.03 \text{ mL base} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.2152 \text{ mol KOH}}{1 \text{ L base}}} = 58.03 \text{ g/mol OH}^-$$

This means that one mole of maleic acid (116.1 g/mol) reacts with two moles of hydroxide ion. Maleic acid is a diprotic acid:  $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ .

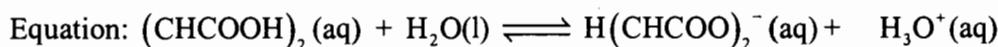
- (c) Maleic acid has two—COOH groups joined together by a bridging C<sub>2</sub>H<sub>2</sub> group. A plausible Lewis structure is shown below:



- (d) We first determine  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-1.80} = 0.016 \text{ M}$  and then the initial concentration of acid.

$$[(\text{CHCOOH})_2]_{\text{initial}} = \frac{0.215 \text{ g}}{50.00 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol}}{116.1 \text{ g}} = 0.0370 \text{ M}$$

We use the first ionization to determine the value of  $K_{a_1}$



$$\text{Initial: } 0.0370 \text{ M} \quad 0 \text{ M} \quad \approx 0 \text{ M}$$

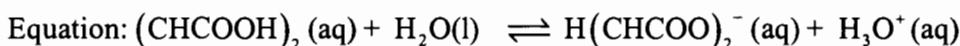
$$\text{Changes: } -0.016 \text{ M} \quad +0.016 \text{ M} \quad +0.016 \text{ M}$$

$$\text{Equil: } 0.021 \text{ M} \quad 0.016 \text{ M} \quad 0.016 \text{ M}$$

$$K_{a_1} = \frac{[\text{H}(\text{CHCOO})_2^-][\text{H}_3\text{O}^+]}{[(\text{CHCOOH})_2]} = \frac{(0.016)(0.016)}{0.021} = 1.2 \times 10^{-2}$$

$K_{a_2}$  could be determined if we had some way to measure the total concentration of all ions in solution, or if we could determine  $[(\text{CHCOO})_2^{2-}] = K_{a_2}$

- (e) Practically all the  $[\text{H}_3\text{O}^+]$  arises from the first ionization.



$$\text{Initial: } 0.0500 \text{ M} \quad 0 \text{ M} \quad \approx 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (0.0500 - x) \text{ M} \quad x \text{ M} \quad x \text{ M}$$

$$K_{a_1} = \frac{[\text{H}(\text{CHCOO})_2^-][\text{H}_3\text{O}^+]}{[(\text{CHCOOH})_2]} = \frac{x^2}{0.0500 - x} = 1.2 \times 10^{-2}$$

$$x^2 = 0.00060 - 0.012 x \quad x^2 + 0.012 x - 0.00060 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.012 \pm \sqrt{0.00014 + 0.0024}}{2} = 0.019 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.019) = 1.72$$

106. (a) 
$$\frac{x^2}{0.00250 - x} \approx \frac{x^2}{0.00250} \approx 4.2 \times 10^{-4} \quad x_1 \approx 0.00102$$

$$\frac{x^2}{0.00250 - 0.00102} = \frac{x^2}{0.00148} \approx 4.2 \times 10^{-4} \quad x_2 \approx 0.000788$$

$$\frac{x^2}{0.00250 - 0.000788} = \frac{x^2}{0.00171} \approx 4.2 \times 10^{-4} \quad x_3 \approx 0.000848$$

$$\frac{x^2}{0.00250 - 0.000848} = \frac{x^2}{0.00165} \approx 4.2 \times 10^{-4} \quad x_4 \approx 0.000833$$

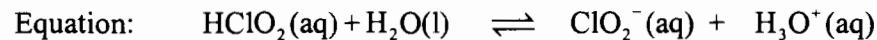
$$\frac{x^2}{0.00250 - 0.000833} = \frac{x^2}{0.00167} \approx 4.2 \times 10^{-4} \quad x_5 \approx 0.000837$$

$$\frac{x^2}{0.00250 - 0.000837} = \frac{x^2}{0.00166} \approx 4.2 \times 10^{-4} \quad x_6 \approx 0.000836$$

$x_6 \approx 0.000836 \quad \text{or } \approx 8.4 \times 10^{-4},$

which is the same as the value obtained with the quadratic equation on page 681.

- (b) We organize the solution around the balanced chemical equation, as we have done before.



$$K_a = \frac{[\text{ClO}_2^-][\text{H}_3\text{O}^+]}{[\text{HClO}_2]} = \frac{x^2}{0.500 - x} = 1.1 \times 10^{-2} \approx \frac{x^2}{0.500} \quad \text{Assuming } x \ll 0.500 \text{ M,}$$

$$x = \sqrt{x^2} = \sqrt{0.500 \times 1.1 \times 10^{-2}} = 0.074 \text{ M} \quad \text{This is not greatly smaller than 0.500 M.}$$

$$\text{Assume } x = 0.074 \quad x = \sqrt{(0.500 - 0.074) \times 1.1 \times 10^{-2}} = 0.068 \text{ M} \quad \text{Try once more.}$$

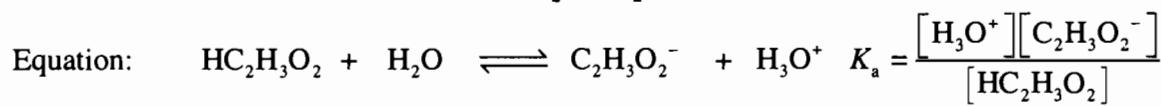
$$\text{Assume } x = 0.068 \quad x = \sqrt{(0.500 - 0.068) \times 1.1 \times 10^{-2}} = 0.069 \text{ M} \quad \text{One more time.}$$

$$\text{Assume } x = 0.069 \quad x = \sqrt{(0.500 - 0.069) \times 1.1 \times 10^{-2}} = 0.069 \text{ M} \quad \text{Final result!}$$

$$[\text{H}_3\text{O}^+] = 0.069 \text{ M}, \quad \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.069) = 1.16$$

107. (a) In this case, two equilibria must be satisfied simultaneously.

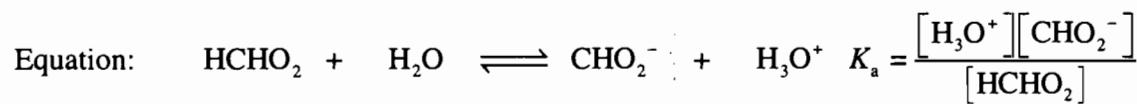
The two have a common variable,  $[\text{H}_3\text{O}^+] = z$ .



Initial:  $0.315\text{ M}$   $0\text{ M}$   $\approx 0\text{ M}$

Changes:  $+x\text{ M}$   $+x\text{ M}$   $+z\text{ M}$   $= \frac{xz}{0.315-x} = 1.8 \times 10^{-5}$

Equil:  $(0.315-x)\text{ M}$   $x\text{ M}$   $z\text{ M}$



Initial:  $0.250\text{ M}$   $0\text{ M}$   $0\text{ M}$

Changes:  $+y\text{ M}$   $+y\text{ M}$   $+z\text{ M}$   $= \frac{yz}{0.250-y} = 1.8 \times 10^{-4}$

Equil:  $(0.250-y)\text{ M}$   $y\text{ M}$   $z\text{ M}$

In this system, there are three variables,  $x = [\text{C}_2\text{H}_3\text{O}_2^-]$ ,  $y = [\text{CHO}_2^-]$ , and  $z = [\text{H}_3\text{O}^+]$ .

These three variables also represent the concentrations of the only charged species in the reaction, and thus  $x + y = z$ . We solve the two  $K_a$  expressions for  $x$  or  $y$  respectively. (Before we do so, however, we take advantages of the fact that  $x$  and  $y$  are quite small:  $x \ll 0.315$  and  $y \ll 0.250$ .) Then we substitute these results into the expression for  $z$ , and solve to obtain a value of that variable.

$$xz = 1.8 \times 10^{-5} (0.315) = 5.7 \times 10^{-6}$$

$$x = \frac{5.7 \times 10^{-6}}{z}$$

$$yz = 1.8 \times 10^{-4} (0.250) = 4.5 \times 10^{-5}$$

$$y = \frac{4.5 \times 10^{-5}}{z}$$

$$z = x + y = \frac{5.7 \times 10^{-6}}{z} + \frac{4.5 \times 10^{-5}}{z} = \frac{5.07 \times 10^{-5}}{z} \quad z = \sqrt{5.07 \times 10^{-5}} = 7.1 \times 10^{-3}\text{ M} = [\text{H}_3\text{O}^+]$$

$\text{pH} = -\log(7.1 \times 10^{-3}) = 2.15$  We see that our assumptions about the sizes of  $x$  and  $y$  must be valid, since each of them is smaller than  $z$ . (Remember that  $x + y = z$ .)

(b) We first determine the initial concentration of each solute.

$$[\text{NH}_3] = \frac{12.5 \text{ g NH}_2}{0.375 \text{ L soln}} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} = 1.96 \text{ M} \quad K_b = 1.8 \times 10^{-5}$$

$$[\text{CH}_3\text{NH}_2] = \frac{1.55 \text{ g CH}_3\text{NH}_2}{0.375 \text{ L soln}} \times \frac{1 \text{ mol CH}_3\text{NH}_2}{31.06 \text{ g CH}_3\text{NH}_2} = 0.113 \text{ M} \quad K_b = 4.2 \times 10^{-4}$$

Now we solve simultaneously two equilibria, which have a common variable,  $[\text{OH}^-] = z$ .

$$\text{Equation: } \text{NH}_3 \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ \text{ (aq)} + \text{OH}^- \text{ (aq)} \quad K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

$$\text{Initial: } 1.96 \text{ M} \quad 0 \text{ M} \quad \approx 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +z \text{ M} \quad = \frac{xz}{1.96 - x} \approx \frac{xz}{1.96}$$

$$\text{Equil: } (1.96 - x) \text{ M} \quad x \text{ M} \quad z \text{ M}$$

$$\text{Eqn: } \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^- \text{ (aq)} \quad K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

$$\text{Initial: } 0.113 \text{ M} \quad 0 \text{ M} \quad \approx 0 \text{ M}$$

$$\text{Changes: } -y \text{ M} \quad +y \text{ M} \quad +z \text{ M} \quad = 4.2 \times 10^{-4} = \frac{yz}{0.113 - y} = \frac{yz}{0.113}$$

$$\text{Equil: } (0.113 - y) \text{ M} \quad y \text{ M} \quad z \text{ M}$$

In this system, there are three variables,  $x = [\text{NH}_4^+]$ ,  $y = [\text{CH}_3\text{NH}_3^+]$ , and  $z = [\text{OH}^-]$ .

These three variables also represent the concentrations of the only charged species in solution, and thus  $x + y = z$ . We solve the two  $K_b$  expressions for  $x$  and  $y$  respectively. Then we substitute these results into the expression for  $z$ , and solve to obtain the value of that variable.

$$xz = 1.96 \times 1.8 \times 10^{-5} = 3.41 \times 10^{-5}$$

$$yz = 0.113 \times 4.2 \times 10^{-4} = 4.75 \times 10^{-5}$$

$$x = \frac{3.41 \times 10^{-5}}{z}$$

$$y = \frac{4.75 \times 10^{-5}}{z}$$

$$z = x + y = \frac{3.41 \times 10^{-5}}{z} + \frac{4.75 \times 10^{-5}}{z} = \frac{8.16 \times 10^{-5}}{z} \quad z^2 = 8.16 \times 10^{-5}$$

$$z = 9.0 \times 10^{-3} \text{ M} = [\text{OH}^-] \quad \text{pOH} = -\log(9.0 \times 10^{-3}) = 2.05 \quad \text{pH} = 14.00 - 2.05 = 11.95$$

We see that our assumptions about  $x$  and  $y$  (that  $x \ll 1.96 \text{ M}$  and  $y \ll 0.113 \text{ M}$ ) must be valid, since each of them is smaller than  $z$ . (Remember that  $x + y = z$ .)

- (c) In 1.0 M  $\text{NH}_4\text{CN}$  there are the following species:  $\text{NH}_4^+$ (aq),  $\text{NH}_3$ (aq),  $\text{CN}^-$ (aq),  $\text{HCN}$ (aq),  $\text{H}_3\text{O}^+$ (aq), and  $\text{OH}^-$ (aq). These species are related by the following six equations.

$$(1) K_w = 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+] [\text{OH}^-] \quad [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$$

$$(2) K_a = 6.2 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+] [\text{CN}^-]}{[\text{HCN}]} \quad (3) K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]}$$

$$(4) [\text{NH}_3] + [\text{NH}_4^+] = 1.0 \text{ M} \quad [\text{NH}_3] = 1.0 - [\text{NH}_4^+]$$

$$(5) [\text{HCN}] + [\text{CN}^-] = 1.0 \text{ M} \quad [\text{HCN}] = 1.0 - [\text{CN}^-]$$

$$(6) [\text{NH}_4^+] + [\text{H}_3\text{O}^+] = [\text{CN}^-] + [\text{OH}^-] \text{ or } [\text{NH}_4^+] \approx [\text{CN}^-]$$

Equation (6) is the result of charge balance, that there must be the same quantity of positive and negative charge in the solution. The approximation is the result of remembering that not much  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  will be formed as the result of hydrolysis of ions.

Substitute equation (4) into equation (3), and equation (5) into equation (2).

$$(3') K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{1.0 - [\text{NH}_4^+]} \quad (2') K_a = 4.0 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+] [\text{CN}^-]}{1.0 - [\text{CN}^-]}$$

Now substitute equation (6) into equation (2'), and equation (1) into equation (3').

$$(2'') K_a = 6.2 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+] [\text{NH}_4^+]}{1.0 - [\text{NH}_4^+]} \quad (3'') \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = \frac{[\text{NH}_4^+]}{[\text{H}_3\text{O}^+] (1.0 - [\text{NH}_4^+])}$$

Now we solve both of these equations for  $[\text{NH}_4^+]$ .

$$(2'): 6.2 \times 10^{-10} - 6.2 \times 10^{-10} [\text{NH}_4^+] = [\text{H}_3\text{O}^+] [\text{NH}_4^+] \quad [\text{NH}_4^+] = \frac{6.2 \times 10^{-10}}{6.2 \times 10^{-10} + [\text{H}_3\text{O}^+]}$$

$$(3'): 1.8 \times 10^{-5} [\text{H}_3\text{O}^+] - 1.8 \times 10^{-5} [\text{H}_3\text{O}^+] [\text{NH}_4^+] = [\text{NH}_4^+] \quad [\text{NH}_4^+] = \frac{1.8 \times 10^{-5} [\text{H}_3\text{O}^+]}{1.00 + 1.8 \times 10^{-5} [\text{H}_3\text{O}^+]}$$

$$\text{We equate the two results and solve for } [\text{H}_3\text{O}^+]. \frac{6.2 \times 10^{-10}}{6.2 \times 10^{-10} + [\text{H}_3\text{O}^+]} = \frac{1.8 \times 10^{-5} [\text{H}_3\text{O}^+]}{1.00 + 1.8 \times 10^{-5} [\text{H}_3\text{O}^+]}$$

$$6.2 \times 10^{-10} + 1.1 [\text{H}_3\text{O}^+] = 1.1 [\text{H}_3\text{O}^+] + 1.8 \times 10^{-5} [\text{H}_3\text{O}^+]^2 \quad 6.2 \times 10^{-10} = 1.8 \times 10^{-5} [\text{H}_3\text{O}^+]^2$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{6.2 \times 10^{-10}}{1.8 \times 10^{-5}}} = 5.9 \times 10^{-10} \text{ M} \quad \text{pH} = -\log(5.9 \times 10^{-10}) = 9.23$$

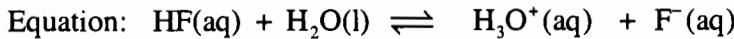
$$\text{Note that } [\text{H}_3\text{O}^+] = \sqrt{\frac{K_a \times K_w}{K_b}} \quad \text{or} \quad \text{pH} = 0.500 (\text{p}K_a + \text{p}K_w - \text{p}K_b)$$

# CHAPTER 18

## ADDITIONAL ASPECTS OF ACID—BASE EQUILIBRIA

### PRACTICE EXAMPLES

**1A** Organize the solution around the balanced chemical equation, as we have done before.



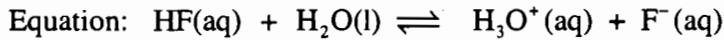
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.500 - x} = 6.6 \times 10^{-4} \approx \frac{x^2}{0.500} \quad \text{assuming } x \ll 0.500$$

$$x = \sqrt{0.500 \times 6.6 \times 10^{-4}} = 0.018\text{ M} \quad \text{One further cycle of approximations gives:}$$

$$x = \sqrt{(0.500 - 0.018) \times 6.6 \times 10^{-4}} = 0.018\text{ M} = [\text{H}_3\text{O}^+]$$

$$[\text{HF}] = 0.500\text{ M} - 0.018\text{ M} = 0.482\text{ M}$$

Recognize that  $0.100\text{ M HCl}$  means  $[\text{H}_3\text{O}^+]_{\text{initial}} = 0.100\text{ M}$ , since HCl is a strong acid.



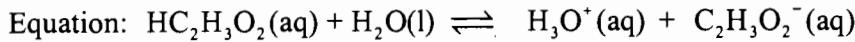
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(0.100 + x)}{0.500 - x} = 6.6 \times 10^{-4} \approx \frac{0.100x}{0.500} \quad \text{assuming } x \ll 0.100$$

$$x = \frac{6.6 \times 10^{-4} \times 0.500}{0.100} = 3.3 \times 10^{-3}\text{ M} = [\text{F}^-] \quad \text{The assumption is valid.}$$

$$[\text{HF}] = 0.500\text{ M} - 0.003\text{ M} = 0.497\text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.100\text{ M} + x = 0.103\text{ M} = 0.100\text{ M} + 0.003\text{ M} = 0.103\text{ M}$$

**1B** From Example 17-6 in the text, we know that  $[\text{H}_3\text{O}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 1.3 \times 10^{-3}\text{ M}$  in  $0.100\text{ M HC}_2\text{H}_3\text{O}_2$ . We base our calculation, as usual, on the balanced chemical equation. The concentration of  $\text{H}_3\text{O}^+$  from the added HCl is represented by  $x$ .



Initial: 0.100 M  $\approx 0\text{M}$  0M

Changes:  $-0.00010\text{M}$   $+0.00010\text{M}$   $+0.00010\text{M}$

From HCl:  $+x\text{M}$

Equil: 0.100 M  $(0.00010+x)\text{M}$   $+0.00010\text{M}$

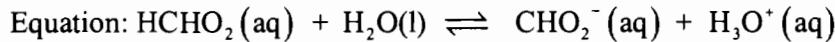
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(0.00010+x)0.00010}{0.100} = 1.8 \times 10^{-5}$$

$$0.00010+x = \frac{1.8 \times 10^{-5} \times 0.100}{0.00010} = 0.018\text{M} \quad x = 0.018\text{M} - 0.00010\text{M} = 0.018\text{M}$$

$$V_{12\text{M HCl}} = 1.00\text{ L} \times \frac{0.018\text{ mol H}_3\text{O}^+}{1\text{ L}} \times \frac{1\text{ mol HCl}}{1\text{ mol H}_3\text{O}^+} \times \frac{1\text{ L soln}}{12\text{ mol HCl}} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1\text{ drop}}{0.050\text{ mL}} = 30\text{ drops}$$

Since 30. drops corresponds to 1.5 mL of 12 M solution, we see that the volume of solution does indeed remain 1.00 L after addition of the 12 M HCl.

**2A** We again organize the solution around the balanced chemical equation.



Initial: 0.100 M 0.150M  $\approx 0\text{M}$

Changes:  $-x\text{M}$   $+x\text{M}$   $+x\text{M}$

Equil:  $(0.100-x)\text{M}$   $(0.150+x)\text{M}$   $x\text{M}$

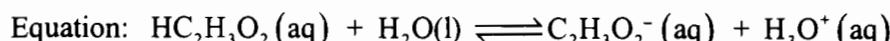
$$K_a = \frac{[\text{CHO}_2^-][\text{H}_3\text{O}^+]}{[\text{HCHO}_2]} = \frac{(0.150+x)(x)}{0.100-x} = 1.8 \times 10^{-4} \approx \frac{0.150x}{0.100} \quad \text{assuming } x \ll 0.100$$

$$x = \frac{0.100 \times 1.8 \times 10^{-4}}{0.150} = 1.2 \times 10^{-4}\text{M} = [\text{H}_3\text{O}^+], \text{ valid assumption}$$

$$[\text{CHO}_2^-] = 0.150\text{M} + 0.00012\text{M} = 0.150\text{M}$$

**2B** This time a solid sample of a weak base is being added to a solution of its conjugate acid. We let  $x$  represent the concentration of acetate ion from the added sodium acetate. Notice that sodium acetate is a strong electrolyte, completely dissociated in aqueous solution.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.00} = 1.0 \times 10^{-5}\text{M} = 0.000010\text{M}$$



Initial: 0.100 M 0M  $\approx 0\text{M}$

Changes:  $-0.000010\text{M}$   $+0.000010\text{M}$   $+0.000010\text{M}$

From NaAc:  $+x\text{M}$

Equil: 0.100M  $(0.000010+x)\text{M}$  0.000010M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{0.000010(0.000010+x)}{0.100} = 1.8 \times 10^{-5}$$

$$0.000010+x = \frac{1.8 \times 10^{-5} \times 0.100}{0.000010} = 0.18 \text{ M} \quad x = 0.18 \text{ M} - 0.000010 \text{ M} = 0.18 \text{ M}$$

$$\text{mass of NaC}_2\text{H}_3\text{O}_2 = 1.00 \text{ L} \times \frac{0.18 \text{ mol C}_2\text{H}_3\text{O}_2^-}{1 \text{ L}} \times \frac{1 \text{ mol NaC}_2\text{H}_3\text{O}_2}{1 \text{ mol C}_2\text{H}_3\text{O}_2^-} \times \frac{82.03 \text{ g NaC}_2\text{H}_3\text{O}_2}{1 \text{ mol NaC}_2\text{H}_3\text{O}_2}$$

$$= 15 \text{ g NaC}_2\text{H}_3\text{O}_2$$

**3A** A strong acid dissociates completely, and essentially is a source of  $\text{H}_3\text{O}^+$ .  $\text{NaC}_2\text{H}_3\text{O}_2$  also dissociates completely in solution. The hydronium ion and the acetate ion react to form acetic acid:  $\text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$

All that is necessary to form a buffer is to have approximately equal amounts of a weak acid and its conjugate base in solution. This will be achieved if we add an amount of HCl equal to approximately half the original amount of acetate ion.

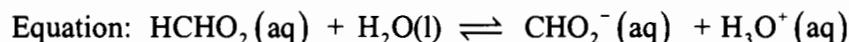
**3B** HCl dissociates completely and serves as a source of hydronium ion. This reacts with ammonia to form ammonium ion:  $\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$ .

Because a buffer contains approximately equal amounts of a weak base ( $\text{NH}_3$ ) and its conjugate acid ( $\text{NH}_4^+$ ), to prepare a buffer we simply add an amount of HCl equal to approximately half the amount of  $\text{NH}_3(\text{aq})$  initially present.

**4A** We first find the formate ion concentration, remembering that  $\text{NaCHO}_2$  is a strong electrolyte, existing in solution as  $\text{Na}^+(\text{aq})$  and  $\text{CHO}_2^-(\text{aq})$ .

$$[\text{CHO}_2^-] = \frac{23.1 \text{ g NaCHO}_2}{500.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol NaCHO}_2}{68.01 \text{ g NaCHO}_2} \times \frac{1 \text{ mol CHO}_2^-}{1 \text{ mol NaCHO}_2} = 0.679 \text{ M}$$

As usual, the solution to the problem is organized around the balanced chemical equation.



Initial:  $0.432 \text{ M}$   $0.679 \text{ M}$   $\approx 0 \text{ M}$

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

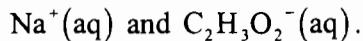
Equil:  $(0.432 - x) \text{ M}$   $(0.679 + x) \text{ M}$   $x \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = \frac{x(0.679+x)}{0.432-x} = 1.8 \times 10^{-4} \approx \frac{0.679x}{0.432} \quad x = \frac{0.432 \times 1.8 \times 10^{-4}}{0.679}$$

This gives  $[\text{H}_3\text{O}^+] = 0.0892 \text{ M}$ . The assumption that  $x \ll 0.432$  is clearly correct.

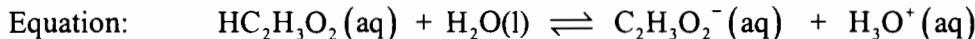
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.1 \times 10^{-4}) = 3.96$$

- 4B** The concentrations of the components in the 100.0 mL of buffer solution are found by dilution. Remember that  $\text{NaC}_2\text{H}_3\text{O}_2$  is a strong electrolyte, existing in solution as



$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.200 \text{ M} \times \frac{63.0 \text{ mL}}{100.0 \text{ mL}} = 0.126 \text{ M} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = 0.200 \text{ M} \times \frac{37.0 \text{ mL}}{100.0 \text{ mL}} = 0.0740 \text{ M}$$

As usual, the solution to the problem is organized around the balanced chemical equation.



$$\text{Initial: } 0.126 \text{ M} \quad 0.0740 \text{ M} \quad \approx 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (0.126 - x) \text{ M} \quad (0.0740 + x) \text{ M} \quad x \text{ M}$$

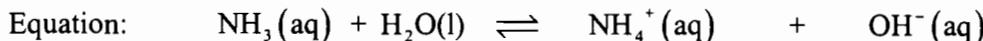
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x(0.0740 + x)}{0.126 - x} = 1.8 \times 10^{-5} \approx \frac{0.0740x}{0.126}$$

$$x = \frac{1.8 \times 10^{-5} \times 0.126}{0.0740} = 3.1 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]; \quad \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 3.1 \times 10^{-5} = 4.51$$

Note: assumption valid:  $x \ll 0.0740 < 0.126$ ;  $x$  is neglected when added or subtracted

- 5A** We know the initial concentration of  $\text{NH}_3$  in the buffer solution and can use the pH to find the equilibrium  $[\text{OH}^-]$ . The rest of the solution is organized around the balanced chemical equation. Our first goal is to determine the initial concentration of  $\text{NH}_4^+$ .

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00 \quad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.00} = 1.0 \times 10^{-5} \text{ M}$$



$$\text{Initial: } 0.35 \text{ M} \quad x \text{ M} \quad \approx 0 \text{ M}$$

$$\text{Changes: } -1.0 \times 10^{-5} \text{ M} \quad +1.0 \times 10^{-5} \text{ M} \quad +1.0 \times 10^{-5} \text{ M}$$

$$\text{Equil: } (0.35 - 1.0 \times 10^{-5}) \text{ M} \quad (x + 1.0 \times 10^{-5}) \text{ M} \quad 1.0 \times 10^{-5} \text{ M}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x + 1.0 \times 10^{-5})(1.0 \times 10^{-5})}{0.35 - 1.0 \times 10^{-5}} = \frac{1.0 \times 10^{-5} \times x}{0.35}$$

$$\text{Assume } x \gg 1.0 \times 10^{-5} \quad x = \frac{0.35 \times 1.8 \times 10^{-5}}{1.0 \times 10^{-5}} = 0.63 \text{ M} = \text{initial } \text{NH}_4^+ \text{ concentration}$$

$$\text{mass}(\text{NH}_4)_2\text{SO}_4 = 0.500 \text{ L} \times \frac{0.63 \text{ mol } \text{NH}_4^+}{1 \text{ L soln}} \times \frac{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4}{2 \text{ mol } \text{NH}_4^+} \times \frac{132.1 \text{ g } (\text{NH}_4)_2\text{SO}_4}{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4}$$

$$\text{Mass of } (\text{NH}_4)_2\text{SO}_4 = 21 \text{ g}$$

- 5B** The solution is composed of 33.05 g  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$  dissolved in 300.0 mL of 0.250 M HCl.  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$ , a strong electrolyte, exists in solution as  $\text{Na}^+$ (aq),  $\text{C}_2\text{H}_3\text{O}_2^-$ (aq) ions and  $\text{H}_2\text{O}$ . First calculate the moles of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$ , which based on the 1:1 stoichiometry will also be the number of moles of  $\text{C}_2\text{H}_3\text{O}_2^-$ . From this, we may calculate the initial  $[\text{C}_2\text{H}_3\text{O}_2^-]$ , assuming the solution's volume remains at 300. mL.

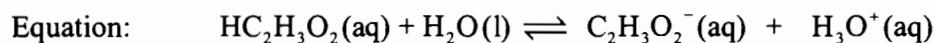
moles of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$  (and moles of  $\text{C}_2\text{H}_3\text{O}_2^-$ )

$$= \frac{33.05 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}}{1 \text{ mole } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}} = 0.243 \text{ moles } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O} = \text{moles } \text{C}_2\text{H}_3\text{O}_2^-$$

$$138.08 \text{ g } \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.243 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-}{0.300 \text{ L soln}} = 0.810 \text{ M} \quad (\text{Note: } [\text{HCl}] \text{ assume unchanged at } 0.250 \text{ M})$$

We organize this information around the balanced chemical equation, as before. We recognize that as much hydronium ion (a strong acid) as possible will react to produce the weak acid, acetic acid.



Initial:  $0 \text{ M}$   $0.810 \text{ M}$   $0.250 \text{ M}$

Form HAc:  $+0.250 \text{ M}$   $-0.250 \text{ M}$   $-0.250 \text{ M}$

 $0.250 \text{ M}$   $0.560 \text{ M}$   $\approx 0 \text{ M}$ 

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.250 - x) \text{ M}$   $(0.560 + x) \text{ M}$   $+x \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x(0.560 + x)}{0.250 - x} = 1.8 \times 10^{-5} \approx \frac{0.560x}{0.250}$$

$$x = \frac{1.8 \times 10^{-5} \times 0.250}{0.560} = 8.0 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 8.0 \times 10^{-6} = 5.09 \approx 5.1$$

- 6A (a)** For formic acid,  $\text{p}K_a = -\log(1.8 \times 10^{-4}) = 3.74$ . The Henderson-Hasselbalch equation provides the pH of the original buffer solution:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 3.74 + \log \frac{0.350}{0.550} = 3.54$$

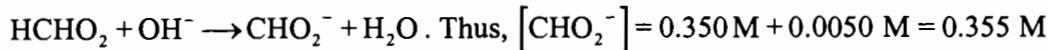
- (b)** The added acid completely reacts with formate ion and produces formic acid. Each mole/L of added acid consumes one 1 M of formate ion and forms 1 M of formic acid:  $\text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ .

Thus,  $[\text{CHO}_2^-] = 0.350 \text{ M} - 0.0050 \text{ M} = 0.345 \text{ M}$  and

$[\text{HCHO}_2] = 0.550 \text{ M} + 0.0050 \text{ M} = 0.555 \text{ M}$ . Use Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 3.74 + \log \frac{0.345}{0.555} = 3.53$$

- (c) Added base reacts completely with formic acid and produces formate ion. Each mole/L of added base consumes 1 M of formic acid and forms 1 M of formate ion:



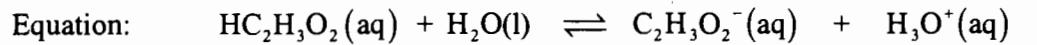
and  $[\text{HCHO}_2] = 0.550 \text{ M} - 0.0050 \text{ M} = 0.545 \text{ M}$ .

With the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 3.74 + \log \frac{0.355}{0.545} = 3.55$$

- 6B** The buffer cited has the same concentration of weak acid and its anion as does the buffer of Example 18-6. Our goal is  $\text{pH} = 5.03$  or  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.03} = 9.3 \times 10^{-6} \text{ M}$ .

Adding strong acid ( $\text{H}_3\text{O}^+$ ), of course, produces  $\text{HC}_2\text{H}_3\text{O}_2$  at the expense of  $\text{C}_2\text{H}_3\text{O}_2^-$ ; it drives the reaction to the left. Again, we use the data around the balanced chemical equation.



Initial:  $0.250 \text{ M}$   $0.560 \text{ M}$   $8.0 \times 10^{-6} \text{ M}$

Add acid:  $+y \text{ M}$   $+y \text{ M}$

Form HAc:  $+y \text{ M}$   $-y \text{ M}$   $-y \text{ M}$   
 $(0.250 + y) \text{ M}$   $(0.560 - y) \text{ M}$   $\approx 0 \text{ M}$

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.250 + y - x) \text{ M}$   $(0.560 - y + x) \text{ M}$   $9.3 \times 10^{-6} \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{9.3 \times 10^{-6}(0.560 - y + x)}{0.250 + y - x} = 1.8 \times 10^{-5} \approx \frac{9.3 \times 10^{-6}(0.560 - y)}{0.250 + y}$$

(Assume that  $x$  is negligible compared to  $y$ )

$$\frac{1.8 \times 10^{-5} \times (0.250 + y)}{9.3 \times 10^{-6}} = 0.484 + 1.94 y = 0.560 - y \quad y = \frac{0.560 - 0.484}{1.94 + 1.00} = 0.026 \text{ M}$$

Notice that our assumption is valid:  $x \ll 0.250 + y (= 0.276) < 0.560 - y (= 0.534)$ .

$$V_{\text{HNO}_3} = 300.0 \text{ mL buffer} \times \frac{0.026 \text{ mmol H}_3\text{O}^+}{1 \text{ mL buffer}} \times \frac{1 \text{ mL HNO}_3 \text{ (aq)}}{6.0 \text{ mmol H}_3\text{O}^+} = 1.3 \text{ mL of } 6.0 \text{ M HNO}_3$$

Instead of the algebraic solution, we use the Henderson-Hasselbalch equation, since the final pH falls within one pH unit of the  $\text{p}K_a$  of acetic acid. We let  $z$  indicate the increase in  $[\text{HC}_2\text{H}_3\text{O}_2]$ , and also the decrease in  $[\text{C}_2\text{H}_3\text{O}_2^-]$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \frac{0.560 - z}{0.250 + z} = 5.03 \quad \frac{0.560 - z}{0.250 + z} = 10^{5.03 - 4.74} = 1.95$$

$$0.560 - z = 1.95(0.250 + z) = 0.488 + 1.95 z \quad z = \frac{0.560 - 0.488}{1.95 + 1.00} = 0.024 \text{ M}$$

This is—and should be—almost exactly the value of  $y$  we obtained by the other method. The differences are due to imprecision: rounding errors.

- 7A (a)** The initial pH is the pH of 0.150 M HCl, which we obtain from  $[\text{H}_3\text{O}^+]$  of that strong acid solution.

$$[\text{H}_3\text{O}^+] = \frac{0.150 \text{ mol HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HCl}} = 0.150 \text{ M,}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.150) = 0.824$$

- (b)** To determine  $[\text{H}_3\text{O}^+]$  and then pH at the 50.0% point, we need the volume of the solution and the amount of  $\text{H}_3\text{O}^+$  unreacted. First we calculate the amount of hydronium ion present and then the volume of base solution needed for its complete neutralization.

$$\text{amount H}_3\text{O}^+ = 25.00 \text{ mL} \times \frac{0.150 \text{ mmol HCl}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HCl}} = 3.75 \text{ mmol H}_3\text{O}^+$$

$$V_{\text{acid}} = 3.75 \text{ mmol H}_3\text{O}^+ \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol H}_3\text{O}^+} \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol OH}^-} \times \frac{1 \text{ mL titrant}}{0.250 \text{ mmol NaOH}} \\ = 15.0 \text{ mL titrant}$$

At the 50.0% point, half (1.88 mmol  $\text{H}_3\text{O}^+$ ) will remain unreacted and only half (7.50 mL titrant) of the titrant solution will be added. From this information, and the original 25.00-mL volume of the solution, we calculate  $[\text{H}_3\text{O}^+]$  and then pH.

$$[\text{H}_3\text{O}^+] = \frac{1.88 \text{ mmol H}_3\text{O}^+ \text{ left}}{25.00 \text{ mL original} + 7.50 \text{ mL titrant}} = 0.0578 \text{ M}$$

$$\text{pH} = -\log (0.0578) = 1.238$$

- (c)** Since this is the titration of a strong acid by a strong base, at the neutralization point  $\text{pH} = 7.00$ . This is a solution of  $\text{NaCl}(\text{aq})$ , in which neither ion hydrolyzes.
- (d)** Beyond the equivalence point, the added titrant contains the only species that determine solution pH. The volume of the solution is  $25.00 \text{ mL} + 1.00 \text{ mL} = 26.00 \text{ mL}$ . The amount of hydroxide ion in the excess titrant is calculated and used to determine  $[\text{OH}^-]$ , from which pH is computed.

$$\text{amount of OH}^- = 1.00 \text{ mL} \times \frac{0.250 \text{ mmol NaOH}}{1 \text{ mL}} = 0.250 \text{ mmol OH}^-$$

$$[\text{OH}^-] = \frac{0.250 \text{ mmol OH}^-}{26.00 \text{ mL}} = 0.00962 \text{ M}$$

$$pOH = -\log(0.00962) = 2.017; pH = 14.00 - 2.017 = 11.983$$

- 7B (a)** The initial pH is simply the pH of 0.00812 M  $\text{Ba}(\text{OH})_2$ , which we obtain from  $[\text{OH}^-]$  for the solution.

$$[\text{OH}^-] = \frac{0.00812 \text{ mol Ba}(\text{OH})_2}{1 \text{ L soln}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(\text{OH})_2} = 0.01624 \text{ M}$$

$$pOH = -\log[\text{OH}^-] = -\log(0.0162) = 1.790; pH = 14.00 - pOH = 14.00 - 1.790 = 12.21$$

- (b)** To determine  $[\text{OH}^-]$  and then pH at the 50.0% point, we need the volume of the solution and the amount of  $\text{OH}^-$  unreacted. First we calculate the amount of hydroxide ion present and then the volume of acid solution needed for its complete neutralization.

$$\text{amount OH}^- = 50.00 \text{ mL} \times \frac{0.00812 \text{ mmol Ba}(\text{OH})_2}{1 \text{ mL soln}} \times \frac{2 \text{ mmol OH}^-}{1 \text{ mmol Ba}(\text{OH})_2} = 0.812 \text{ mmol OH}^-$$

$$V_{\text{acid}} = 0.812 \text{ mmol OH}^- \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol OH}^-} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol H}_3\text{O}^+} \times \frac{1 \text{ mL titrant}}{0.0250 \text{ mmol HCl}} \\ = 32.48 \text{ mL titrant}$$

At the 50.0 % point, half (0.406 mmol  $\text{OH}^-$ ) will remain unreacted and only half (16.24 mL titrant) of the titrant solution will be added. From this information, and the original 50.00-mL volume of the solution, we calculate  $[\text{OH}^-]$  and then pH.

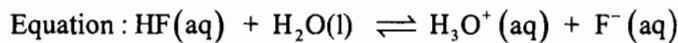
$$[\text{OH}^-] = \frac{0.406 \text{ mmol OH}^- \text{ left}}{50.00 \text{ mL original} + 16.24 \text{ mL titrant}} = 0.00613 \text{ M}$$

$$pOH = -\log(0.00613) = 2.213; pH = 14.00 - pOH = 11.79$$

- (c)** Since this is the titration of a strong base by a strong acid, at the neutralization point, pH = 7.00 . This is a solution of  $\text{BaCl}_2(\text{aq})$ , in which neither ion hydrolyzes.

- 8A (a)** Initial pH is just that of 0.150 M HF ( $pK_a = -\log(6.6 \times 10^{-4}) = 3.18$  ).

$$[\text{Initial solution contains } 20.00 \text{ mL} \times \frac{0.150 \text{ mmol HF}}{1 \text{ mL}} = 3.00 \text{ mmol HF}].$$



Initial: 0.150 M  $\approx 0 \text{ M}$  0 M

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.150 - x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x \cdot x}{0.150 - x} \approx \frac{x^2}{0.150} = 6.6 \times 10^{-4}$$

$$x = \sqrt{0.150 \times 6.6 \times 10^{-4}} = 9.9 \times 10^{-3} \text{ M}$$

$x > 0.05(0.150)$ . The assumption is invalid. After a 2<sup>nd</sup> cycle of approximation cycle,  $[\text{H}_3\text{O}^+] = 9.6 \times 10^{-3} \text{ M}$ ;  $\text{pH} = -\log(9.6 \times 10^{-3}) = 2.02$

- (b) When the titration is 25.0% complete, there are  $(0.25 \times 3.00 =) 0.75 \text{ mmol F}^-$  for every 3.00 mmol HF that were present initially.  $(3.00 - 0.75 =) 2.25 \text{ mmol HF}$  remain untitrated. We designate the solution volume (the volume holding these 3.00 mmol total) as  $V$  and use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.18 + \log \frac{0.75 \text{ mmol}/V}{2.25 \text{ mmol}/V} = 2.70$$

- (c) At the midpoint of the titration of a weak base,  $\text{pH} = \text{p}K_a = 3.18$
- (d) At the endpoint of the titration, the anion of the weak acid hydrolyzes. We calculate the amount of that anion and the volume of the solution in order to calculate its initial concentration.

$$\text{amount F}^- = 20.00 \text{ mL} \times \frac{0.150 \text{ mmol HF}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol F}^-}{1 \text{ mmol HF}} = 3.00 \text{ mmol F}^-$$

$$\text{volume titrant} = 3.00 \text{ mmol HF} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol HF}} \times \frac{1 \text{ mL titrant}}{0.250 \text{ mmol OH}^-} = 12.0 \text{ mL titrant}$$

$$[\text{F}^-] = \frac{3.00 \text{ mmol F}^-}{25.00 \text{ mL original volume} + 12.0 \text{ mL titrant}} = 0.0811 \text{ M}$$

We organize the solution of the hydrolysis problem around its balanced equation.

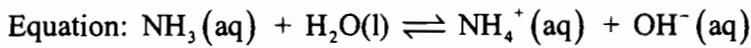
Equation :	$\text{F}^- (\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HF(aq)} + \text{OH}^-(\text{aq})$
Initial:	0.0811 M
Changes:	$-x \text{ M}$
Equil:	$(0.0811 - x) \text{ M}$

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-4}} = 1.5 \times 10^{-11} = \frac{x \cdot x}{0.0811 - x} \approx \frac{x^2}{0.0811}$$

$$x = \sqrt{0.0811 \times 1.5 \times 10^{-11}} = 1.1 \times 10^{-6} \text{ M} = [\text{OH}^-] \quad \text{The assumption is valid.}$$

$$\text{pOH} = -\log(1.1 \times 10^{-6}) = 5.96; \quad \text{pH} = 14.00 - \text{pOH} = 14.00 - 5.96 = 8.04$$

**8B (a)** The initial pH is simply that of 0.106 M  $\text{NH}_3$ .



Initial:	0.106 M	0 M	$\approx 0$ M
Changes:	$-x$ M	$+x$ M	$+x$ M
Equil:	$(0.106 - x)$ M	$x$ M	$x$ M

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x \cdot x}{0.106 - x} \approx \frac{x^2}{0.106} = 1.8 \times 10^{-5}$$

$$x = \sqrt{0.106 \times 1.8 \times 10^{-5}} = 1.4 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 1.4 \times 10^{-3} \text{ M} \quad \text{Assumption is valid.} \quad \text{pOH} = -\log(0.0014) = 2.85$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.85 = 11.15$$

**(b)** When the titration is 25.0% complete, there are 25.0 mmol  $\text{NH}_4^+$  for every 100.0 mmol of  $\text{NH}_3$  that were present initially (i.e. there are 1.33 mmol of  $\text{NH}_4^+$  in solution) 3.98 mmol  $\text{NH}_3$  remain untitrated. We designate the solution volume (the volume holding these 5.30 mmol total) as  $V$  and use a version of the Henderson-Hasselbalch equation.

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.74 + \log \frac{\frac{1.33 \text{ mmol}}{V}}{\frac{3.98 \text{ mmol}}{V}} = 4.26$$

$$\text{pH} = 14.00 - 4.26 = 9.74$$

**(c)** At the midpoint of the titration of a weak base,  
 $\text{pOH} = \text{p}K_b = 4.74$  and  $\text{pH} = 14.00 - 4.74 = 9.26$

**(d)** At the endpoint of the titration, the cation of the weak base hydrolyzes. We calculate the amount of that cation and the volume of the solution in order to calculate its initial concentration.

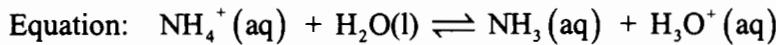
$$\text{amount } \text{NH}_4^+ = 50.00 \text{ mL} \times \frac{0.106 \text{ mmol NH}_3}{1 \text{ mL soln}} \times \frac{1 \text{ mmol NH}_4^+}{1 \text{ mmol NH}_3}$$

$$\text{amount } \text{NH}_4^+ = 5.30 \text{ mmol NH}_4^+$$

$$V_{\text{titrant}} = 5.30 \text{ mmol NH}_3 \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol NH}_3} \times \frac{1 \text{ mL titrant}}{0.225 \text{ mmol H}_3\text{O}^+} = 23.6 \text{ mL titrant}$$

$$[\text{NH}_4^+] = \frac{5.30 \text{ mmol NH}_4^+}{50.00 \text{ mL original volume} + 23.6 \text{ mL titrant}} = 0.0720 \text{ M}$$

We organize the solution of the hydrolysis problem around its balanced chemical equation.



Initial:  $0.0720 \text{ M}$   $0 \text{ M}$   $\approx 0 \text{ M}$

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

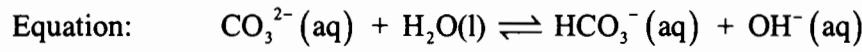
Equil:  $(0.0720 - x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x \cdot x}{0.0720 - x} \approx \frac{x^2}{0.0720}$$

$$x = \sqrt{0.0720 \times 5.6 \times 10^{-10}} = 6.3 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+] \quad \text{The assumption is valid.}$$

$$\text{pH} = -\log(6.3 \times 10^{-6}) = 5.20$$

**9A** The acidity of the solution is principally due to the hydrolysis of the carbonate ion, considered first.



Initial:  $1.0 \text{ M}$   $0 \text{ M}$   $\approx 0 \text{ M}$

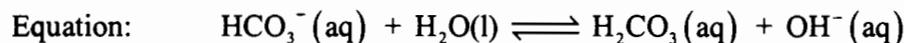
Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(1.0 - x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_b = \frac{K_w}{K_a(\text{HCO}_3^-)} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x \cdot x}{1.0 - x} \approx \frac{x^2}{1.0}$$

$$x = \sqrt{1.0 \times 2.1 \times 10^{-4}} = 1.5 \times 10^{-2} \text{ M} = 0.015 \text{ M} = [\text{OH}^-] \quad \text{The assumption is valid.}$$

Now we consider the hydrolysis of the bicarbonate ion.



Initial:  $0.015 \text{ M}$   $0 \text{ M}$   $0.015 \text{ M}$

Changes:  $-y \text{ M}$   $+y \text{ M}$   $+y \text{ M}$

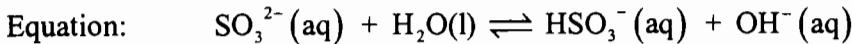
Equil:  $(0.015 - y) \text{ M}$   $y \text{ M}$   $(0.015 + y) \text{ M}$

$$K_b = \frac{K_w}{K_a(\text{H}_2\text{CO}_3)} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-7}} = 2.3 \times 10^{-8} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = \frac{y(0.015 + y)}{0.015 - x} \approx \frac{0.015y}{0.015} = y$$

The assumption is valid and  $y = [\text{H}_2\text{CO}_3] = 2.3 \times 10^{-8} \text{ M}$ . The second hydrolysis makes a negligible contribution to the acidity of the solution. For the entire solution, then

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.015) = 1.82 \quad \text{pH} = 14.00 - 1.82 = 12.18$$

**9B** The acidity of the solution is principally due to the hydrolysis of the sulfite ion.



Initial: 0.500 M 0 M  $\approx 0$  M

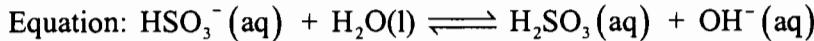
Changes:  $-x$  M  $+x$  M  $+x$  M

Equil:  $(0.500 - x)$  M  $x$  M  $x$  M

$$K_b = \frac{K_w}{K_a \text{HSO}_3^-} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} = \frac{[\text{HSO}_3^-][\text{OH}^-]}{[\text{SO}_3^{2-}]} = \frac{x \cdot x}{0.500 - x} \approx \frac{x^2}{0.500}$$

$$x = \sqrt{0.500 \times 1.6 \times 10^{-7}} = 2.8 \times 10^{-4} \text{ M} = 0.00028 \text{ M} = [\text{OH}^-] \quad \text{The assumption is valid.}$$

Next we consider the hydrolysis of the bisulfite ion.



Initial: 0.00028 M 0 M 0.00028 M

Changes:  $-y$  M  $+y$  M  $+y$  M

Equil:  $(0.00028 - y)$  M  $y$  M  $(0.00028 + y)$  M

$$K_b = \frac{K_w}{K_a \text{H}_2\text{SO}_3} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-2}} = 7.7 \times 10^{-13}$$

$$K_b = 7.7 \times 10^{-13} = \frac{[\text{H}_2\text{SO}_3][\text{OH}^-]}{[\text{HSO}_3^-]} = \frac{y(0.00028 + y)}{0.00028 - y} \approx \frac{0.00028y}{0.00028} = y$$

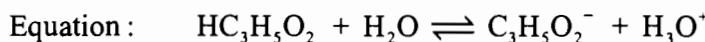
The assumption is valid and  $y = [\text{H}_2\text{CO}_3] = 7.7 \times 10^{-13} \text{ M}$ . The second hydrolysis makes a negligible contribution to the acidity of the solution. For the entire solution, then

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.00028) = 3.55 \quad \text{pH} = 14.00 - 3.55 = 10.45$$

## REVIEW QUESTIONS

- The abbreviation “mmol” stands for millimole, one thousandth of a mole. This amount of material often is a convenient one to use in calculations involving solutions where volumes are measured in mL.
  - HIn is the generic symbol for the formula of the acid form of an acid/base indicator.
  - The equivalence point of a titration is that point when sufficient added titrant is present to react with all of the substance being titrated, with no titrant left over.
  - A titration curve is a plot of the pH of solution versus the volume of added titrant (or sometimes versus the percentage of substance that has been titrated).

2. (a) The common-ion effect refers to the suppression of an ionization equilibrium caused by the presence (or addition) of one or more of the ions produced by the ionization.
- (b) A buffer solution maintains constant pH by consuming added strong acid or added strong base. The buffer solution contains components that react with each.
- (c) The value of  $pK_a$  can be determined from the titration curve of a monoprotic weak acid since the pH at the half equivalence point is equal to the  $pK_a$  of the weak acid.
- (d) pH is measured with a series of acid-base indicators that change color at different pH values. By determining the color of each indicator in a sample of the solution being tested, the pH of that solution can be placed within a narrow range.
3. (a) Buffer capacity is the amount of strong acid or base that can be added to a specified volume of a buffer before a significant change in pH occurs. Buffer range is the range of pH values within which a buffer solution will resist changes in pH.
- (b) Hydrolysis refers to the reaction of an ion with water to produce either  $\text{H}_3\text{O}^+(\text{aq})$  or  $\text{OH}^-(\text{aq})$ . Neutralization refers to the reaction of an acid with a base to produce a solution with a pH close to 7.0.
- (c) The first and second equivalence points of a weak diprotic acid are the points where, respectively, the first proton has been completely ionized, and the second proton has been completely ionized.
- (d) The equivalence point of a titration is the point where stoichiometric amounts of acid and base have been combined. The end point is when the indicator changes color. Careful selection of the indicator can ensure that these two points nearly coincide.
4. (a) Note that HI is a strong acid and the initial  $[\text{H}_3\text{O}^+] = [\text{HI}] = 0.0892\text{M}$



$$K_a = \frac{[\text{C}_3\text{H}_5\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]} = 1.3 \times 10^{-5} = \frac{x(0.0892 + x)}{0.275 - x} \approx \frac{0.0892x}{0.275} \quad x = 4.0 \times 10^{-5} \text{ M}$$

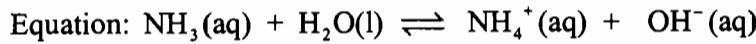
The assumption that  $x \ll 0.0892 \text{ M}$  is correct.  $[\text{H}_3\text{O}^+] = 0.0892\text{M}$

(b)  $[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.0892} = 1.1 \times 10^{-13} \text{ M}$

(c)  $[\text{C}_3\text{H}_5\text{O}_2^-] = x = 4.0 \times 10^{-5} \text{ M}$

(d)  $[\text{I}^-] = [\text{HI}]_{\text{int}} = 0.0892 \text{ M}$

5. (a) The  $\text{NH}_4\text{Cl}$  dissociates completely, and thus,  $[\text{NH}_4^+]_{\text{int}} = [\text{Cl}^-]_{\text{int}} = 0.102 \text{ M}$



Initial:  $0.164 \text{ M}$   $0.102 \text{ M}$   $\approx 0 \text{ M}$

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.164 - x)\text{M}$   $(0.102 + x)\text{M}$   $x \text{ M}$

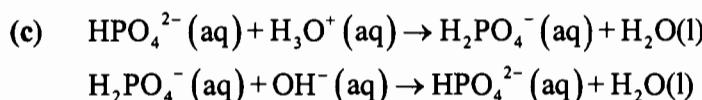
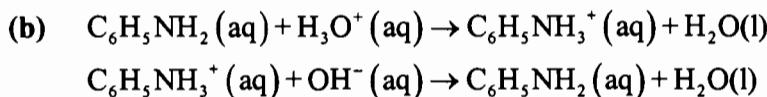
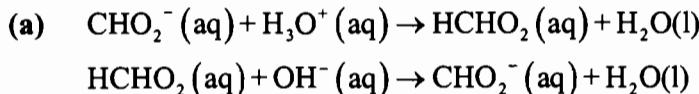
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.102 + x)x}{0.164 - x} = 1.8 \times 10^{-5} \approx \frac{0.102x}{0.164}; x = 2.9 \times 10^{-5} \text{ M}$$

Assumed  $x \ll 0.102 \text{ M}$ , a clearly valid assumption.  $[\text{OH}^-] = x = 2.9 \times 10^{-5} \text{ M}$

(b)  $[\text{NH}_4^+] = 0.102 + x = 0.102 \text{ M}$  (c)  $[\text{Cl}^-] = 0.102 \text{ M}$

(d)  $[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-5}} = 3.4 \times 10^{-10} \text{ M}$

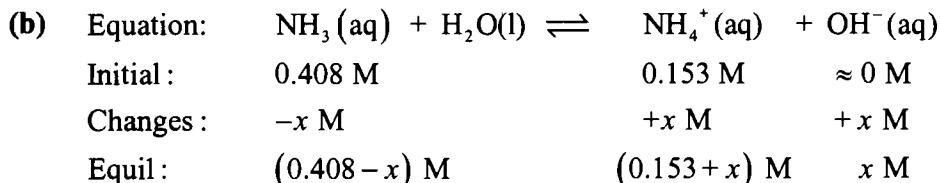
6. Adding  $\text{H}_3\text{O}^+(\text{aq})$  represents reaction with strong acid; adding  $\text{OH}^-(\text{aq})$  represents reaction with strong base.



7. (a) Equation:  $\text{HC}_7\text{H}_5\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_7\text{H}_5\text{O}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$   
Initial:  $0.012 \text{ M}$   $0.033 \text{ M}$   $\approx 0 \text{ M}$   
Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$   
Equil:  $(0.012 - x)\text{M}$   $(0.033 + x)\text{M}$   $x \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = 6.3 \times 10^{-5} = \frac{x(0.033 + x)}{0.012 - x} \approx \frac{0.033x}{0.012} \quad x = 2.3 \times 10^{-5} \text{ M}$$

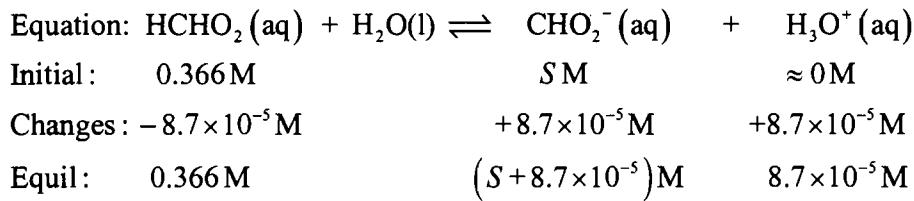
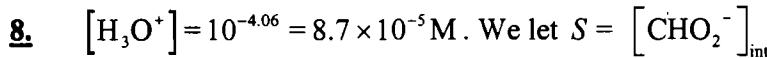
To determine the value of  $x$ , we assumed  $x \ll 0.012 \text{ M}$ , an assumption that clearly is correct.  $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-5} \text{ M}$   $\text{pH} = -\log(2.3 \times 10^{-5}) = 4.64$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{x(0.153 + x)}{0.408 - x} \approx \frac{0.153x}{0.408} \quad x = 4.8 \times 10^{-5} \text{ M}$$

To determine the value of  $x$ , we assumed  $x \ll 0.153$ , a clearly valid assumption.

$$[\text{OH}^-] = 4.8 \times 10^{-5} \text{ M}; \text{pOH} = -\log(4.8 \times 10^{-5}) = 4.32; \text{pH} = 14.00 - 4.32 = 9.68$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = 1.8 \times 10^{-4} = \frac{(S + 8.7 \times 10^{-5})(8.7 \times 10^{-5})}{0.366} \approx \frac{8.7 \times 10^{-5}S}{0.366}; S = 0.76 \text{ M}$$

To determine  $S$ , we assumed  $S \gg 8.7 \times 10^{-5}$  M, clearly a valid assumption. Or, we could have used the Henderson-Hasselbalch equation.  $\text{p}K_a = -\log(1.8 \times 10^{-4}) = 3.74$

$$4.06 = 3.74 + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]}; \quad \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 2.1; \quad [\text{CHO}_2^-] = 2.1 \times 0.366 = 0.77 \text{ M}$$

The difference in the two answers is due simply to rounding.



$$\text{p}K_a = 14.00 - \text{p}K_b = 14.00 - 4.74 = 9.26 \quad \text{pH} = 9.12 = 9.26 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{-0.14} = 0.72 \quad [\text{NH}_3] = 0.72 \times [\text{NH}_4^+] = 0.72 \times 0.732 \text{ M} = 0.53 \text{ M}$$

10. 0.60 mol  $\text{NaC}_2\text{H}_3\text{O}_2$  will raise the pH of 1.00 L of 0.50 M HCl to the greatest extent. Both  $\text{OH}^-$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  are bases that will react with the strong acid ( $\text{H}_3\text{O}^+$ ) in HCl(aq), resulting in an increase in the pH of the solution. Since there is more acetate ion available than hydroxide ion, 0.60 mol  $\text{NaC}_2\text{H}_3\text{O}_2$  will consume more  $\text{H}_3\text{O}^+$  than will 0.40 mol NaOH, causing a greater increase in the pH of the solution. In fact, 0.60 mol  $\text{NaC}_2\text{H}_3\text{O}_2$  will consume all of the  $\text{H}_3\text{O}^+$  in 1.00 L of 0.50 M HCl, leaving only a solution of acetic acid and sodium acetate, while 0.40 mol NaOH will leave a solution of HCl (with a concentration of 0.10 M) and NaCl. With regard to the other two possibilities, 0.70 mol NaCl will not affect the pH and 0.50 mol  $\text{HC}_2\text{H}_3\text{O}_2$  will lower the pH because  $\text{HC}_2\text{H}_3\text{O}_2$  is an acid.

11. We use the Henderson-Hasselbalch equation to determine  $K_a$  of lactic acid.

$$[\text{C}_3\text{H}_5\text{O}_3^-] = \frac{1.00 \text{ g NaC}_3\text{H}_5\text{O}_3}{100.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \times \frac{1 \text{ mol NaC}_3\text{H}_5\text{O}_3}{112.1 \text{ g NaC}_3\text{H}_5\text{O}_3} \times \frac{1 \text{ mol C}_3\text{H}_5\text{O}_3^-}{1 \text{ mol NaC}_3\text{H}_5\text{O}_3} = 0.0892 \text{ M}$$

$$\text{pH} = 4.11 = \text{p}K_a + \log \frac{[\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \text{p}K_a + \log \frac{0.0892 \text{ M}}{0.0500 \text{ M}} = \text{p}K_a + 0.251$$

$$\text{p}K_a = 4.11 - 0.251 = 3.86; \quad K_a = 10^{-3.86} = 1.4 \times 10^{-4}$$

12. (a) Use the Henderson-Hasselbalch equation to determine  $[\text{CHO}_2^-]$  in the buffer solution.

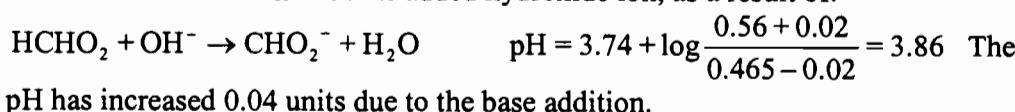
$$\text{pH} = \text{p}K_a + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]}; \quad 3.82 = 3.74 + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]}; \quad \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 3.82 - 3.74 = 0.08$$

$$\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 1.2; \quad [\text{CHO}_2^-] = 1.2[\text{HCHO}_2] = 1.2 \times 0.465 \text{ M} = 0.56 \text{ M}$$

$$\begin{aligned} \text{mass NaCHO}_2 &= 0.250 \text{ L} \times \frac{0.56 \text{ mol CHO}_2^-}{1 \text{ L soln}} \times \frac{1 \text{ mol NaCHO}_2}{1 \text{ mol CHO}_2^-} \times \frac{68.0 \text{ g NaCHO}_2}{1 \text{ mol NaCHO}_2} \\ &= 9.5 \text{ g NaCHO}_2 \quad [\text{Note that } \text{p}K_a = -\log K_a = -\log(1.8 \times 10^{-4}) = 3.74] \end{aligned}$$

$$(b) [\text{OH}^-]_{\text{int}} = \frac{0.20 \text{ g NaOH}}{0.250 \text{ L}} \times \frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.020 \text{ M OH}^-$$

Thus,  $[\text{HCHO}_2]$  will decrease by 0.020 M and  $[\text{CHO}_2^-]$  will increase by 0.020 M because of the reaction with the added hydroxide ion, as a result of:



- 13. (a)** The pH color change range is 1.00 pH unit on either side of  $pK_{\text{HIn}}$ . If the pH color change range is below pH = 7.00, the indicator changes color in acidic solution. If it is above pH = 7.00, the indicator changes color in alkaline solution. If pH = 7.00 falls within the pH color change range, the indicator changes color near the neutral point.

indicator	$K_{\text{HIn}}$	$pK_{\text{HIn}}$	pH color change range	changes color in?
bromophenol blue	$1.4 \times 10^{-4}$	3.85	2.9 (yellow) to 4.9 (blue)	acidic solution
bromocresol green	$2.1 \times 10^{-5}$	4.68	3.7 (yellow) to 5.7 (blue)	acidic solution
bromothymol blue	$7.9 \times 10^{-8}$	7.10	6.1 (yellow) to 8.1 (blue)	neutral solution
2,4-dinitrophenol	$1.3 \times 10^{-4}$	3.89	2.9 (colorless) to 4.9 (yellow)	acidic solution
chlorophenol red	$1.0 \times 10^{-6}$	6.00	5.0 (yellow) to 7.0 (red)	acidic solution
thymolphthalein	$1.0 \times 10^{-10}$	10.00	9.0 (colorless) to 11.0 (blue)	basic solution

- (b)** If bromcresol green is green, the pH is between 3.7 and 5.7, probably about pH = 4.7.

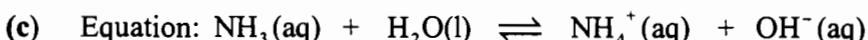
If chlorophenol red is orange, the pH is between 5.0 and 7.0, probably about pH = 6.0.

- 14.** We first determine the pH of each solution, and then use the answer in Exercise 13(a) to predict the color of the indicator. (The weakly acidic or basic character of the indicator does not affect the pH of the solution, since the very little indicator is added.)

**(a)**  $[\text{H}_3\text{O}^+] = 0.100 \text{ M HCl} \times \frac{1 \text{ mol H}_3\text{O}^+}{1 \text{ mol HCl}} = 0.100 \text{ M}; \text{ pH} = -\log(0.100 \text{ M}) = 1.000$

2,4-dinitrophenol assumes its acid color in a solution with pH = 1.000. The solution is colorless.

- (b)** Solutions of NaCl(aq) are pH neutral, with pH = 7.000. Chlorophenol red assumes its neutral color in such a solution; the solution is red/orange.



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00} \quad x = 4.2 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log(4.2 \times 10^{-3}) = 2.38 \quad \text{pH} = 14.00 - 2.38 = 11.62$$

Thymolphthalein assumes its basic color in a solution with pH = 11.62; the solution is blue.

- (d)** From Figure 17-6, seawater has pH = 7.00 to 8.50. Bromcresol green assumes its basic color in this solution; the solution is blue.

15. (a) The titration reaction is  $\text{KOH}(\text{aq}) + \text{HI}(\text{aq}) \rightarrow \text{KI}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$\text{vol. KOH soln} = 25.00 \text{ mL} \times \frac{0.212 \text{ mmol HI}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol KOH}}{1 \text{ mmol HI}} \times \frac{1 \text{ mL soln}}{0.146 \text{ mmol KOH}} \\ = 36.3 \text{ mL KOH soln}$$

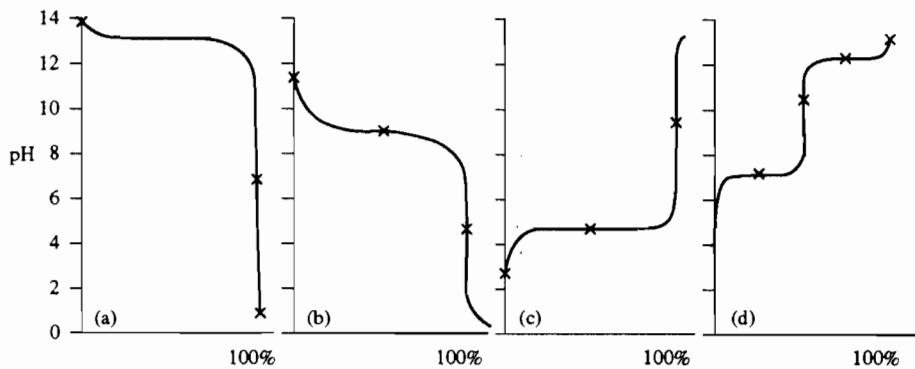
- (b) The titration reaction is  $2\text{KOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{K}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

$$\text{vol. KOH soln} = 20.00 \text{ mL} \times \frac{0.0942 \text{ mol H}_2\text{SO}_4}{1 \text{ L soln}} \times \frac{2 \text{ mol KOH}}{1 \text{ mol H}_2\text{SO}_4} \times \frac{1 \text{ mL soln}}{0.146 \text{ mmol KOH}} \\ = 25.8 \text{ mL KOH soln}$$

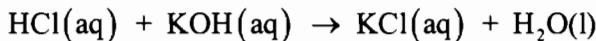
16. We can just sketch approximate titration curves of pH vs. percent of titration, since we do not have the concentration of the acid or the base, or the volume of solution being titrated. We can, however, precisely determine the pH at the half-equivalence point [mid-way between untitrated and completely titrated for a weak acid (or base)]; this is equal to the  $pK_a$  of the weak acid (or  $p\text{OH} = pK_b$  of the weak base). Further, if we assume all solutions are 1.00 M, we can determine the pH at each equivalence point. For a weak base, the pH at the equivalence point equals  $-\log \sqrt{0.50(K_a)}$ . For a weak acid, the pH at the equivalence point equals  $14.00 + \log \sqrt{0.50(K_b)}$  or  $14.00 + \log \sqrt{0.50(K_w / K_a)}$  [Indicator choices are given in square brackets.]

- (a) In this titration (assuming 1.00 M NaOH and 1.00 M  $\text{HNO}_3$ ), the initial pH = 14.00 and at the equivalence point pH = 7.00. The pH drops rapidly after the equivalence point, rapidly reaching pH = 1.00. [Bromothymol blue changes from blue at pH = 8 to yellow at pH = 6].
- (b) The initial pH is that of 1.00 M  $\text{NH}_3$ , pH = 11.6. The half-equivalence point is  $p\text{OH} = pK_b = 4.74$  and thus pH = 9.26. That of the equivalence point is  $-\log \sqrt{0.50(K_a)} = 4.78$ . The pH then drops rapidly with added strong acid to pH = 1.00. [Methyl red changes from yellow at pH = 6.2 to red at pH = 4.5]
- (c) The initial pH is that of 1.00 M  $\text{HC}_2\text{H}_3\text{O}_2$ , pH = 2.38. That of the half-equivalence point is  $pH = pK_a = 4.74$ . The pH at the equivalence point is  $pH = 14.00 + \log \sqrt{0.50(K_w / K_a)}$  or pH = 9.22. The pH then rises rapidly with the addition of strong base, rapidly reaching pH = 13.00. [Phenolphthalein changes from colorless at pH = 8 to red at pH = 10.]
- (d) The initial pH is that of a 1.00 M  $\text{H}_2\text{PO}_4^-$ , pH = 3.60. The first half-equivalence point is  $pH = pK_{a_2} = 7.20$ . The pH of the first equivalence point is about pH = 10.4. (the  $\text{OH}^-$  ions are formed via hydrolysis of  $\text{HPO}_4^{2-}$ ) That for the second half equivalence point would be  $pH = pK_{a_3} = 12.37$ , but this will be difficult to reach; the

solution is becoming pretty dilute. Finally, the pH for the second equivalence point is about  $\text{pH} = 12.9$  (here  $\text{OH}^-$  is formed via hydrolysis of  $\text{PO}_4^{3-}$ ) which again will be hard to reach without adding excessively concentrated base. [Alizarin yellow R changes from yellow at  $\text{pH} = 10$  to violet at  $\text{pH} = 12$ . These is no suitable indicator given in Figure 18-8 for the second equivalence point.] The curves are sketched below.



17. First we calculate the amount of HCl. The titration reaction is



$$\text{amount HCl} = 25.00 \text{ mL} \times \frac{0.160 \text{ mmol HCl}}{1 \text{ mL soln}} = 4.00 \text{ mmol HCl} = 4.00 \text{ mmol H}_3\text{O}^+ \text{ present}$$

Then, in each case, we calculate the amount of  $\text{OH}^-$  that has been added, determine which ion,  $\text{OH}^-(\text{aq})$  or  $\text{H}_3\text{O}^+(\text{aq})$ , is in excess, compute the concentration of that ion, and determine the pH.

(a) amount  $\text{OH}^- = 10.00 \text{ mL} \times \frac{0.242 \text{ mmol OH}^-}{1 \text{ mL soln}} = 2.42 \text{ mmol OH}^-$ ;  $\text{H}_3\text{O}^+$  is in excess.

$$[\text{H}_3\text{O}^+] = \frac{4.00 \text{ mmol H}_3\text{O}^+ - \left( 2.42 \text{ mmol OH}^- \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol OH}^-} \right)}{25.00 \text{ mL originally} + 10.00 \text{ mL titrant}} = 0.0451 \text{ M}$$

$$\text{pH} = -\log(0.0451) = 1.346$$

(b) amount  $\text{OH}^- = 15.00 \text{ mL} \times \frac{0.242 \text{ mmol OH}^-}{1 \text{ mL soln}} = 3.63 \text{ mmol OH}^-$ ;  $\text{H}_3\text{O}^+$  is in excess.

$$[\text{H}_3\text{O}^+] = \frac{4.00 \text{ mmol H}_3\text{O}^+ - \left( 3.63 \text{ mmol OH}^- \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol OH}^-} \right)}{25.00 \text{ mL originally} + 15.00 \text{ mL titrant}} = 0.00925 \text{ M}$$

$$\text{pH} = -\log(0.00925) = 2.034$$

18. The titration reaction is  $\text{KOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$\text{mmol of KOH} = 20.00 \text{ mL} \times \frac{0.275 \text{ mmol KOH}}{1 \text{ mL soln}} = 5.50 \text{ mmol KOH}$$

- (a) The total volume of the solution is  $V = 20.00 \text{ mL} + 15.00 \text{ mL} = 35.00 \text{ mL}$

$$\text{mmol HCl} = 15.00 \text{ mL} \times \frac{0.350 \text{ mmol HCl}}{1 \text{ mL soln}} = 5.25 \text{ mmol HCl}$$

$$\text{mmol excess OH}^- = (5.50 \text{ mmol KOH} - 5.25 \text{ mmol HCl}) \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 0.25 \text{ mmol OH}^-$$

$$[\text{OH}^-] = \frac{0.25 \text{ mmol OH}^-}{35.00 \text{ mL soln}} = 0.0071 \text{ M} \quad \text{pOH} = -\log(0.0071) = 2.15$$

$$\text{pH} = 14.00 - 2.15 = 11.85$$

- (b) The total volume of solution is  $V = 20.00 \text{ mL} + 20.00 \text{ mL} = 40.00 \text{ mL}$

$$\text{mmol HCl} = 20.00 \text{ mL} \times \frac{0.350 \text{ mmol HCl}}{1 \text{ mL soln}} = 7.00 \text{ mmol HCl}$$

$$\begin{aligned} \text{mmol excess H}_3\text{O}^+ &= (7.00 \text{ mmol HCl} - 5.50 \text{ mmol KOH}) \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HCl}} \\ &= 1.50 \text{ mmol H}_3\text{O}^+ \end{aligned}$$

$$[\text{H}_3\text{O}^+] = \frac{1.50 \text{ mmol H}_3\text{O}^+}{40.00 \text{ mL}} = 0.0375 \text{ M} \quad \text{pH} = -\log(0.0375) = 1.426$$

19. The titration reaction is  $\text{HNO}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$\text{amount HNO}_2 = 25.00 \text{ mL} \times \frac{0.132 \text{ mmol HNO}_2}{1 \text{ mL soln}} = 3.30 \text{ mmol HNO}_2$$

- (a) The volume of the solution is  $25.00 \text{ mL} + 10.00 \text{ mL} = 35.00 \text{ mL}$

$$\text{amount NaOH} = 10.00 \text{ mL} \times \frac{0.116 \text{ mmol NaOH}}{1 \text{ mL soln}} = 1.16 \text{ mmol NaOH}$$

1.16 mmol  $\text{NaNO}_2$  are formed in this reaction and there is an excess of  $(3.30 \text{ mmol HNO}_2 - 1.16 \text{ mmol NaOH}) = 2.14 \text{ mmol HNO}_2$ . We can use the Henderson-Hasselbalch equation to determine the pH of the solution.

$$\text{p}K_a = -\log(7.2 \times 10^{-4}) = 3.14$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = 3.14 + \log \frac{1.16 \text{ mmol NO}_2^- / 35.00 \text{ mL}}{2.14 \text{ mmol HNO}_2 / 35.00 \text{ mL}} = 2.87$$

- (b) The volume of the solution is  $25.00 \text{ mL} + 20.00 \text{ mL} = 45.00 \text{ mL}$

$$\text{amount NaOH} = 20.00 \text{ mL} \times \frac{0.116 \text{ mmol NaOH}}{1 \text{ mL soln}} = 2.32 \text{ mmol NaOH}$$

2.32 mmol  $\text{NaNO}_2^-$  are formed in this reaction and there is an excess of  $(3.30 \text{ mmol HNO}_2 - 2.32 \text{ mmol NaOH}) = 0.98 \text{ mmol HNO}_2$ .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = 3.14 + \log \frac{2.32 \text{ mmol NO}_2^- / 45.00 \text{ mL}}{0.98 \text{ mmol HNO}_2 / 45.00 \text{ mL}} = 3.51$$

- 20.** The calculation is very similar to that of Review Question 19. In this case, however, the titration reaction is  $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$\text{amount NH}_3 = 20.00 \text{ mL} \times \frac{0.318 \text{ mmol NH}_3}{1 \text{ mL soln}} = 6.36 \text{ mmol NH}_3$$

- (a) The volume of the solution is  $20.00 \text{ mL} + 10.00 \text{ mL} = 30.00 \text{ mL}$

$$\text{amount HCl} = 10.00 \text{ mL} \times \frac{0.475 \text{ mmol NaOH}}{1 \text{ mL soln}} = 4.75 \text{ mmol HCl}$$

4.75 mmol  $\text{NH}_4\text{Cl}$  is formed in this reaction and there is an excess of  $(6.36 \text{ mmol NH}_3 - 4.75 \text{ mmol HCl}) = 1.61 \text{ mmol NH}_3$ . We can use the Henderson-Hasselbalch equation to determine the pH of the solution.

$$\text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.74; \quad \text{p}K_a = 14.00 - \text{p}K_b = 14.00 - 4.74 = 9.26$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log \frac{1.61 \text{ mmol NH}_3 / 30.00 \text{ mL}}{4.75 \text{ mmol NH}_4^+ / 30.00 \text{ mL}} = 8.79$$

- (b) The volume of the solution is  $20.00 \text{ mL} + 15.00 \text{ mL} = 35.00 \text{ mL}$

$$\text{amount HCl} = 15.00 \text{ mL} \times \frac{0.475 \text{ mmol NaOH}}{1 \text{ mL soln}} = 7.13 \text{ mmol HCl}$$

6.36 mmol  $\text{NH}_4\text{Cl}$  is formed in this reaction and there is an excess of  $(7.13 \text{ mmol HCl} - 6.36 \text{ mmol NH}_3) = 0.77 \text{ mmol HCl}$ ; this excess HCl determines the pH of the solution.

$$[\text{H}_3\text{O}^+] = \frac{0.77 \text{ mmol HCl}}{35.00 \text{ mL soln}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HCl}} = 0.022 \text{ M} \quad \text{pH} = -\log(0.022) = 1.66$$

- 21. (a)** First we calculate the pH of a 0.01000 M  $\text{HC}_7\text{H}_5\text{O}_2$  solution with an ICE table.



Initial: 0.01000 M 0 M  $\approx 0 \text{ M}$

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.01000 - x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_a = \frac{[\text{C}_7\text{H}_5\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_7\text{H}_5\text{O}_2]} = 6.3 \times 10^{-5} = \frac{x^2}{0.0100 - x} \approx \frac{x^2}{0.0100}$$

$$x = 7.9 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+] \quad \text{pH} = -\log(7.9 \times 10^{-4}) = 3.10$$

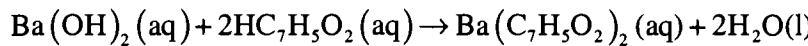
(Note:  $x$  is about 8% of the value of 0.0100, thus it is not much smaller than 0.0100)  
A more accurate calculation requires solution of the quadratic:

$$x^2 + 6.3 \times 10^{-5}x - 6.3 \times 10^{-7} = 0 \quad \text{where } x = 7.6 \times 10^{-4} \text{ M and pH} = 3.12$$

- (b)** amount of  $\text{HC}_7\text{H}_5\text{O}_2 = 25.0 \text{ mL} \times 0.01000 \text{ M} = 0.250 \text{ mmol HC}_7\text{H}_5\text{O}_2$

We determine the volume of 0.01000 M  $\text{Ba}(\text{OH})_2$  to reach the equivalence point.

The titration reaction is:



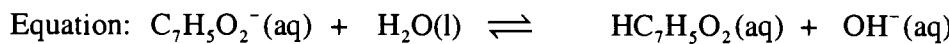
$$V_{\text{base}} = 0.250 \text{ mmol HC}_7\text{H}_5\text{O}_2 \times \frac{1 \text{ mmol Ba}(\text{OH})_2}{2 \text{ mmol HC}_7\text{H}_5\text{O}_2} \times \frac{1 \text{ mL soln}}{0.01000 \text{ mmol Ba}(\text{OH})_2}$$

$$V_{\text{base}} = 12.5 \text{ mL}$$

Thus, the addition of 6.25 mL of 0.01000 M  $\text{Ba}(\text{OH})_2$  brings us to the half-equivalence point, where  $\text{pH} = \text{p}K_a = 4.20$ .

- (c)** At the equivalence point, stoichiometric amounts of  $\text{HC}_7\text{H}_5\text{O}_2$  and  $\text{OH}^-$  are found in solution. There is complete conversion to  $\text{C}_7\text{H}_5\text{O}_2^-$ , hence, there is 0.250 mmol  $\text{C}_7\text{H}_5\text{O}_2^-$  in  $25.00 + 12.50 = 37.50 \text{ mL}$  solution. It is the hydrolysis of this anion that determines the pH of the solution at the equivalence point.

$$[\text{C}_7\text{H}_5\text{O}_2^-] = \frac{0.250 \text{ mmol C}_7\text{H}_5\text{O}_2^-}{37.50 \text{ mL soln}} = 6.67 \times 10^{-3} \text{ M}$$



Initial: 0.00667 M 0 M 0 M

Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(0.00667 - x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10} = \frac{x^2}{0.00667 - x} \approx \frac{x^2}{0.00667} \quad x = 1.03 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log(1.03 \times 10^{-6}) = 5.99 \quad \text{pH} = 14.00 - 5.99 = 8.01$$

- (d) The excess added base determines the pH of the solution.

$$\text{excess OH}^- = 2.50 \text{ mL} \times \frac{0.0100 \text{ mmol Ba(OH)}_2}{1 \text{ mL Ba(OH)}_2} \times \frac{2 \text{ mmol OH}^-}{1 \text{ mmol Ba(OH)}_2}$$

$$\text{excess OH}^- = 0.0500 \text{ mmol OH}^-$$

$$[\text{OH}^-] = \frac{0.0500 \text{ mmol OH}^-}{25.00 \text{ mL} + 15.00 \text{ mL}} = 1.25 \times 10^{-3} \text{ M}$$

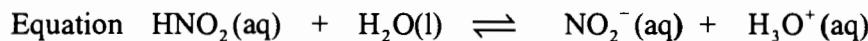
$$\text{pOH} = -\log(1.25 \times 10^{-3}) = 2.903 \quad \text{pH} = 14.000 - 2.903 = 11.097$$

22. The 0.10 M solutions of  $\text{NaHSO}_4$  is the most acidic. The  $\text{Na}^+$  cation does not contribute to the acidity of the solution; it does not hydrolyze. Of the anions involved,  $\text{S}^{2-}$  hydrolyzes to produce an alkaline solution. Each of the other anions ( $\text{HSO}_4^-$ ,  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ) can ionize further to yield  $\text{H}_3\text{O}^+$ , but  $\text{HSO}_4^-$  does so to a far greater extent than do the other two; it is quite strong for a weak acid. In fact,  $\text{HPO}_4^{2-}$  is expected to hydrolyze to form a basic solution.

## EXERCISES

### The Common Ion Effect

23. (a) We first determine the pH of 0.100 M  $\text{HNO}_2$ .



$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = 7.2 \times 10^{-4} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

Via successive approximations,  $x = 8.1 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$ .

$$\text{Then pH} = -\log(8.1 \times 10^{-3}) = 2.09$$

When 0.100 mol  $\text{NaNO}_2$  is added to 1.00 L of a 0.100 M  $\text{HNO}_2$ , a solution with  $[\text{NO}_2^-] = 0.100 \text{ M} = [\text{HNO}_2]$  is produced. The answer obtained with the Henderson-Hasselbalch equation, is  $\text{pH} = \text{p}K_a = -\log(7.2 \times 10^{-4}) = 3.14$ . Thus, the addition has caused a pH change of 1.05 units.

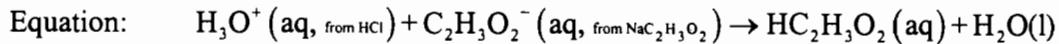
- (b)  $\text{NaNO}_3$  contributes nitrate ion,  $\text{NO}_3^-$ , to the solution. Since, however, there is no molecular  $\text{HNO}_3(\text{aq})$  in equilibrium with hydrogen and nitrate ions, there is no equilibrium to be shifted by the addition of nitrate ions. The  $[\text{H}_3\text{O}^+]$  and the pH are thus unaffected by the addition of  $\text{NaNO}_3$  to a solution of nitric acid. The pH changes are not the same because there is an equilibrium system to be shifted in the first solution, whereas there is no equilibrium, just total ionization, in the second solution.
25. (a) The strong acid  $\text{HCl}$  suppresses the ionization of the weak acid  $\text{HOCl}$  so much that a negligible concentration of  $\text{H}_3\text{O}^+$  is contributed to the solution by  $\text{HOCl}$ . Thus,  $[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.035\text{ M}$

- (b) This is a buffer solution. We can use the Henderson-Hasselbalch equation to determine its pH.  $\text{p}K_a = -\log(7.2 \times 10^{-4}) = 3.14$ ;

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = 3.14 + \log \frac{0.100\text{ M}}{0.0550\text{ M}} = 3.40$$

$$[\text{H}_3\text{O}^+] = 10^{-3.40} = 4.0 \times 10^{-4} \text{ M}$$

- (c) This also is a buffer solution, as we see by an analysis of the reaction between the components.



In soln:	0.0525 M	0.0768 M	0 M
Produce HAc:	-0.0525 M	-0.0525 M	+0.0525 M
Initial:	≈ 0 M	0.0243 M	0.0525 M

Now the Henderson-Hasselbalch equation can be used.

$$\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \frac{0.0243\text{ M}}{0.0525\text{ M}} = 4.41$$

$$[\text{H}_3\text{O}^+] = 10^{-4.41} = 3.9 \times 10^{-5} \text{ M}$$

## Buffer Solutions

- 27.** (a) 0.100 M NaCl is not a buffer solution. Neither a weak acid nor a weak base present.
- (b) 0.100 M NaCl—0.100 M  $\text{NH}_4\text{Cl}$  is not a buffer solution. Although a weak acid,  $\text{NH}_4^+$ , is present, its conjugate base is not.
- (c) 0.100 M  $\text{CH}_3\text{NH}_2$  and 0.150 M  $\text{CH}_3\text{NH}_3^+\text{Cl}^-$  is a buffer solution. Both a weak base,  $\text{CH}_3\text{NH}_2$ , and its conjugate acid,  $\text{CH}_3\text{NH}_3^+$ , are present in approximately equal concentrations.
- (d) 0.100 M HCl—0.050 M  $\text{NaNO}_2$  is not a buffer solution. All the  $\text{NO}_2^-$  is converted to  $\text{HNO}_2$ , and thus the solution is a mixture of a strong acid and a weak acid.
- (e) 0.100 M HCl—0.200 M  $\text{NaC}_2\text{H}_3\text{O}_2$  is a buffer solution. All of the HCl reacts with half of the  $\text{C}_2\text{H}_3\text{O}_2^-$  to form a solution with 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$ , a weak acid, and 0.100 M  $\text{C}_2\text{H}_3\text{O}_2^-$ , its conjugate base.
- (f) 0.100 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.125 M  $\text{NaC}_3\text{H}_5\text{O}_2$  is not a buffer in the strict sense because it does not contain a weak acid and its conjugate base, but rather the conjugate base of another weak acid. These two weak acids (acetic,  $K_a = 1.8 \times 10^{-5}$  and propionic,  $K_a = 1.35 \times 10^{-5}$ ) have approximately the same strength, however, this solution would resist changes in its pH on the addition of strong acid or strong base and thus, it could be argued that this system should also be called a buffer.

**29.** amount of solute =  $1.15 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-}{129.6 \text{ g}} \times \frac{1 \text{ mol C}_6\text{H}_5\text{NH}_3^+}{1 \text{ mol C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-}$   
 $= 8.87 \times 10^{-6} \text{ mol C}_6\text{H}_5\text{NH}_3^+$

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = \frac{8.87 \times 10^{-6} \text{ mol C}_6\text{H}_5\text{NH}_3^+}{3.18 \text{ L soln}} = 2.79 \times 10^{-6} \text{ M}$$

Equation:	$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
Initial:	$0.105 \text{ M}$
Changes:	$-x \text{ M}$
Equil:	$(0.105 - x) \text{ M}$

$$\begin{array}{rcl} & & 2.79 \times 10^{-6} \text{ M} \approx 0 \text{ M} \\ & & +x \text{ M} \quad +x \text{ M} \\ & & (2.79 \times 10^{-6} + x) \text{ M} \quad x \text{ M} \end{array}$$

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = 7.4 \times 10^{-10} = \frac{(2.79 \times 10^{-6} + x)x}{0.105 - x}$$

$$7.4 \times 10^{-10} (0.105 - x) = (2.79 \times 10^{-6} + x)x; \quad 7.8 \times 10^{-11} - 7.4 \times 10^{-10}x = 2.79 \times 10^{-6}x + x^2$$

$$x^2 + (2.79 \times 10^{-6} + 7.4 \times 10^{-10})x - 7.8 \times 10^{-11} = 0; \quad x^2 + 2.79 \times 10^{-6}x - 7.8 \times 10^{-11} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-2.79 \times 10^{-6} \pm \sqrt{7.78 \times 10^{-12} + 3.1 \times 10^{-10}}}{2} = 7.5 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log(7.5 \times 10^{-6}) = 5.12 \quad \text{pH} = 14.00 - 5.12 = 8.88$$

31. (a) First use the Henderson-Hasselbalch equation

$[\text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.74, \text{p}K_a = 14.00 - 4.74 = 9.26]$  to determine  $[\text{NH}_4^+]$  in the buffer solution.

$$\text{pH} = 9.45 = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \quad \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.45 - 9.26 = +0.19$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{0.19} = 1.55 \quad [\text{NH}_4^+] = \frac{[\text{NH}_3]}{1.55} = \frac{0.258 \text{ M}}{1.55} = 0.17 \text{ M}$$

We now assume that the volume of the solution does not change significantly when the solid is added.

$$\begin{aligned} \text{mass}(\text{NH}_4)_2\text{SO}_4 &= 425 \text{ mL} \times \frac{1 \text{ L soln}}{1000 \text{ mL}} \times \frac{0.17 \text{ mol NH}_4^+}{1 \text{ L soln}} \times \frac{1 \text{ mol}(\text{NH}_4)_2\text{SO}_4}{2 \text{ mol NH}_4^+} \\ &\times \frac{132.2 \text{ g}(\text{NH}_4)_2\text{SO}_4}{1 \text{ mol}(\text{NH}_4)_2\text{SO}_4} = 4.8 \text{ g}(\text{NH}_4)_2\text{SO}_4 \end{aligned}$$

- (b) Let's use the Henderson-Hasselbalch equation to determine the ratio of concentrations of cation and weak base in the altered solution.

$$\text{pH} = 9.30 = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \quad \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.30 - 9.26 = +0.04$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{0.04} = 1.1 = \frac{0.258}{0.17 \text{ M} + x \text{ M}} \quad 0.19 + 1.1x = 0.258 \quad x = 0.062 \text{ M}$$

The reason we decided to add  $x$  to the numerator follows. (Notice we cannot remove a component.) A pH of 9.30 is more acidic than a pH of 9.45 and therefore the conjugate acid's ( $\text{NH}_4^+$ ) concentration must increase. Additionally, mathematics tells us that for the concentration ratio to decrease from 1.55 to 1.1, its denominator must increase. We solve this expression for  $x$  to find a value of 0.062 M. We need to add  $\text{NH}_4^+$  to increase its concentration by 0.062 M in 100 mL of solution.

$$\begin{aligned}
 (\text{NH}_4)_2\text{SO}_4 \text{ mass} &= 0.100 \text{ L} \times \frac{0.062 \text{ mol NH}_4^+}{1 \text{ L}} \times \frac{1 \text{ mol} (\text{NH}_4)_2\text{SO}_4}{2 \text{ mol NH}_4^+} \times \frac{132.1 \text{ g} (\text{NH}_4)_2\text{SO}_4}{1 \text{ mol} (\text{NH}_4)_2\text{SO}_4} \\
 &= 0.41 \text{ g} (\text{NH}_4)_2\text{SO}_4 \quad \text{Hence, need to add} \approx 0.4 \text{ g}
 \end{aligned}$$

33. The added HCl will react with the ammonia, and the pH of the buffer solution will decrease. The original buffer solution has  $[\text{NH}_3] = 0.258 \text{ M}$  and  $[\text{NH}_4^+] = 0.17 \text{ M}$ . We first calculate the  $[\text{HCl}]$  in solution, reduced from 12 M because of dilution.  $[\text{HCl}]_{\text{added}} = 12 \text{ M} \times \frac{0.55 \text{ mL}}{100.6 \text{ mL}} = 0.066 \text{ M}$  We determine  $\text{p}K_a$  for ammonium ion:

$$\text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.74 \quad \text{p}K_a = 14.00 - 4.74 = 9.26$$

Equation:	$\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O(l)}$
Buffer:	0.258 M
Added:	+0.066 M
Changes:	-0.066 M
Final:	0.192 M
	0 M
	0.24 M

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log \frac{0.192}{0.24} = 9.16$$

35. The  $\text{p}K_a$ 's of the three acids help us choose the one to be used in the buffer. It is the acid with a  $\text{p}K_a$  within 1.00 pH unit of 3.50.  $\text{p}K_a = 3.74$  for  $\text{HCHO}_2$ ,  $\text{p}K_a = 4.74$  for  $\text{HC}_2\text{H}_3\text{O}_2$ , and  $\text{p}K_1 = 2.15$  for  $\text{H}_3\text{PO}_4$ . Thus, we choose  $\text{HCHO}_2$  and  $\text{NaCHO}_2$  to prepare a buffer with  $\text{pH} = 3.50$ . The Henderson-Hasselbalch equation is used to determine the relative amounts of each component present in the buffer solution.

$$\text{pH} = 3.50 = 3.74 + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} \quad \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 3.50 - 3.74 = -0.24$$

$$\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = 10^{-0.24} = 0.58$$

This ratio of concentrations is also the ratio of the number of moles of each component in the buffer solution, since both concentrations are a number of moles in a certain volume, and the volumes are the same (the two solutes are in the same solution). This ratio also is the ratio of the volumes of the two solutions, since both solutions being mixed contain the same concentration of solute. If we assume 100. mL of acid solution,  $V_{\text{acid}} = 100. \text{ mL}$ .

Then the volume of salt solution is  $V_{\text{salt}} = 0.58 \times 100. \text{ mL} = 58 \text{ mL}$  0.100 M  $\text{NaCHO}_2$

37. (a) The pH of the buffer is determined via the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = 4.89 + \log \frac{0.100\text{M}}{0.100\text{M}} = 4.89$$

The effective pH range is the same for every propionate buffer: from  $\text{pH} = 3.89$  to  $\text{pH} = 5.89$ , one pH unit on either side of  $\text{p}K_a$  for propionic acid.

- (b) To each liter of 0.100 M  $\text{HC}_3\text{H}_5\text{O}_2$  — 0.100M  $\text{NaC}_3\text{H}_5\text{O}_2$  we can add 0.100 mol  $\text{OH}^-$  before all of the  $\text{HC}_3\text{H}_5\text{O}_2$  is consumed, and we can add 0.100 mol  $\text{H}_3\text{O}^+$  before all of the  $\text{C}_3\text{H}_5\text{O}_2^-$  is consumed. The buffer capacity thus is 100. millimoles (0.100 mol) of acid or base per liter of buffer solution.

39. (a) pH of this buffer solution is determined with the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = -\log(1.8 \times 10^{-4}) + \log \frac{8.5 \text{ mmol}/75.0 \text{ mL}}{15.5 \text{ mmol}/75.0 \text{ mL}} \\ = 3.74 - 0.26 = 3.48$$

[Note: solution is not a good buffer, as  $[\text{CHO}_2^-] = 1.1 \times 10^{-1} \sim 600$  times  $K_a$ ]

- (b) Amount of added  $\text{OH}^- = 0.25 \text{ mmol Ba(OH)}_2 \times \frac{2 \text{ mmol OH}^-}{1 \text{ mmol Ba(OH)}_2} = 0.50 \text{ mmol OH}^-$

The  $\text{OH}^-$  added reacts with the formic acid and produces formate ion.

Equation:	$\text{HCHO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Buffer:	15.5 mmol $\approx 0\text{M}$ 8.5 mmol
Add base:	+0.50 mmol
React:	-0.50 mmol -0.50 mmol +0.50 mmol
Final:	15.0 mmol 0 mmol 9.0 mmol

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = -\log(1.8 \times 10^{-4}) + \log \frac{9.0 \text{ mmol}/75.0 \text{ mL}}{15.0 \text{ mmol}/75.0 \text{ mL}} \\ = 3.74 - 0.22 = 3.52$$

- (c) Amount of added  $\text{H}_3\text{O}^+ = 1.05 \text{ mL acid} \times \frac{12 \text{ mmol HCl}}{1 \text{ mL acid}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HCl}} = 13 \text{ mmol H}_3\text{O}^+$

The  $\text{H}_3\text{O}^+$  added reacts with the formate ion and produces formic acid.

Equation:	$\text{CHO}_2^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq}) \rightleftharpoons \text{HCHO}_2 (\text{aq}) + \text{H}_2\text{O}(\text{l})$
Buffer :	8.5 mmol $\approx$ 0 mmol 15.5 mmol
Add acid :	+ 13 mmol
React :	- 8.5 mmol - 8.5 mmol + 8.5 mmol
Final :	0 mmol 4.5 mmol 24.0 mmol

The buffer's capacity has been exceeded. The pH of the solution is determined by the strong acid present.

$$[\text{H}_3\text{O}^+] = \frac{4.5 \text{ mmol}}{75.0 \text{ mL} + 1.05 \text{ mL}} = 0.059 \text{ M}; \quad \text{pH} = -\log(0.059) = 1.23$$

- 41. (a)** We use the Henderson-Hasselbalch equation to determine the pH of the solution. The total solution volume is

$$36.00 \text{ mL} + 64.00 \text{ mL} = 100.00 \text{ mL}. \quad \text{p}K_a = 14.00 - \text{p}K_b = 14.00 + \log(1.8 \times 10^{-5}) = 9.26$$

$$[\text{NH}_3] = \frac{36.00 \text{ mL} \times 0.200 \text{ M NH}_3}{100.00 \text{ mL}} = \frac{7.20 \text{ mmol NH}_3}{100.0 \text{ mL}} = 0.0720 \text{ M}$$

$$[\text{NH}_4^+] = \frac{64.00 \text{ mL} \times 0.200 \text{ M NH}_4^+}{100.00 \text{ mL}} = \frac{12.8 \text{ mmol NH}_4^+}{100.0 \text{ mL}} = 0.128 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log \frac{0.0720}{0.128 \text{ M}} = 9.01$$

- (b)** The solution has  $[\text{OH}^-] = 10^{-4.99} = 1.0 \times 10^{-5} \text{ M}$

The Henderson-Hasselbalch equation depends on the assumption:

$$[\text{NH}_3] \gg 1.8 \times 10^{-5} \text{ M} \ll [\text{NH}_4^+]$$

If the solution is diluted to 1.00 L,  $[\text{NH}_3] = 7.20 \times 10^{-3} \text{ M}$ , and

$[\text{NH}_4^+] = 1.28 \times 10^{-2} \text{ M}$ . These concentrations are consistent with the assumption.

However, if the solution is diluted to 1000. L,  $[\text{NH}_3] = 7.2 \times 10^{-6} \text{ M}$ , and

$[\text{NH}_3] = 1.28 \times 10^{-5} \text{ M}$ , and these two concentrations are not consistent with the

assumption. Thus, in 1000. L of solution, the given quantities of  $\text{NH}_3$  and  $\text{NH}_4^+$  will not produce a solution with  $\text{pH} = 9.00$ . With sufficient dilution, the solution will become indistinguishable from pure water; its pH will equal 7.00.

- (c)** The 0.20 mL of added 1.00 M HCl does not significantly affect the volume of the solution, but it does add  $0.20 \text{ mL} \times 1.00 \text{ M HCl} = 0.20 \text{ mmol H}_3\text{O}^+$ . This added  $\text{H}_3\text{O}^+$

reacts with  $\text{NH}_3$ , decreasing its amount from 7.20 mmol  $\text{NH}_3$  to 7.00 mmol  $\text{NH}_3$ , and increasing the amount of  $\text{NH}_4^+$  from 12.8 mmol  $\text{NH}_4^+$  to 13.0 mmol  $\text{NH}_4^+$ , through the reaction:  $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$

$$\text{pH} = 9.26 + \log \frac{7.00 \text{ mmol } \text{NH}_3 / 100.20 \text{ mL}}{13.0 \text{ mmol } \text{NH}_4^+ / 100.20 \text{ mL}} = 8.99$$

- (d) We see in the calculation of part (c) that the total volume of the solution does not affect the pOH of the solution, at least as long as the Henderson-Hasselbalch equation is obeyed. We let  $x$  represent the number of millimoles of  $\text{H}_3\text{O}^+$  added, through 1.00 M HCl. This increases the amount of  $\text{NH}_4^+$  and decreases the amount of  $\text{NH}_3$ , through the reaction  $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$

$$\text{pH} = 8.90 = 9.26 + \log \frac{7.20 - x}{12.8 + x}; \quad \log \frac{7.20 - x}{12.8 + x} = 8.90 - 9.26 = -0.36$$

Inverting, we have:

$$\frac{12.8 + x}{7.20 - x} = 10^{-0.36} = 2.29; \quad 12.8 + x = 2.29(7.20 - x) = 16.5 - 2.29x$$

$$x = \frac{16.5 - 12.8}{1.00 + 2.29} = 1.1 \text{ mmol } \text{H}_3\text{O}^+$$

$$\text{vol 1.00 M HCl} = 1.1 \text{ mmol } \text{H}_3\text{O}^+ \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol } \text{H}_3\text{O}^+} \times \frac{1 \text{ mL soln}}{1.00 \text{ mmol HCl}} = 1.1 \text{ mL 1.00 M HCl}$$

## Acid-Base Indicators

- 43.** (a) In an acid-base titration, the pH of the solution changes sharply at a definite pH that is known prior to titration. (This pH change occurs during the addition of a very small volume of titrant.) Determining the pH of a solution, on the other hand, is more difficult because the pH of the solution is not known precisely in advance. Since each indicator only serves to fix the pH over a quite small region, often less than 2.0 pH units, several indicators—carefully chosen to span the entire range of 14 pH units—must be employed to narrow the pH to  $\pm 1$  pH unit or possibly lower.
- (b) An indicator is, after all, a weak acid. Its addition to a solution will affect the acidity of that solution. Thus, one adds only enough indicator to show a color change and not enough to affect solution acidity.
- 45.** (a) 0.10 M KOH is an alkaline solution and phenol red will display its basic color in such a solution; the solution will be red.
- (b) 0.10 M  $\text{HC}_2\text{H}_3\text{O}_2$  is an acidic solution, although that of a weak acid, and phenol red will display its acidic color in such a solution; the solution will be yellow.

- (c) 0.10 M  $\text{NH}_4\text{NO}_3$  is an acidic solution due to the hydrolysis of the ammonium ion. Phenol red will display its acidic color, that is, yellow, in this solution.
- (d) 0.10 M HBr is an acidic solution, the aqueous solution of a strong acid. Phenol red will display its acidic color in this solution; the solution will be yellow.
- (e) 0.10 M NaCN is an alkaline solution because of the hydrolysis of the cyanide ion. Phenol red will display its basic color, red, in this solution.
- (f) An equimolar acetic acid–potassium acetate buffer has  $\text{pH} = \text{p}K_a = 4.74$  for acetic acid. In this solution phenol red will display its acid color, yellow.

47. Moles of HCl =  $C \times V = 0.04050 \text{ M} \times 0.01000 \text{ L} = 4.050 \times 10^{-4} \text{ moles}$

Moles of  $\text{Ba}(\text{OH})_2$  at endpoint =  $C \times V = 0.01120 \text{ M} \times 0.01790 \text{ L} = 2.005 \times 10^{-4} \text{ moles}$ .

Moles of HCl that react with  $\text{Ba}(\text{OH})_2 = 2 \times \text{moles } \text{Ba}(\text{OH})_2$

Moles of HCl in excess  $4.050 \times 10^{-4} \text{ moles} - 4.010 \times 10^{-4} \text{ moles} = 4.04 \times 10^{-6} \text{ moles}$

Total volume at the equivalence point =  $(10.00 \text{ mL} + 17.90 \text{ mL}) = 27.90 \text{ mL}$

$$[\text{HCl}]_{\text{excess}} = \frac{4.04 \times 10^{-6} \text{ mole HCl}}{0.02790 \text{ L}} = 1.45 \times 10^{-4} \text{ M}; \text{ pH} = -\log(1.45 \times 10^{-4}) = 3.84$$

a) The approximate  $\text{pK}_{\text{HIn}} = 3.84$  (generally  $\pm 1$  pH unit)

b) This is a relatively good indicator (with  $\approx 1\%$  of the equivalence point volume), however,  $\text{pK}_{\text{HIn}}$  is not very close to the theoretical pH at the equivalence point (pH = 7.000). For very accurate work, a better indicator is needed (i.e. bromothymol blue ( $\text{pK}_{\text{HIn}} = 7.1$ )). Note: 2,4-dinitrophenol works relatively well here because the pH near the equivalence point of a strong acid/strong base titration rises very sharply ( $\approx 6$  pH units for an addition of only 2 drops (0.10 mL))

## Neutralization Reactions

49. The reaction (to 2<sup>nd</sup> equiv. pt.) is:  $\text{H}_3\text{PO}_4 \text{ (aq)} + 2 \text{KOH (aq)} \longrightarrow \text{K}_2\text{HPO}_4 \text{ (aq)} + 2 \text{H}_2\text{O(l)}$ .

The molarity of the  $\text{H}_3\text{PO}_4$  solution is determined in the following manner.

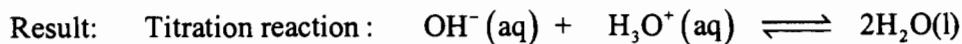
$$\text{H}_3\text{PO}_4 \text{ molarity} = \frac{31.15 \text{ mL KOH soln} \times \frac{0.2420 \text{ mmol KOH}}{1 \text{ mL KOH soln}} \times \frac{1 \text{ mmol H}_3\text{PO}_4}{2 \text{ mmol KOH}}}{25.00 \text{ mL H}_3\text{PO}_4 \text{ soln}} = 0.1508 \text{ M}$$

51. Determine amount of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  in each solution, and the amount of excess reagent.

A. amount  $\text{H}_3\text{O}^+ = 50.00 \text{ mL} \times \frac{0.0150 \text{ mmol H}_2\text{SO}_4}{1 \text{ mL soln}} \times \frac{2 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol H}_2\text{SO}_4} = 1.50 \text{ mmol H}_3\text{O}^+$

(assuming complete ionization of  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$  in the presence of  $\text{OH}^-$ )

B. amount  $\text{OH}^- = 50.00 \text{ mL} \times \frac{0.0385 \text{ mmol NaOH}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol NaOH}} = 1.93 \text{ mmol OH}^-$



Initial amounts : 1.93 mmol 1.50 mmol

After reaction : 0.43 mmol 0 mmol

$$[\text{OH}^-] = \frac{0.43 \text{ mmol OH}^-}{100.0 \text{ mL soln}} = 4.3 \times 10^{-3} \text{ M}$$

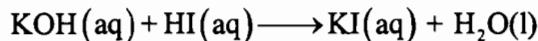
$$\text{pOH} = -\log(4.3 \times 10^{-3}) = 2.37 \quad \text{pH} = 14.00 - 2.37 = 11.63$$

## Titration Curves

53. In each case, the volume of acid and its molarity are the same. Thus, also the amount of acid is the same in each case. The volume of titrant needed to reach the equivalence point will also be the same in both cases, since the titrant has the same concentration in each case, and it is the same amount of base that reacts with a given amount (in moles) of acid. Realize that, as the titration of a weak acid proceeds, the weak acid will ionize, replenishing the  $\text{H}_3\text{O}^+$  in solution. This will occur until all of the weak acid has ionized and subsequently reacted with the strong base. At the equivalence point in the titration of a strong acid with a strong base is an aqueous solution of ions that do not hydrolyze. But the equivalence point solution of the titration of a weak acid with a strong base contains the anion of a weak acid, which will hydrolyze to produce a basic (alkaline) solution. (Don't forget, however, that the inert cation of a strong base is also present.)

55. (a) Initial  $[\text{OH}^-] = 0.100 \text{ M OH}^- \quad \text{pOH} = -\log(0.100) = 1.000 \quad \text{pH} = 13.00$

Since this is the titration of a strong base with a strong acid, KI is the solute present at the equivalence point and thus, the  $\text{pH} = 7.00$ . The titration reaction is:



$$V_{\text{HI}} = 25.0 \text{ mL KOH soln} \times \frac{0.100 \text{ mmol KOH soln}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol HI}}{1 \text{ mmol KOH}} \times \frac{1 \text{ mL HI soln}}{0.200 \text{ mmol HI}} \\ = 12.5 \text{ mL HI soln}$$

Initial amount of KOH present =  $25.0 \text{ mL KOH soln} \times 0.100 \text{ M} = 2.50 \text{ mmol KOH}$

At the 40% titration point:  $5.00 \text{ mL HI soln} \times 0.200 \text{ M HI} = 1.00 \text{ mmol HI}$

excess KOH =  $2.50 \text{ mmol KOH} - 1.00 \text{ mmol HI} = 1.50 \text{ mmol KOH}$

$$[\text{OH}^-] = \frac{1.50 \text{ mmol KOH}}{30.0 \text{ mL total}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 0.0500 \text{ M} \quad \text{pOH} = -\log(0.0500) = 1.30$$

$$\text{pH} = 14.00 - 1.30 = 12.70$$

At the 80% titration point:  $10.00 \text{ mL HI soln} \times 0.200 \text{ M HI} = 2.00 \text{ mmol HI}$   
 excess KOH =  $2.50 \text{ mmol KOH} - 2.00 \text{ mmol HI} = 0.50 \text{ mmol KOH}$

$$[\text{OH}^-] = \frac{0.50 \text{ mmol KOH}}{35.0 \text{ mL total}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 0.0143 \text{ M} \quad \text{pOH} = -\log(0.0143) = 1.84$$

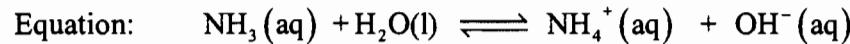
$$\text{pH} = 14.00 - 1.84 = 12.16$$

At the 110% titration point:  $13.75 \text{ mL HI soln} \times 0.200 \text{ M HI} = 2.75 \text{ mmol HI}$   
 excess HI =  $2.75 \text{ mmol HI} - 2.50 \text{ mmol HI} = 0.25 \text{ mmol HI}$

$$[\text{H}_3\text{O}^+] = \frac{0.25 \text{ mmol HI}}{38.8 \text{ mL total}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HI}} = 0.0064 \text{ M}; \quad \text{pH} = -\log(0.0064) = 2.19$$

Since the pH changes very rapidly at the equivalence point, from about pH = 10 to about pH = 4, most of the indicators in Figure 18-6 can be used. The main exceptions are alizarin yellow R, bromophenol blue, thymol blue (in its acid range), and methyl violet.

**(b) Initial pH:**



Initial:  $1.00 \text{ M}$   $0 \text{ M}$   $\approx 0 \text{ M}$

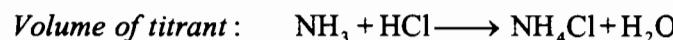
Changes:  $-x \text{ M}$   $+x \text{ M}$   $+x \text{ M}$

Equil:  $(1.00 - x) \text{ M}$   $x \text{ M}$   $x \text{ M}$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00}$$

$$x = 4.2 \times 10^{-3} \text{ M} = [\text{OH}^-], \quad \text{pOH} = -\log(4.2 \times 10^{-3}) = 2.38,$$

$$\text{pH} = 14.00 - 2.38 = 11.62 = \text{initial pH}$$

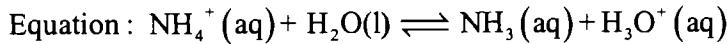


$$V_{\text{HCl}} = 10.0 \text{ mL} \times \frac{1.00 \text{ mmol NH}_3}{1 \text{ mL soln}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NH}_3} \times \frac{1 \text{ mL HCl soln}}{0.250 \text{ mmol HCl}} = 40.0 \text{ mL soln}$$

pH at equivalence point: The total solution volume at the equivalence point is  $10.0 + 40.0 = 50.0 \text{ mL}$

Also at the equivalence point, all of the  $\text{NH}_3$  has reacted to form  $\text{NH}_4^+$ . It is this  $\text{NH}_4^+$  that hydrolyzes to determine the pH of the solution.

$$[\text{NH}_4^+] = \frac{10.0 \text{ mL} \times \frac{1.00 \text{ mmol NH}_3}{1 \text{ mL soln}} \times \frac{1 \text{ mmol NH}_4^+}{1 \text{ mmol NH}_3}}{50.0 \text{ mL total solution}} = 0.200 \text{ M}$$



$$\text{Initial: } 0.200 \text{ M} \quad 0 \text{ M} \quad \approx 0 \text{ M}$$

$$\text{Changes: } -x \text{ M} \quad +x \text{ M} \quad +x \text{ M}$$

$$\text{Equil: } (0.200 - x) \text{ M} \quad x \text{ M} \quad x \text{ M}$$

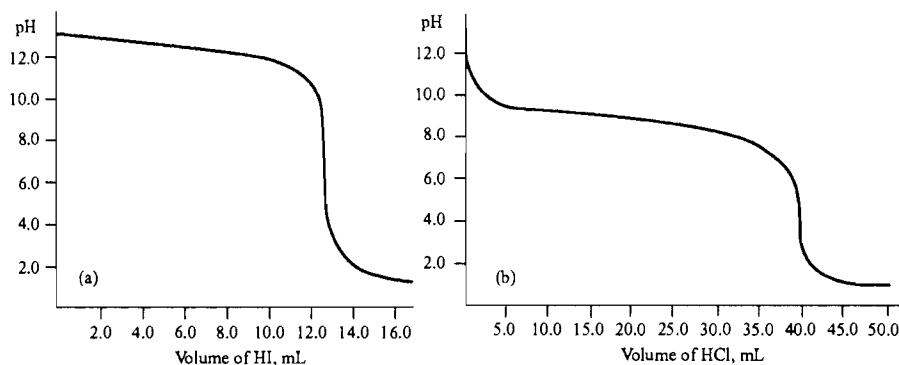
$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_3]} = \frac{x^2}{0.200 - x} \approx \frac{x^2}{0.200}$$

$$x = 1.1 \times 10^{-5} \text{ M}; \quad [\text{H}_3\text{O}^+] = 1.1 \times 10^{-5} \text{ M}; \quad \text{pH} = -\log(1.1 \times 10^{-5}) = 4.96$$

Of the indicators in Figure 18-6, one that has the pH of the equivalence point within its pH color change range is methyl red (yellow at pH = 6.2 and red at pH = 4.5); Bromcresol green would be another choice. At the 50 % titration point,

$$[\text{NH}_3] = [\text{NH}_4^+] \quad \text{pOH} = \text{pK}_b = 4.74 \quad \text{pH} = 14.00 - 4.74 = 9.26$$

The titration curves for parts (a) and (b) follow.



- 57.** A pH greater than 7.00 in the titration of a strong base with a strong acid means that the base is not completely titrated. A pH less than 7.00 means that excess acid has been added.

- (a) We can determine  $[\text{OH}^-]$  of the solution from the pH.  $[\text{OH}^-]$  is also the quotient of the amount of hydroxide ion in excess divided by the volume of the solution: 20.00 mL base  $+x$  mL added acid.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 12.55 = 1.45 \quad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-1.45} = 0.035 \text{ M}$$

$$[\text{OH}^-] = \frac{\left(20.00 \text{ mL base} \times \frac{0.175 \text{ mmol OH}^-}{1 \text{ mL base}}\right) - \left(x \text{ mL acid} \times \frac{0.200 \text{ mmol H}_3\text{O}^+}{1 \text{ mL acid}}\right)}{20.00 \text{ mL} + x \text{ mL}} = 0.035 \text{ M}$$

$$3.50 - 0.200x = 0.70 + 0.035x; \quad 3.50 - 0.70 = 0.035x + 0.200x; \quad 2.80 = 0.235x$$

$$x = \frac{2.80}{0.235} = 11.9 \text{ mL acid added.}$$

- (b) The set-up here is the same as for part (a).

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.80 = 3.20 \quad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-3.20} = 0.00063 \text{ M}$$

$$[\text{OH}^-] = \frac{\left(20.00 \text{ mL base} \times \frac{0.175 \text{ mmol OH}^-}{1 \text{ mL base}}\right) - \left(x \text{ mL acid} \times \frac{0.200 \text{ mmol H}_3\text{O}^+}{1 \text{ mL acid}}\right)}{20.00 \text{ mL} + x \text{ mL}}$$

$$[\text{OH}^-] = 0.00063 \frac{\text{mmol}}{\text{mL}} = 0.00063 \text{ M}$$

$$3.50 - 0.200x = 0.0126 + 0.00063x; \quad 3.50 - 0.0126 = 0.00063x + 0.200x; \quad 3.49 = 0.201x$$

$$x = \frac{3.49}{0.201} = 17.4 \text{ mL acid added. This is close to the equivalence point at 17.5 mL.}$$

- (c) Here the acid is in excess, so we reverse the set-up of part (a). We are just slightly beyond the equivalence point. This is close to the "mirror image" of part (b).

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.25} = 0.000056 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{\left(x \text{ mL acid} \times \frac{0.200 \text{ mmol H}_3\text{O}^+}{1 \text{ mL acid}}\right) - \left(20.00 \text{ mL base} \times \frac{0.175 \text{ mmol OH}^-}{1 \text{ mL base}}\right)}{20.00 \text{ mL} + x \text{ mL}}$$

$$= 5.6 \times 10^{-5} \text{ M}$$

$$0.200x - 3.50 = 0.0011 + 5.6 \times 10^{-5}x; \quad 3.50 + 0.0011 = -5.6 \times 10^{-5}x + 0.200x;$$

$$3.50 = 0.200x$$

$$x = \frac{3.50}{0.200} = 17.5, \text{ mL acid added. Just beyond the equivalence point at 17.5 mL.}$$

- 59.** For each of the titrations, the pH at the half-equivalence point equals the  $\text{p}K_a$  of the acid.

The initial pH is that of 0.1000 M weak acid:  $K_a = \frac{x^2}{0.1000} \quad x = \sqrt{0.1000 \times K_a} = [\text{H}_3\text{O}^+]$

The pH at the equivalence point is that of 0.05000 M anion of the weak acid, for which the

$[\text{OH}^-]$  is determined as follows.  $K_b = \frac{K_w}{K_a} = \frac{x^2}{0.05000} \quad x = \sqrt{\frac{K_w}{K_a} \times 0.05000} = [\text{OH}^-]$

And finally when 0.100 mL of base has been added beyond the equivalence point, the pH is determined by the excess added base, as follows (for all three titrations).

$$[\text{OH}^-] = \frac{0.100 \text{ mL} \times \frac{0.1000 \text{ mmol NaOH}}{1 \text{ mL NaOH soln}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol NaOH}}}{20.1 \text{ mL soln total}} = 4.98 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(4.98 \times 10^{-4}) = 3.303 \quad \text{pH} = 14.000 - 3.303 = 10.697$$

(a) Initial:  $[\text{H}_3\text{O}^+] = \sqrt{0.1000 \times 7.0 \times 10^{-3}} = 0.026 \text{ M} \quad \text{pH} = 1.59$

Equiv:  $[\text{OH}^-] = \sqrt{\frac{1.0 \times 10^{-14}}{7.0 \times 10^{-3}}} \times 0.05000 = 2.7 \times 10^{-7} \quad \text{pOH} = 6.57$   
 $\text{pH} = 14.00 - 6.57 = 7.43$

Indicator: bromothymol blue, yellow at pH = 6.2 and blue at pH = 7.8

(b) Initial:  $[\text{H}_3\text{O}^+] = \sqrt{0.1000 \times 3.0 \times 10^{-4}} = 0.0055 \text{ M} \quad \text{pH} = 2.26$

Equiv:  $[\text{OH}^-] = \sqrt{\frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}}} \times 0.05000 = 1.3 \times 10^{-6} \quad \text{pOH} = 5.89$   
 $\text{pH} = 14.00 - 5.89 = 8.11$

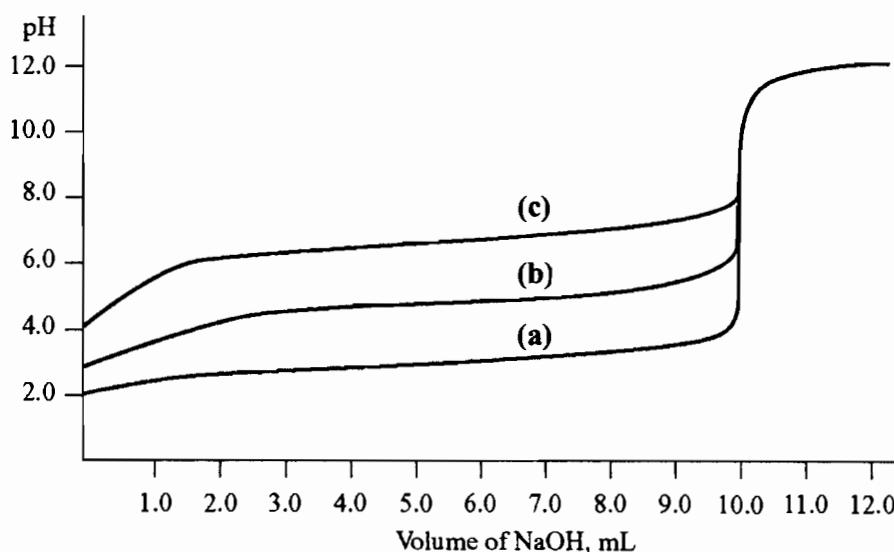
Indicator: thymol blue, yellow at pH = 8.0 and blue at pH = 9.6

(c) Initial:  $[\text{H}_3\text{O}^+] = \sqrt{0.1000 \times 2.0 \times 10^{-8}} = 0.000045 \text{ M} \quad \text{pH} = 4.35$

Equiv:  $[\text{OH}^-] = \sqrt{\frac{1.0 \times 10^{-14}}{2.0 \times 10^{-8}}} \times 0.0500 = 1.6 \times 10^{-4} \quad \text{pOH} = 3.80$   
 $\text{pH} = 14.00 - 3.80 = 10.20$

Indicator: alizarin yellow R, yellow at pH = 10.0 and violet at pH = 12.0

The three titration curves are drawn with respect to the same axes in the diagram below.



- 61.** 25.00 mL of 0.100 M NaOH titrated with 0.100 M HCl

(i) Initial pOH for 0.100 M NaOH:  $[\text{OH}^-] = 0.100 \text{ M}$ ,  $\text{pOH} = 1.000$  or  $\text{pH} = 13.000$

$$\text{(ii) After addition of 24 mL: } [\text{NaOH}] = 0.100 \text{ M} \times \frac{25.00 \text{ mL}}{49.00 \text{ mL}} = 0.0510 \text{ M}$$

$$[\text{HCl}] = 0.100 \text{ M} \times \frac{24.00 \text{ mL}}{49.00 \text{ mL}} = 0.0490 \text{ M}$$

NaOH is in excess by 0.0020 M =  $[\text{OH}^-]$   $\text{pOH} = 2.70$

(iii) At the equivalence point (25.00 mL), the pOH should be 7.000 and pH = 7.000

$$\text{(iv) After addition of 26 mL: } [\text{NaOH}] = 0.100 \text{ M} \times \frac{25.00 \text{ mL}}{51.00 \text{ mL}} = 0.0490 \text{ M}$$

$$[\text{HCl}] = 0.100 \text{ M} \times \frac{26.00 \text{ mL}}{51.00 \text{ mL}} = 0.0510 \text{ M}$$

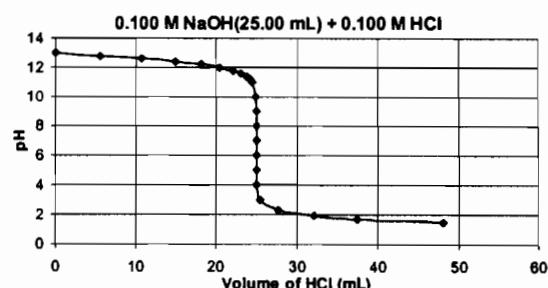
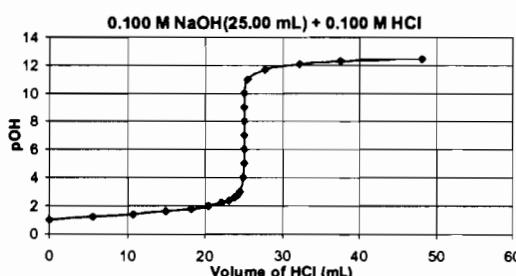
HCl is in excess by 0.0020 M =  $[\text{H}_3\text{O}^+]$   $\text{pH} = 2.70$  or  $\text{pOH} = 11.30$

$$\text{(v) After addition of 33.00 mL HCl (xs) } [\text{NaOH}] = 0.100 \text{ M} \times \frac{25.00 \text{ mL}}{58.00 \text{ mL}} = 0.0431 \text{ M}$$

$$[\text{HCl}] = 0.100 \text{ M} \times \frac{33.00 \text{ mL}}{58.00 \text{ mL}} = 0.0569 \text{ M} \quad [\text{HCl}]_{\text{excess}} = 0.0138 \text{ M}$$

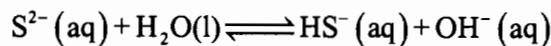
pH = 1.860 and pOH = 12.140

The graphs look to be mirror images of one another. In reality, one must reflect about a horizontal line centered at pH or pOH = 7 to obtain the other curve.

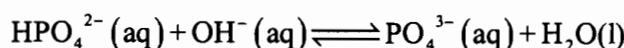


## pH of Salts of Polyprotic Acids

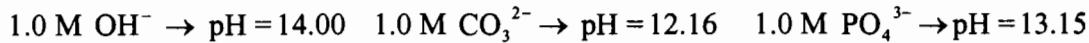
- 63.** We expect a solution of  $\text{Na}_2\text{S}$  to be alkaline, or basic. This alkalinity is created by the hydrolysis of the sulfide ion, the anion of a very weak acid ( $K_2 = 1 \times 10^{-19}$  for  $\text{H}_2\text{S}$ ).



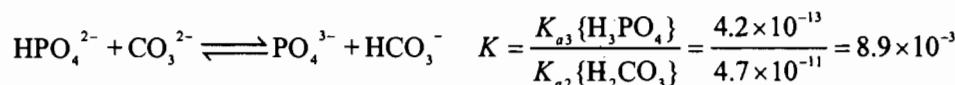
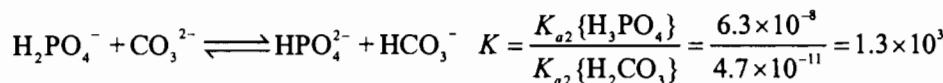
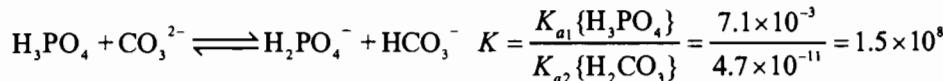
- 65. (a)**  $\text{H}_3\text{PO}_4(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{HCO}_3^-(\text{aq})$



- (b) The pH values of 1.00 M solutions of the three ions are;



Thus, we see that  $\text{CO}_3^{2-}$  is not a strong enough base to remove the third proton from  $\text{H}_3\text{PO}_4$ . As an alternative method of solving this problem, we can compute the equilibrium constant the reactions of carbonate ion with  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ .



Since the equilibrium constant for the third reaction is much smaller than 1.00, we conclude that it proceeds to the right to only a negligible extent and thus is not a practical method of producing  $\text{PO}_4^{3-}$ . The other two reactions have large equilibrium constants, and products are expected to strongly predominate. They have the advantage of involving an inexpensive base and, even if they do not go to completion, they will be drawn to completion by reaction with  $\text{OH}^-$  in the last step of the process.

67.  $\text{H}_2\text{C}_3\text{H}_2\text{O}_4 \text{ MM} = 104.06 \frac{\text{g}}{\text{mol}}$  Moles of  $\text{H}_2\text{C}_3\text{H}_2\text{O}_4 = 19.5 \text{ g} \times \frac{1 \text{ mol}}{104.06 \text{ g}} = 0.187 \text{ mol}$

$$\text{Concentration of } \text{H}_2\text{C}_3\text{H}_2\text{O}_4 = \frac{\text{moles}}{V} = \frac{0.187 \text{ moles}}{0.250 \text{ L}} = 0.748 \text{ M}$$

The second proton that can dissociate has a negligible effect on pH ( $K_{a_2}$  very small)

$\text{H}_2\text{A}(\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{HA}^-(\text{aq})$	$+$	$\text{H}_3\text{O}^+(\text{aq})$
initial	0.748 M			0 M		$\sim 0 \text{ M}$
change	$-x$			$+x$		$+x$
equil	$0.748-x$			$x$		$x$

$$\text{pH} = 1.47, \text{ therefore, } [\text{H}_3\text{O}^+] = 0.034 \text{ M} = x, \quad K_{a_1} = \frac{(0.034)^2}{0.748 - 0.034} = 1.6 \times 10^{-3}$$

( $1.5 \times 10^{-3}$  in tables, difference owing to ionization of the second proton)

$\text{HA}^-(\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{A}^{2-}(\text{aq})$	$+$	$\text{H}_3\text{O}^+(\text{aq})$
initial	0.300 M			0 M		$\sim 0 \text{ M}$
change	$-x$			$+x$		$+x$
equil	$0.300-x$			$x$		$x$

$$\text{pH} = 4.26, \text{ therefore, } [\text{H}_3\text{O}^+] = 5.5 \times 10^{-5} \text{ M} = x, \quad K_{\text{a}_2} = \frac{(5.5 \times 10^{-5})^2}{0.300 - 5.5 \times 10^{-5}} = 1.0 \times 10^{-8}$$

## General Acid-Base Equilibria

**69. (a)**  $\text{Ba}(\text{OH})_2$  is a strong base.  $\text{pOH} = 14.00 - 11.88 = 2.12 \quad [\text{OH}^-] = 10^{-2.12} = 0.0076 \text{ M}$

$$[\text{Ba}(\text{OH})_2] = \frac{0.0076 \text{ mol OH}^-}{1 \text{ L}} \times \frac{1 \text{ mol Ba}(\text{OH})_2}{2 \text{ mol OH}^-} = 0.0038 \text{ M}$$

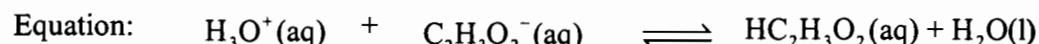
$$\begin{aligned} \text{(b)} \quad \text{pH} = 4.52 &= \text{p}K_{\text{a}} + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \frac{0.294 \text{ M}}{[\text{HC}_2\text{H}_3\text{O}_2]} \\ \log \frac{0.294 \text{ M}}{[\text{HC}_2\text{H}_3\text{O}_2]} &= 4.52 - 4.74 \quad \frac{0.294 \text{ M}}{[\text{HC}_2\text{H}_3\text{O}_2]} = 10^{-0.22} = 0.60 \\ [\text{HC}_2\text{H}_3\text{O}_2] &= \frac{0.294 \text{ M}}{0.60} = 0.49 \text{ M} \end{aligned}$$

**71. (a)**  $\text{pOH} = 14.00 - 6.07 = 7.93 \quad [\text{OH}^-] = 10^{-7.93} = 1.2 \times 10^{-8} \text{ M}$

$$Q_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.10 \text{ M})(1.2 \times 10^{-8} \text{ M})}{0.10} = 1.2 \times 10^{-8}$$

Since the value of  $Q_b$  does not equal the tabulated value of  $K_b = 1.8 \times 10^{-5}$ , the solution described cannot exist. (The assumption here is that equilibrium has been established)

**(b)** These solutes can be added to the same solution, but the final solution will have an appreciable  $[\text{HC}_2\text{H}_3\text{O}_2]$  because of the reaction of  $\text{H}_3\text{O}^+(\text{aq})$  with  $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$



Initial  $0.058 \text{ M}$   $0.10 \text{ M}$   $0 \text{ M}$

Changes:  $-0.058 \text{ M}$   $-0.058 \text{ M}$   $+0.058 \text{ M}$

Equil:  $0.000 \text{ M}$   $0.04 \text{ M}$   $0.058 \text{ M}$

Of course, some  $\text{H}_3\text{O}^+$  will exist in the final solution, but not equivalent to  $0.058 \text{ M HI}$ .

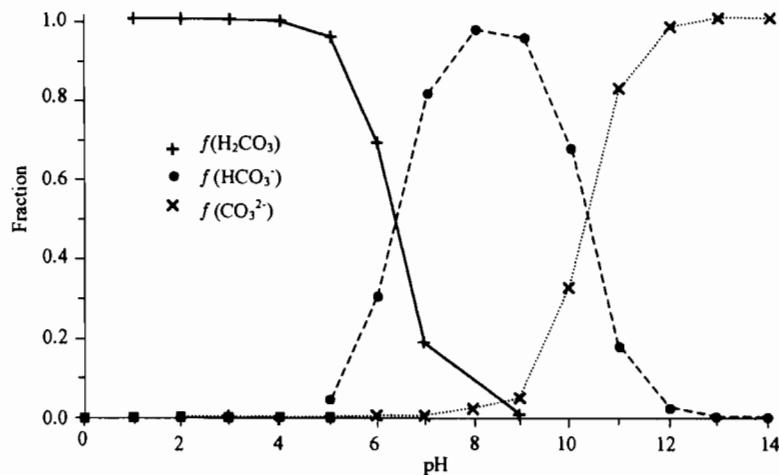
**(c)** Both  $0.10 \text{ M KNO}_2$  and  $0.25 \text{ M KNO}_3$  can exist together. Some hydrolysis of the  $\text{NO}_2^-(\text{aq})$  ion will occur, forming  $\text{HNO}_2(\text{aq})$ .

**(d)**  $\text{Ba}(\text{OH})_2$  is a strong base and will react as much as possible with the weak conjugate acid  $\text{NH}_4^+$ , to form  $\text{NH}_3(\text{aq})$ . We will end up with a solution of  $\text{BaCl}_2(\text{aq})$ ,  $\text{NH}_3(\text{aq})$ , and unreacted  $\text{NH}_4\text{Cl}(\text{aq})$ .

- (e) This will be a benzoic acid-benzoate ion buffer solution. Since the two components have the same concentration, the buffer solution will have  $\text{pH} = \text{p}K_a = -\log(6.3 \times 10^{-5}) = 4.20$ . This solution can indeed exist.
- (f) The first three components contain no ions that will hydrolyze. But  $\text{C}_2\text{H}_3\text{O}_2^-$  is the anion of a weak acid and will hydrolyze to form a slightly basic solution. Since  $\text{pH} = 6.4$  is an acidic solution, the solution described cannot exist.

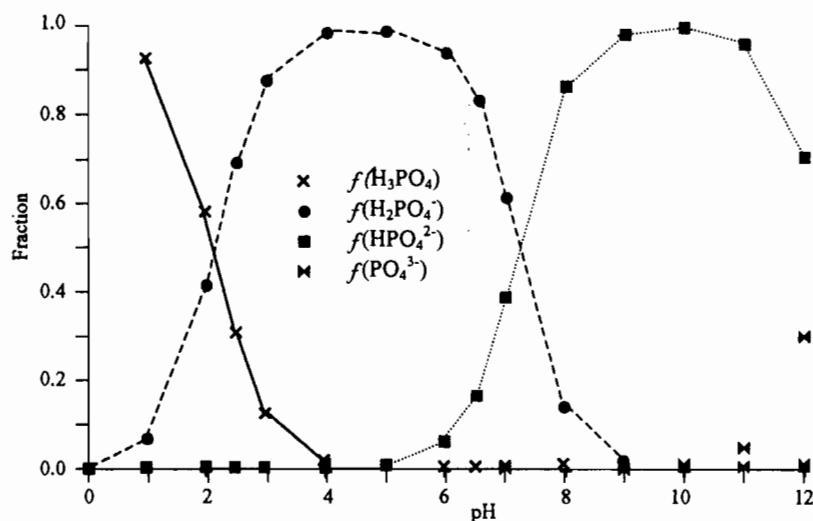
## FEATURE PROBLEMS

- 98.** (a) The two curves cross the point at which half of the total acetate is present as acetic acid and half is present as acetate ion. This is the half equivalence point in a titration, where  $\text{pH} = \text{p}K_a = 4.74$ .
- (b) For carbonic acid, there are three carbonate containing species: " $\text{H}_2\text{CO}_3$ " which predominates at low pH,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  which predominates in alkaline solution. The points of intersection should occur at the half-equivalence points in each step-wise titration: at  $\text{pH} = \text{p}K_{a_1} = -\log(4.4 \times 10^{-7}) = 6.36$  and at  $\text{pH} = \text{p}K_{a_2} = -\log(4.7 \times 10^{-11}) = 10.33$ . The following graph was computer-calculated (and then drawn) from these equations.  $f$  in each instance represents the fraction of the species whose formula is in parentheses.

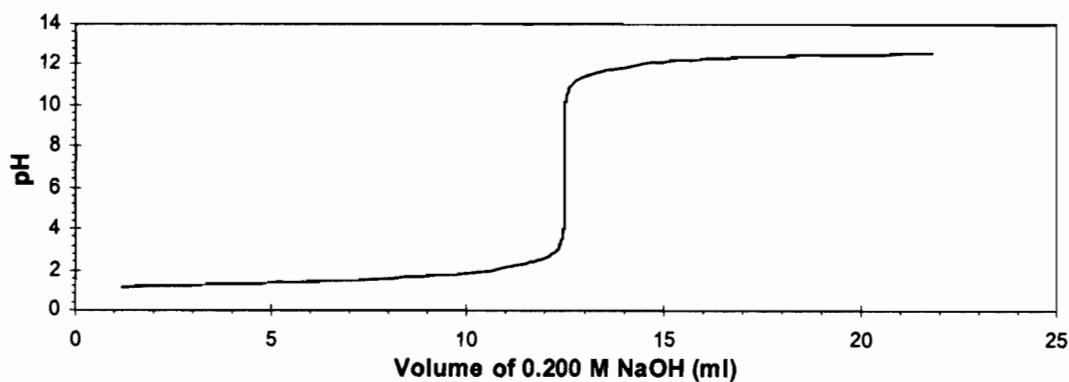


$$\frac{1}{f(\text{H}_2\text{A})} = 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}; \quad \frac{1}{f(\text{HA}^-)} = \frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]}; \quad \frac{1}{f(\text{A}^{2-})} = \frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1$$

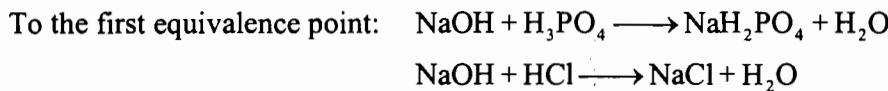
- (c) For phosphoric acid, there are four phosphate containing species:  $\text{H}_3\text{PO}_4$  under acidic conditions,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  which predominates in alkaline solution. The points of intersection should occur at  $\text{pH} = \text{p}K_{a_1} = -\log(7.1 \times 10^{-3}) = 2.15$ ,  $\text{pH} = \text{p}K_{a_2} = -\log(6.3 \times 10^{-8}) = 7.20$ , and  $\text{pH} = \text{p}K_{a_3} = -\log(4.2 \times 10^{-13}) = 12.38$ , a quite alkaline solution. The graph that follows was computer-calculated and drawn.



99. (a) This is exactly the same titration curve we would obtain for the titration of 25.00 mL of 0.200 M HCl with 0.200 M NaOH, because the acid species being titrated is  $\text{H}_3\text{O}^+$ . Both acids are strong acids and have ionized completely before titration begins. The initial pH is that of 0.200 M  $\text{H}_3\text{O}^+ = [\text{HCl}] + [\text{HNO}_3]$ ;  $\text{pH} = -\log(0.200) = 0.70$ . At the equivalence point,  $\text{pH} = 7.000$ . We treat this problem in the same way we would for the titration of a single strong acid with a strong base.



- (b) In Figure 18-9, we note that the equivalence point of the titration of a strong acid occurs at  $\text{pH} = 7.00$ , but that the strong acid is essentially completely neutralized at  $\text{pH} = 4$ . In Figure 18-13, we see that the first equivalence point of  $\text{H}_3\text{PO}_4$  occurs at about  $\text{pH} = 4.6$ . Thus, the first equivalence point represents the complete neutralization of  $\text{HCl}$  and the neutralization of  $\text{H}_3\text{PO}_4$  to  $\text{H}_2\text{PO}_4^-$ . Then, the second equivalence point represents the neutralization of  $\text{H}_2\text{PO}_4^-$  to  $\text{HPO}_4^{2-}$ . To reach the first equivalence point requires about 20.0 mL of 0.216 M  $\text{NaOH}$ , while to reach the second one requires a total of 30.0 mL of 0.216 M  $\text{NaOH}$ , or an additional 10.0 mL of base beyond the first equivalence point. The equations for the two titration reactions are as follows.



There is a third equivalence point, not shown in the figure, that would require an additional 10.0 mL of base to reach. Its titration reaction is represented by the following equation.



We determine the molar concentration of  $\text{H}_3\text{PO}_4$  and then of  $\text{HCl}$ . Notice that only 10.0 mL of the  $\text{NaOH}$  needed to reach the first equivalence point reacts with the  $\text{HCl}(\text{aq})$ ; the rest reacts with  $\text{H}_3\text{PO}_4$ .

$$\frac{(30.0 - 20.0) \text{ mL NaOH(aq)} \times \frac{0.216 \text{ mmol NaOH}}{1 \text{ mL NaOH soln}} \times \frac{1 \text{ mmol H}_3\text{PO}_4}{1 \text{ mmol NaOH}}}{10.00 \text{ mL acid soln}} = 0.216 \text{ M H}_3\text{PO}_4$$

$$\frac{(20.0 - 10.0) \text{ mL NaOH(aq)} \times \frac{0.216 \text{ mmol NaOH}}{1 \text{ mL NaOH soln}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{10.00 \text{ mL acid soln}} = 0.216 \text{ M HCl}$$

- (c) We start with a phosphoric acid-dihydrogen phosphate buffer solution and titrate until all of the  $\text{H}_3\text{PO}_4$  is consumed. We begin with

$$10.00 \text{ mL} \times \frac{0.0400 \text{ mmol H}_3\text{PO}_4}{1 \text{ mL}} = 0.400 \text{ mmol H}_3\text{PO}_4 \text{ and the diprotic anion,}$$

$$10.00 \text{ mL} \times \frac{0.0150 \text{ mmol H}_2\text{PO}_4^-}{1 \text{ mL}} = 0.150 \text{ mmol H}_2\text{PO}_4^{2-} \text{. The volume of 0.0200 M}$$

$$\text{NaOH needed is } 0.400 \text{ mmol H}_3\text{PO}_4 \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol H}_3\text{PO}_4} \times \frac{1 \text{ mL NaOH}}{0.0200 \text{ mmol NaOH}} = 20.00 \text{ mL}$$

to reach the first equivalence point. The pH of points during this titration are computed with the Henderson-Hasselbalch equation.

$$\text{Initially: } \text{pH} = \text{p}K_1 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = -\log(7.1 \times 10^{-3}) + \log \frac{0.0150}{0.0400} = 2.15 - 0.43 = 1.62$$

$$\text{At 5.00 mL: } \text{pH} = 2.15 + \log \frac{0.150 + 0.100}{0.400 - 0.100} = 2.15 - 0.08 = 2.07$$

$$\text{At 10.0 mL, pH} = 2.15 + \log \frac{0.150 + 0.200}{0.400 - 0.200} = 2.15 + 0.24 = 2.39$$

$$\text{At 15.0 mL, pH} = 2.15 + \log \frac{0.150 + 0.300}{0.400 - 0.300} = 2.15 + 0.65 = 2.80$$

This is the first equivalence point, a solution of 30.00 mL (= 10.00 mL originally + 20.00 mL titrant), containing 0.400 mmol  $\text{H}_2\text{PO}_4^-$  from the titration and the 0.150 mmol  $\text{H}_2\text{PO}_4^{2-}$  originally present. This is a solution with

$$[\text{H}_2\text{PO}_4^-] = \frac{(0.400 + 0.150) \text{ mmol H}_2\text{PO}_4^-}{30.00 \text{ mL}} = 0.0183 \text{ M, which has}$$

$$\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = 0.50(2.15 - \log(6.3 \times 10^{-8})) = 0.50(2.15 + 7.20) = 4.68$$

To reach the second equivalence point means titrating 0.550 mmol  $\text{H}_2\text{PO}_4^-$ , which requires an additional volume of titrant given by

$$0.550 \text{ mmol H}_2\text{PO}_4^- \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol H}_2\text{PO}_4^-} \times \frac{1 \text{ mL NaOH}}{0.0200 \text{ mmol NaOH}} = 27.5 \text{ mL.}$$

To determine pH during this titration, we divide the region into five equal portions of 5.5 mL and use the Henderson-Hasselbalch equation.

At (20.0 + 5.5) mL,

$$\text{pH} = \text{p}K_2 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7.20 + \log \frac{(0.20 \times 0.550) \text{ mmol HPO}_4^{2-} \text{ formed}}{(0.80 \times 0.550) \text{ mmol H}_2\text{PO}_4^- \text{ remaining}}$$

$$\text{pH} = 7.20 - 0.60 = 6.60$$

$$\text{At (20.0 + 11.0) mL} = 31.0 \text{ mL, pH} = 7.20 + \log \frac{0.40 \times 0.550}{0.60 \times 0.550} = 7.02$$

$$\text{At 36.5 mL, pH} = 7.38 \quad \text{At 42.0 mL, pH} = 7.80$$

The pH at the second equivalence point is given by

$$\text{pH} = \frac{1}{2}(\text{p}K_2 + \text{p}K_3) = 0.50(7.20 - \log(4.2 \times 10^{-13})) = 0.50(7.20 + 12.38) = 9.79.$$

Another 27.50 mL of 0.020 M NaOH would be required to reach the third equivalence point. pH values at each of four equally spaced volumes of 5.50 mL additional 0.0200 M NaOH are computed as before, assuming the Henderson-Hasselbalch equation is valid.

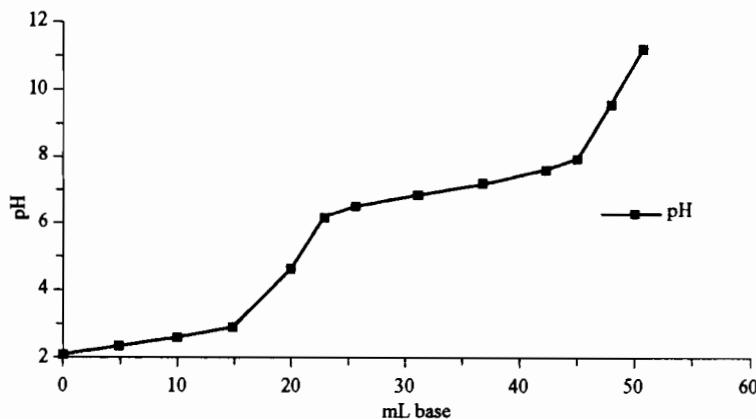
$$\text{At } (47.50 + 5.50) \text{ mL} = 53.00 \text{ mL, } \text{pH} = \text{p}K_3 + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 12.38 + \log \frac{0.20 \times 0.550}{0.80 \times 0.550} \\ = 12.38 - 0.60 = 11.78$$

At 58.50 mL, pH = 12.20      At 64.50 mL, pH = 12.56      At 70.00 mL, pH = 12.98  
But at infinite dilution with 0.0200 M NaOH, the pH = 12.30, so this point can't be reached.

At the last equivalence point, the solution will contain 0.550 mmol  $\text{PO}_4^{3-}$  in a total of  $10.00 + 20.00 + 27.50 + 27.50 \text{ mL} = 85.00 \text{ mL}$  of solution, with

$$[\text{PO}_4^{3-}] = \frac{0.550 \text{ mmol}}{85.00 \text{ mL}} = 0.00647 \text{ M. But we can never reach this point, because the}$$

pH of the 0.0200 M NaOH titrant is 12.30. Moreover, the titrant is diluted by its addition to the solution. Thus, our titration will cease sometime shortly after the second equivalence point. We never will see the third equivalence point, largely because the titrant is too dilute. Our results are plotted on the next page.



100.  $\text{p}K_{a_1} = 2.34$ ;  $K_{a_1} = 4.6 \times 10^{-3}$  and  $\text{p}K_{a_2} = 9.69$ ;  $K_{a_2} = 2.0 \times 10^{-10}$

- (a) Since the  $K_a$  values are so different, we can treat alanine ( $\text{H}_2\text{A}^+$ ) as a monoprotic acid with  $K_{a_1} = 4.6 \times 10^{-3}$ . Hence:

	$\text{H}_2\text{A}^+(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{HA}(\text{aq})$	+	$\text{H}_3\text{O}^+(\text{aq})$
Initial	0.500 M		-		0 M		$\approx 0$ M
Change	$-x$ M		-		$+x$ M		$+x$ M
Equilibrium	$(0.500 - x)$ M		-		$x$ M		$x$ M

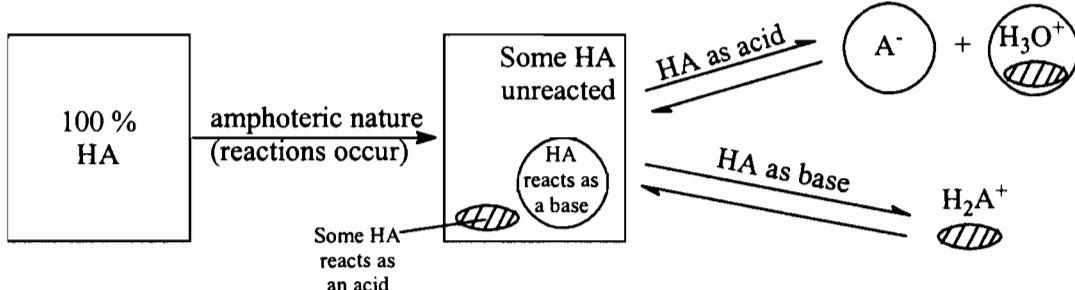
$$K_{a_1} = \frac{[\text{HA}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}^+]} = \frac{(x)(x)}{(0.500 - x)} = 4.6 \times 10^{-3} \approx \frac{x^2}{0.500}$$

$$x = 0.048 \text{ M} = [\text{H}_3\text{O}^+] \quad (x = 0.0457 \text{ solving the quadratic equation})$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.046) = 1.34$$

- (b) At the first half-neutralization point a buffer made up of  $\text{H}_2\text{A}^+/\text{HA}$  is formed, where  $[\text{H}_2\text{A}^+] = [\text{HA}]$ . The Henderson Hasselbalch equation gives  $\text{pH} = \text{p}K_a = 2.34$
- (c) At the 1<sup>st</sup> equivalence point all of the  $\text{H}_2\text{A}^+(\text{aq})$  is converted to  $\text{HA}(\text{aq})$ .  $\text{HA}(\text{aq})$  is involved in both  $K_{a_1}$  and  $K_{a_2}$ , both ionizations must be considered.

If we assume that the solution is converted to 100% HA, we must consider two reactions. HA may act as a weak acid ( $\text{HA} \rightarrow \text{A}^- + \text{H}^+$ ) or HA may act as a base ( $\text{HA} + \text{H}^+ \rightarrow \text{H}_2\text{A}^+$ ). See Diagram on below:



Using the diagram above, we see the following relations must hold true.

$$[\text{A}^-] = [\text{H}_3\text{O}^+] + [\text{H}_2\text{A}^+]$$

$$K_{a_2} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \text{ or } [\text{A}^-] = \frac{K_{a_2}[\text{HA}]}{[\text{H}_3\text{O}^+]} \quad \& \quad K_{a_1} = \frac{[\text{HA}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}^+]} \text{ or } [\text{H}_2\text{A}^+] = \frac{[\text{H}_3\text{O}^+][\text{HA}]}{K_{a_1}}$$

Substitute for  $[\text{A}^-]$  and  $[\text{H}_2\text{A}^+]$  in  $[\text{A}^-] = [\text{H}_3\text{O}^+] + [\text{H}_2\text{A}^+]$

$$\frac{K_{a_2}[\text{HA}]}{[\text{H}_3\text{O}^+]} = [\text{H}_3\text{O}^+] + \frac{[\text{H}_3\text{O}^+][\text{HA}]}{K_{a_1}} \quad (\text{multiply both sides by } K_{a_1} [\text{H}_3\text{O}^+])$$

$$K_{a_1} K_{a_2} [\text{HA}] = K_{a_1} [\text{H}_3\text{O}^+][\text{H}_3\text{O}^+] + [\text{H}_3\text{O}^+][\text{H}_3\text{O}^+][\text{HA}]$$

$$K_{a_1} K_{a_2} [\text{HA}] = [\text{H}_3\text{O}^+]^2 (K_{a_1} + [\text{HA}])$$

$$[\text{H}_3\text{O}^+]^2 = \frac{K_{a_1} K_{a_2} [\text{HA}]}{(K_{a_1} + [\text{HA}])} \quad \text{Usually, } [\text{HA}] \gg K_{a_1} \quad (\text{Here, } 0.500 \gg 4.6 \times 10^{-3})$$

Make the assumption that  $K_{a_1} + [\text{HA}] \approx [\text{HA}]$

$$[\text{H}_3\text{O}^+]^2 = \frac{K_{a_1} K_{a_2} [\text{HA}]}{[\text{HA}]} = K_{a_1} K_{a_2} \quad \text{Take } -\log \text{ of both sides}$$

$$-\log [\text{H}_3\text{O}^+]^2 = -2\log [\text{H}_3\text{O}^+] = 2(\text{pH}) = -\log K_{a_1} K_{a_2} = -\log K_{a_1} - \log K_{a_2} = \text{p}K_{a_1} + \text{p}K_{a_2}$$

$$2(\text{pH}) = \text{p}K_{a_1} + \text{p}K_{a_2}$$

$$\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = \frac{2.34 + 9.69}{2} = 6.02$$

- (d) Half way between the 1<sup>st</sup> and 2<sup>nd</sup> equivalence point, half of HA(aq) is converted to A<sup>-</sup>(aq). We have a HA/A<sup>-</sup> buffer solution where  $[\text{HA}] = [\text{A}^-]$ . The Henderson-Hasselbalch equation yields  $\text{pH} = \text{p}K_{a_2} = 9.69$
- (e) At the second equivalence point, all of the H<sub>2</sub>A<sup>+</sup>(aq) is converted to A<sup>-</sup>(aq). We may treat this simply as a weak base in water having  $K_b = \frac{K_w}{K_{a_2}} = \frac{1 \times 10^{-14}}{2.0 \times 10^{-10}} = 5.0 \times 10^{-5}$

Note: There has been a 1:3 dilution, hence the  $[\text{A}^-] = 0.500 \text{ M} \times \frac{1 \text{ V}}{3 \text{ V}} = 0.167 \text{ M}$

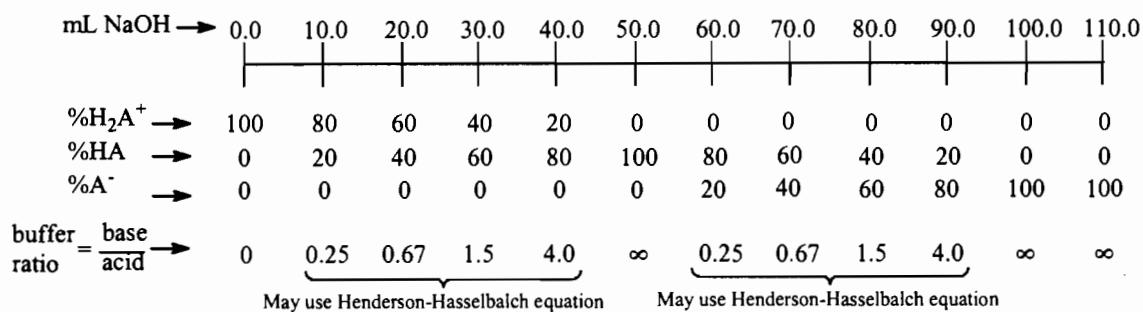
	A <sup>-</sup> (aq)	+	H <sub>2</sub> O(l)	$\rightleftharpoons$	HA(aq)	+	OH <sup>-</sup> (aq)
Initial	0.167 M		-		0 M		$\approx 0 \text{ M}$
Change	$-x \text{ M}$		-		$+x \text{ M}$		$+x \text{ M}$
Equilibrium	$(0.167 - x) \text{ M}$		-		$x \text{ M}$		$x \text{ M}$

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{(x)(x)}{(0.167 - x)} = 5.0 \times 10^{-5} \approx \frac{x^2}{0.167}$$

$$x = 0.0029 \text{ M} = [\text{OH}^-]; \text{pOH} = -\log [\text{OH}^-] = 2.54;$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.54 = 11.46$$

- (f) All of the points required in (f) can be obtained using the Henderson-Hasselbalch equation (the chart on the next page shows that the buffer ratio for each point is within the acceptable range (0.25 to 4.0))



- (i) After 10.0 mL

Here we will show how to obtain the answer using both the Henderson-Hasselbalch equation and setting up the I. C. E. (Initial, Change, Equilibrium) table. The results will differ within accepted experimental limitation of the experiment ( $\pm 0.01$  pH units)

$$n_{H_2A^+} = (C \times V) = (0.500 \text{ M})(0.0500 \text{ L}) = 0.0250 \text{ moles H}_2A^+$$

$$n_{OH^-} = (C \times V) = (0.500 \text{ M})(0.0100 \text{ L}) = 0.00500 \text{ moles OH}^-$$

$$V_{\text{total}} = (50.0 + 10.0) \text{ mL} = 60.0 \text{ mL or } 0.0600 \text{ L}$$

$$[H_2A^+] = \frac{n_{H_2A^+}}{V_{\text{total}}} = \frac{0.0250 \text{ mol}}{0.0600 \text{ L}} = 0.417 \text{ M} \quad [OH^-] = \frac{n_{OH^-}}{V_{\text{total}}} = \frac{0.00500 \text{ mol}}{0.0600 \text{ L}} = 0.0833 \text{ M}$$

$$K_{\text{eq}} \text{ for titration reaction} = \frac{1}{K_{b(HA)}} = \frac{1}{\left( \frac{K_w}{K_{a_1}} \right)} = \frac{K_{a_1}}{K_w} = \frac{4.6 \times 10^{-3}}{1.00 \times 10^{-14}} = 4.6 \times 10^{11}$$

	H <sub>2</sub> A <sup>+</sup> (aq)	+	OH <sup>-</sup> (aq)	↔	HA(aq)	+	H <sub>2</sub> O(l)
Initial:	0.417 M		0.0833 M		0 M		-
100% rxn:	-0.0833		-0.0833 M		+0.0833 M		-
New initial:	0.334 M		0 M		0.0833 M		-
Change:	+x M		+x M		-x M		-
Equilibrium:	≈0.334 M		x M		≈0.0833 M		-

$$4.6 \times 10^{11} = \frac{(0.0833)}{(0.334)(x)} ; x = \frac{(0.0833)}{(0.334)(4.6 \times 10^{11})} = 5.4 \times 10^{-13} \text{ (valid assumption)}$$

$$x = 5.4 \times 10^{-13} = [OH^-]; pOH = -\log(5.4 \times 10^{-13}) = 12.27; pH = 14.00 - pOH = 14.00 - 12.27 = 1.73$$

Alternate method using the Henderson-Hasselbalch equation:

- (i) After 10.0 mL, 20% of H<sub>2</sub>A<sup>+</sup> reacts forming the conjugate base HA. Hence the buffer solution is 80% H<sub>2</sub>A<sup>+</sup> (acid) and 20% HA (base)

$$pH = pK_{a_1} + \log \frac{\text{base}}{\text{acid}} = 2.34 + \log \frac{20.0}{80.0} = 2.34 + (-0.602) = 1.74 \text{ (within } \pm 0.01\text{)}$$

For the remainder of the calculations we will employ the Henderson-Hasselbalch equation with the understanding that using the method that employs the I.C.E. table gives the same result within the limitation of the data.

- (ii) After 20.0 mL, 40% of  $\text{H}_2\text{A}^+$  reacts forming the conjugate base HA  
Hence the buffer solution is 60%  $\text{H}_2\text{A}^+$  (acid) and 40% HA (base)

$$\text{pH} = \text{p}K_{a_1} + \log \frac{\text{base}}{\text{acid}} = 2.34 + \log \frac{40.0}{60.0} = 2.34 + (-0.176) = 2.16$$

- (iii) After 30.0 mL, 60% of  $\text{H}_2\text{A}^+$  reacts forming the conjugate base HA  
Hence the buffer solution is 40%  $\text{H}_2\text{A}^+$  (acid) and 60% HA (base)

$$\text{pH} = \text{p}K_{a_1} + \log \frac{\text{base}}{\text{acid}} = 2.34 + \log \frac{60.0}{40.0} = 2.34 + (+0.176) = 2.52$$

- (iv) After 40.0 mL, 80% of  $\text{H}_2\text{A}^+$  reacts forming the conjugate base HA  
Hence the buffer solution is 20%  $\text{H}_2\text{A}^+$  (acid) and 80% HA (base)

$$\text{pH} = \text{p}K_{a_1} + \log \frac{\text{base}}{\text{acid}} = 2.34 + \log \frac{80.0}{20.0} = 2.34 + (0.602) = 2.94$$

- (v) After 50 mL all of the  $\text{H}_2\text{A}^+$ (aq) has reacted and we begin with essentially 100% HA(aq), which is a weak acid. Addition of base results in the formation of the conjugate base (buffer system)  $\text{A}^-(\text{aq})$ . We employ a similar solution, however, now we must use  $\text{p}K_{a_2} = 9.69$

- (vi) After 60.0 mL, 20% of HA reacts forming the conjugate base  $\text{A}^-$   
Hence the buffer solution is 80% HA (acid) and 20%  $\text{A}^-$  (base)

$$\text{pH} = \text{p}K_{a_2} + \log \frac{\text{base}}{\text{acid}} = 9.69 + \log \frac{20.0}{80.0} = 9.69 + (-0.602) = 9.09$$

- (vii) After 70.0 mL, 40% of HA reacts forming the conjugate base  $\text{A}^-$   
Hence the buffer solution is 60% HA (acid) and 40%  $\text{A}^-$  (base)

$$\text{pH} = \text{p}K_{a_2} + \log \frac{\text{base}}{\text{acid}} = 9.69 + \log \frac{40.0}{60.0} = 9.69 + (-0.176) = 9.51$$

- (viii) After 80.0 mL, 60% of HA reacts forming the conjugate base  $\text{A}^-$   
Hence the buffer solution is 40% HA (acid) and 60%  $\text{A}^-$  (base)

$$\text{pH} = \text{p}K_{a_2} + \log \frac{\text{base}}{\text{acid}} = 9.69 + \log \frac{60.0}{40.0} = 9.69 + (+0.176) = 9.87$$

- (ix) After 90.0 mL, 80% of HA reacts forming the conjugate base  $\text{A}^-$   
Hence the buffer solution is 20% HA (acid) and 80%  $\text{A}^-$  (base)

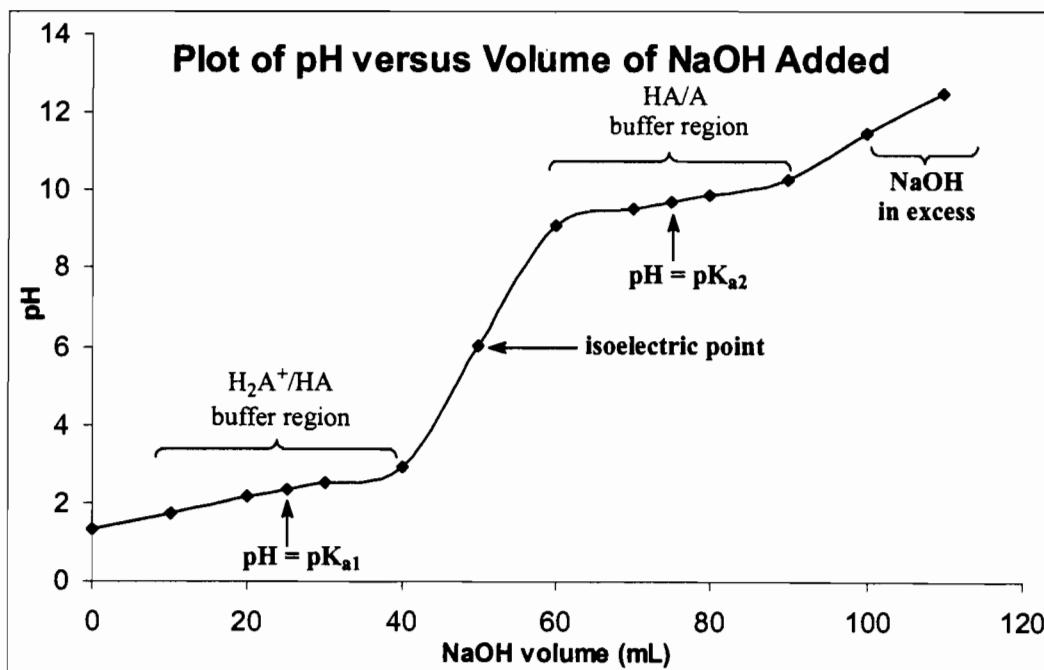
$$\text{pH} = \text{p}K_{a_2} + \log \frac{\text{base}}{\text{acid}} = 9.69 + \log \frac{80.0}{20.0} = 9.69 + (0.602) = 10.29$$

- (x) After the addition of 110.0 mL, NaOH is in excess. (10.0 mL of 0.500 M NaOH is in excess, or, 0.00500 moles of NaOH remains unreacted). The pH of a solution which has NaOH in excess is determined by the  $[\text{OH}^-]$  that is in excess. (For a diprotic acid this occurs after the 2<sup>nd</sup> equivalence point).

$$[\text{OH}^-]_{\text{excess}} = \frac{n_{\text{OH}^-}}{V_{\text{total}}} = \frac{0.00500 \text{ mol}}{0.1600 \text{ L}} = 0.03125 \text{ M} ; \text{pOH} = -\log(0.03125) = 1.51$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.51 = 12.49$$

- (g) A sketch of the titration curve for the 0.500 M solution of alanine hydrochloride, with some significant points labeled on the plot is shown below.

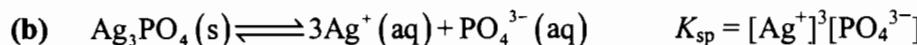


# CHAPTER 19

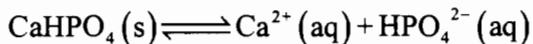
## SOLUBILITY AND COMPLEX-ION EQUILIBRIA

### PRACTICE EXAMPLES

**1A** In each case, we first write the balanced equation for the solubility equilibrium and then the equilibrium constant expression for that equilibrium, the  $K_{sp}$  expression:



**1B (a)** Provided  $[OH^-]$  is not too high, the hydrogen phosphate ion is not expected to ionize in aqueous solution to a significant extent because of the quite small values for the second and third ionization constants of phosphoric acid.

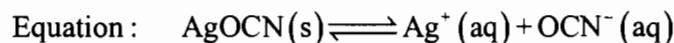


**(b)** The ionization constant is written in the manner of a  $K_c$  expression:

$$K_{sp} = [Ca^{2+}][HPO_4^{2-}] = 1. \times 10^{-7}$$

**2A** We calculate the solubility of silver cyanate,  $s$ , as a molarity. We then use the solubility equation to (1) relate the concentrations of the ions and (2) write the  $K_{sp}$  expression.

$$s = \frac{7 \text{ mg AgOCN}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol AgOCN}}{149.9 \text{ g AgOCN}} = 5 \times 10^{-4} \text{ moles/L}$$

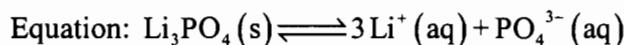


Solubility Product :  $s$   $s$

$$K_{sp} = [Ag^+][OCN^-] = (s) \times (s) = s^2 = (5 \times 10^{-4})^2 = 3 \times 10^{-7}$$

**2B** We calculate the solubility of lithium phosphate,  $s$ , as a molarity. We then use the solubility equation to (1) relate the concentrations of the ions and (2) write the  $K_{sp}$  expression.

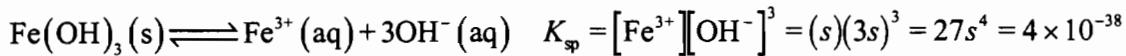
$$s = \frac{0.034 \text{ g Li}_3PO_4}{100 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol Li}_3PO_4}{115.79 \text{ g Li}_3PO_4} = 0.0029 \text{ moles/L}$$



Solubility Product:  $(3s)^3$   $s$

$$K_{sp} = [Li^+]^3[PO_4^{3-}] = (3s)^3 \cdot (s) = 27s^4 = 27(0.0029)^4 = 1.9 \times 10^{-9}$$

**3A** We use the solubility equilibrium to write the  $K_{sp}$  expression, which we then solve to obtain the molar solubility,  $s$ , of  $\text{Fe(OH)}_3$ .



$$\text{Solubility: } s = \sqrt[4]{\frac{4 \times 10^{-38}}{27}} = 2 \times 10^{-10} \text{ M}$$

**3B** First we determine the solubility of  $\text{BaSO}_4$ , and then find the mass dissolved.



The last relationship is true because  $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$  in a solution produced by dissolving  $\text{BaSO}_4$  in pure water. Thus,  $s = \sqrt{K_{sp}} = \sqrt{1.1 \times 10^{-10}} = 1.0 \times 10^{-5} \text{ M}$

$$\text{mass BaSO}_4 = 225 \text{ mL} \times \frac{1.0 \times 10^{-5} \text{ mmol BaSO}_4}{1 \text{ mL sat'd soln}} \times \frac{233.39 \text{ mg BaSO}_4}{1 \text{ mmol BaSO}_4} = 0.55 \text{ mg BaSO}_4$$

**4A** For  $\text{PbI}_2$ ,  $K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = 7.1 \times 10^{-9}$ . The solubility equilibrium is the basis of the calculation.

Equation:	$\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{I}^-(aq)$
Initial:	0.10 M 0 M
Changes:	+ $s$ M + $2s$ M
Equil:	(0.10 + $s$ ) M $2s$ M

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = 7.1 \times 10^{-9} = (0.10 + s)(2s)^2 \approx 0.40s^2 \quad s = \sqrt{\frac{7.1 \times 10^{-9}}{0.40}} = 1.3 \times 10^{-4} \text{ M}$$

(assumption 0.10  $\gg s$  valid)

This value of  $s$  is the solubility of  $\text{PbI}_2$  in 0.10 M  $\text{Pb}(\text{NO}_3)_2(aq)$ .

**4B** We find pOH from the given pH:

$$\text{pOH} = 14.00 - 8.20 = 5.80; \quad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.80} = 1.6 \times 10^{-6} \text{ M}.$$

We assume that pOH remains constant, and use the  $K_{sp}$  expression for  $\text{Fe(OH)}_3$ .

$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 4 \times 10^{-38} = [\text{Fe}^{3+}](1.6 \times 10^{-6})^3 \quad [\text{Fe}^{3+}] = \frac{4 \times 10^{-38}}{(1.6 \times 10^{-6})^3} = 1 \times 10^{-20} \text{ M}$$

Therefore, the molar solubility of  $\text{Fe(OH)}_3$  is  $1 \times 10^{-20} \text{ M}$ .

The dissolved  $\text{Fe(OH)}_3$  does not significantly affect  $[\text{OH}^-]$ .

**5A** First determine  $[I^-]$  as altered by dilution. We then compute  $Q_{sp}$  and compare it with  $K_{sp}$ .

$$[I^-] = \frac{3 \text{ drops} \times \frac{0.05 \text{ mL}}{1 \text{ drop}} \times \frac{0.20 \text{ mmol KI}}{1 \text{ mL}} \times \frac{1 \text{ mmol } I^-}{1 \text{ mmol KI}}}{100.0 \text{ mL soln}} = 3 \times 10^{-4} \text{ M}$$

$$Q_{sp} = [Ag^+][I^-] = (0.010)(3 \times 10^{-4}) = 3 \times 10^{-6}$$

$Q_{sp} > 8.5 \times 10^{-17} = K_{sp}$  Precipitation should occur.

**5B** We first use the solubility product constant expression for  $PbI_2$  to determine the  $[I^-]$  needed in solution to just form a precipitate when  $[Pb^{2+}] = 0.010 \text{ M}$ . We assume that the volume of solution added is small and that  $[Pb^{2+}]$  remains at 0.010 M throughout.

$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9} = (0.010)[I^-]^2 \quad [I^-] = \sqrt{\frac{7.1 \times 10^{-9}}{0.010}} = 8.4 \times 10^{-4} \text{ M}$$

We determine the volume of 0.20 M KI needed.

$$\begin{aligned} \text{volume of KI(aq)} &= 100.0 \text{ mL} \times \frac{8.4 \times 10^{-4} \text{ mmol } I^-}{1 \text{ mL}} \times \frac{1 \text{ mmol KI}}{1 \text{ mmol } I^-} \times \frac{1 \text{ mL KI(aq)}}{0.20 \text{ mmol KI}} \times \frac{1 \text{ drop}}{0.050 \text{ mL}} \\ &= 8.4 \text{ drops} = 9 \text{ drops} \end{aligned}$$

Since one additional drop is needed, 10 drops will be required. This is an insignificant volume compared to the original solution, so that  $[Pb^{2+}]$  remains constant.

**6A** We find  $[Ca^{2+}]$  that can coexist with  $[OH^-] = 0.040 \text{ M}$ .  $K_{sp} = 5.5 \times 10^{-6}$  for  $Ca(OH)_2$ .

$$K_{sp} = 5.5 \times 10^{-6} = [Ca^{2+}][OH^-]^2 = [Ca^{2+}](0.040)^2; \quad [Ca^{2+}] = \frac{5.5 \times 10^{-6}}{(0.040)^2} = 3.4 \times 10^{-3} \text{ M}$$

For precipitation to be considered complete,  $[Ca^{2+}]$  should be less than 0.1% of its original value.  $3.4 \times 10^{-3} \text{ M}$  is 34% of 0.010 M and therefore precipitation of  $Ca(OH)_2$  is not complete under these conditions.

**6B** We begin by finding  $[Mg^{2+}]$  that corresponds to  $1 \mu\text{g } Mg^{2+} / \text{L}$ .

$$[Mg^{2+}] = \frac{1 \mu\text{g } Mg^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ g}}{10^6 \mu\text{g}} \times \frac{1 \text{ mol } Mg^{2+}}{24.3 \text{ g } Mg^{2+}} = 4 \times 10^{-8} \text{ M}$$

Now we use the  $K_{sp}$  expression for  $Mg(OH)_2$  to determine  $[OH^-]$ .

$$K_{sp} = 1.8 \times 10^{-11} = [Mg^{2+}][OH^-]^2 = (4 \times 10^{-8})[OH^-]^2 \quad [OH^-] = \sqrt{\frac{1.8 \times 10^{-11}}{4 \times 10^{-8}}} = 0.02 \text{ M}$$

**7A** Let us first determine  $[\text{Ag}^+]$  when  $\text{AgCl(s)}$  just begins to precipitate. At that point,  $Q_{\text{sp}}$  and  $K_{\text{sp}}$  are equal.

$$K_{\text{sp}} = 1.8 \times 10^{-10} = [\text{Ag}^+] [\text{Cl}^-] = Q_{\text{sp}} = [\text{Ag}^+] \times 0.115\text{M} \quad [\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.115} = 1.6 \times 10^{-9}\text{M}$$

Now let us determine  $[\text{Br}^-]$  that can coexist with this  $[\text{Ag}^+]$ .

$$K_{\text{sp}} = 5.0 \times 10^{-13} = [\text{Ag}^+] [\text{Br}^-] = 1.6 \times 10^{-9}\text{M} \times [\text{Br}^-]; \quad [\text{Br}^-] = \frac{5.0 \times 10^{-13}}{1.6 \times 10^{-9}} = 3.1 \times 10^{-4}\text{M}$$

The remaining bromide ion has precipitated as  $\text{AgBr(s)}$  with the addition of  $\text{AgNO}_3\text{(aq)}$ .

$$\text{Percent of Br}^- \text{ remaining} = \frac{[\text{Br}^-]_{\text{final}}}{[\text{Br}^-]_{\text{initial}}} \times 100\% = \frac{3.1 \times 10^{-4}\text{M}}{0.264\text{M}} \times 100\% = 0.12\%$$

**7B** Since the ions have the same charge and the same concentrations, we look for two  $K_{\text{sp}}$  values with the same anion that are as far apart as possible. The  $K_{\text{sp}}$  values for the carbonates are very close, while those for the sulfates and fluorides are quite different. However, the difference in the  $K_{\text{sp}}$  values is greatest for the chromates;  $K_{\text{sp}}$  for

$\text{BaCrO}_4 (1.2 \times 10^{-10})$  is so much smaller than  $K_{\text{sp}}$  for  $\text{SrCrO}_4 (2.2 \times 10^{-5})$ ,  $\text{BaCrO}_4$  will precipitate first and  $\text{SrCrO}_4$  will begin to precipitate when  $[\text{CrO}_4^{2-}]$  has the value:

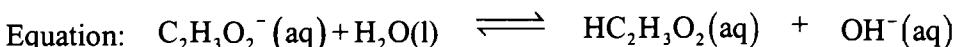
$$[\text{CrO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Sr}^{2+}]} = \frac{2.2 \times 10^{-5}}{0.10} = 2.2 \times 10^{-4}\text{M}.$$

At this point  $[\text{Ba}^{2+}]$  is found as follows.

$$[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{CrO}_4^{2-}]} = \frac{1.2 \times 10^{-10}}{2.2 \times 10^{-4}} = 5.5 \times 10^{-7}\text{M};$$

$[\text{Ba}^{2+}]$  has dropped to 0.00055% of its initial value and therefore is considered to be completely precipitated, before  $\text{SrCrO}_4$  begins to precipitate. The two ions are thus effectively separated as chromates. The best precipitating agent is a group 1 chromate salt.

**8A** First determine  $[\text{OH}^-]$  resulting from the hydrolysis of acetate ion.



Initial:  $0.10\text{M}$   $0\text{M}$   $\approx 0\text{M}$

Changes:  $-x\text{M}$   $+x\text{M}$   $+x\text{M}$

Equil:  $(0.10 - x)\text{M}$   $x\text{M}$   $x\text{M}$

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{x \cdot x}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = [\text{OH}^-] = \sqrt{0.10 \times 5.6 \times 10^{-10}} = 7.5 \times 10^{-6} \text{ M} \quad (\text{the assumption } x \ll 0.10 \text{ was valid})$$

Now compute the value of the ion product in this solution and compare it with the value of  $K_{sp}$  for  $\text{Mg}(\text{OH})_2$ .

$$Q_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.010 \text{ M})(7.5 \times 10^{-6} \text{ M})^2 = 5.6 \times 10^{-13} < 1.8 \times 10^{-11} = K_{sp}[\text{Mg}(\text{OH})_2]$$

Because  $Q_{sp}$  is smaller than  $K_{sp}$ , this solution is unsaturated and precipitation of  $\text{Mg}(\text{OH})_2(\text{s})$  will not occur.

- 8B** Use the Henderson–Hasselbalch equation to determine the pH of the buffer.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = -\log(1.8 \times 10^{-5}) + \log \frac{0.250 \text{ M}}{0.150 \text{ M}} = 4.74 + 0.22 = 4.96$$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 4.96 = 9.04 \quad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.04} = 9.1 \times 10^{-10} \text{ M}$$

Now we determine  $Q_{sp}$  to see if precipitation will occur.

$$Q_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 = (0.013 \text{ M})(9.1 \times 10^{-10})^3 = 9.8 \times 10^{-30}$$

$Q_{sp} > 4 \times 10^{-38} = K_{sp}$ ;  $\text{Fe}(\text{OH})_3$  precipitation should occur.

- 9A** Determine  $[\text{OH}^-]$ , and then the pH necessary to prevent the precipitation of  $\text{Mn}(\text{OH})_2$ .

$$K_{sp} = 1.9 \times 10^{-13} = [\text{Mn}^{2+}][\text{OH}^-]^2 = (0.0050 \text{ M})[\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{1.9 \times 10^{-13}}{0.0050}} = 6.2 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(6.2 \times 10^{-6}) = 5.21 \quad \text{pH} = 14.00 - 5.21 = 8.79$$

We use this pH in the Henderson–Hasselbalch equation to determine  $[\text{NH}_4^+]$ .

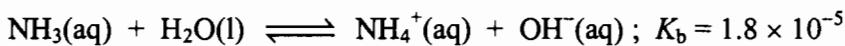
$\text{p}K_b = 4.74$  for  $\text{NH}_3$ .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 8.79 = (14.00 - 4.74) + \log \frac{0.025 \text{ M}}{[\text{NH}_4^+]}$$

$$\log \frac{0.025 \text{ M}}{[\text{NH}_4^+]} = 8.79 - (14.00 - 4.74) = -0.47 \quad \frac{0.025}{[\text{NH}_4^+]} = 10^{-0.47} = 0.34$$

$$[\text{NH}_4^+] = \frac{0.025}{0.34} = 0.074 \text{ M}$$

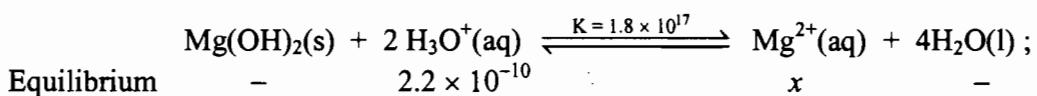
- 9B** First we must calculate the  $[\text{H}_3\text{O}^+]$  in the buffer solution that is being employed to dissolve the magnesium hydroxide:



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[0.100\text{M}][\text{OH}^-]}{[0.250\text{M}]} = 1.8 \times 10^{-5}$$

$$[\text{OH}^-] = 4.5 \times 10^{-5} \text{ M}; [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14} \text{ M}^2}{4.5 \times 10^{-5} \text{ M}} = 2.2 \times 10^{-10} \text{ M}$$

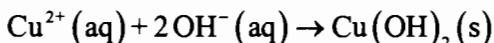
Now we can employ equation 19.4 to calculate the molar solubility of  $\text{Mg}(\text{OH})_2$  in the buffer solution; Molar Solubility  $\text{Mg}(\text{OH})_2 = [\text{Mg}^{2+}]_{\text{equil}}$



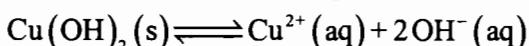
$$K = \frac{[\text{Mg}^{2+}]}{[\text{H}_3\text{O}^+]^2} = \frac{x}{[2.2 \times 10^{-10} \text{ M}]^2} = 1.8 \times 10^{17} \quad x = 8.7 \times 10^{-3} \text{ M} = [\text{Mg}^{2+}]_{\text{equil}}$$

So, the Molar Solubility for  $\text{Mg}(\text{OH})_2 = 8.7 \times 10^{-3} \text{ M}$

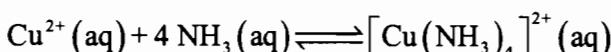
- 10A (a)** In solution are  $\text{Cu}^{2+}(\text{aq})$ ,  $\text{SO}_4^{2-}(\text{aq})$ ,  $\text{Na}^+(\text{aq})$ , and  $\text{OH}^-(\text{aq})$ .



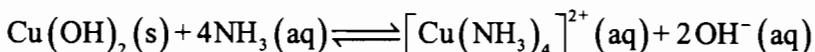
- (b)** In solution above  $\text{Cu}(\text{OH})_2(\text{s})$  is  $\text{Cu}^{2+}(\text{aq})$ :



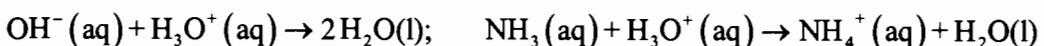
This  $\text{Cu}^{2+}(\text{aq})$  reacts with the added  $\text{NH}_3(\text{aq})$ :



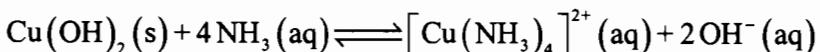
The overall result is:



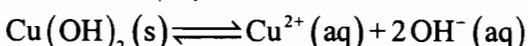
- (c)**  $\text{HNO}_3(\text{aq})$  (strong acid), forms  $\text{H}_3\text{O}^+(\text{aq})$ , which reacts with  $\text{OH}^-(\text{aq})$  and  $\text{NH}_3(\text{aq})$ .



As  $\text{NH}_3(\text{aq})$  is consumed, this reaction shifts to the left.



But as  $\text{OH}^-(\text{aq})$  is consumed, this reaction shifts to the right:

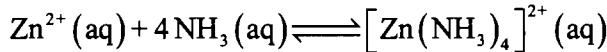


The species in solution at the end of all this are

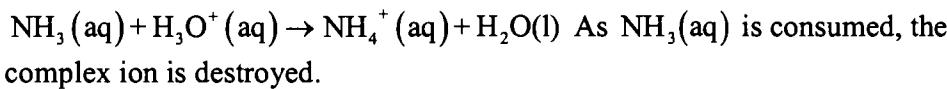
$\text{Cu}^{2+}(\text{aq})$ ,  $\text{NO}_3^-(\text{aq})$ ,  $\text{NH}_4^+(\text{aq})$ , excess  $\text{H}_3\text{O}^+(\text{aq})$ ,  $\text{Na}^+(\text{aq})$ ; and  $\text{SO}_4^{2-}(\text{aq})$

(Probably  $\text{HSO}_4^-(\text{aq})$  as well)

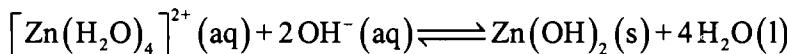
- 10B (a)** In solution are  $\text{Zn}^{2+}$ (aq),  $\text{SO}_4^{2-}$ (aq), and  $\text{NH}_3$ (aq),



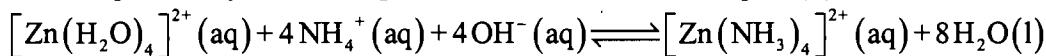
- (b)**  $\text{HNO}_3$ (aq), a strong acid, produces  $\text{H}_3\text{O}^+$ (aq), which reacts with  $\text{NH}_3$ (aq).



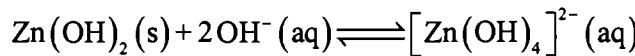
- (c)**  $\text{NaOH}$ (aq) is a strong base that produces  $\text{OH}^-$ (aq), forming a hydroxide precipitate.



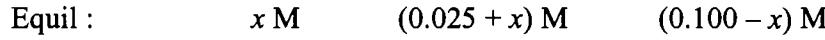
Another possibility is reversing the effect of the reaction of part (b).



- (d)** The precipitate dissolves in excess base.



- 11A** We first determine  $[\text{Ag}^+]$  in a solution that is 0.100 M  $\text{Ag}^+$ (aq) (from  $\text{AgNO}_3$ ) and 0.225 M  $\text{NH}_3$ (aq). Because of the large value of  $K_f = 1.6 \times 10^7$ , we start by having the reagents form as much complex ion as possible, and approach equilibrium from that point.



$$K_f = 1.6 \times 10^7 = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{0.100 - x}{x(0.025 + 2x)^2} \approx \frac{0.100}{x(0.025)^2}$$

$$x = \frac{0.100}{(0.025)^2 1.6 \times 10^7} = 1.0 \times 10^{-5} \text{ M} = [\text{Ag}^+] = \text{concentration of free silver ion}$$

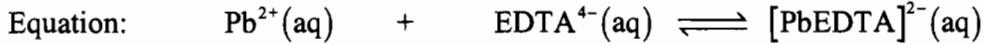
The  $[\text{Cl}^-]$  is diluted:  $[\text{Cl}^-]_{\text{final}} = [\text{Cl}^-]_{\text{initial}} \times \frac{1.00 \text{ mL}_{\text{initial}}}{1,500 \text{ mL}_{\text{final}}} = 3.50 \text{ M} \div 1500 = 0.00233 \text{ M}$

Finally we compare  $Q_{\text{sp}}$  with  $K_{\text{sp}}$  to determine if precipitation of  $\text{AgCl}(\text{s})$  will occur.

$$Q_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-5} \text{ M})(0.00233 \text{ M}) = 2.3 \times 10^{-8} > 1.8 \times 10^{-10} = K_{\text{sp}}$$

Because the value of the  $Q_{\text{sp}}$  is larger than the value of the  $K_{\text{sp}}$ , precipitation should occur.

**11B** We organize the solution around the balanced equation of the formation reaction.



Initial: 0.100 M 0.250 M 0 M

Form Complex: -0.100 M (0.250 - 0.100) M 0.100 M

Equil: x M (0.150 + x) M (0.100 - x) M

$$K_f = \frac{[\text{PbEDTA}]^{2-}}{[\text{Pb}^{2+}][\text{EDTA}^{4-}]} = 2 \times 10^{18} = \frac{0.100 - x}{x(0.150 + x)} \approx \frac{0.100}{0.150x}$$

$$x = \frac{0.100}{0.150 \times 2 \times 10^{18}} = 3 \times 10^{-19} \text{ M}$$

We calculate  $Q_{sp}$  to determine if precipitation should occur.

$$Q_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = (3 \times 10^{-19} \text{ M})(0.10 \text{ M})^2 = 3 \times 10^{-21}.$$

$Q_{sp} < 7.1 \times 10^{-9} = K_{sp}$  Precipitation will not occur.

**12A** We first determine the maximum concentration of free  $\text{Ag}^+$ .

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \quad [\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.0075} = 2.4 \times 10^{-8} \text{ M.}$$

This is so small that we assume that all the  $\text{Ag}^+$  in solution is present as complex ion:

$[\text{Ag}(\text{NH}_3)_2]^+ = 0.13 \text{ M}$ . We use  $K_f$  to determine the concentration of free  $\text{NH}_3$ .

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} = 1.6 \times 10^7 = \frac{0.13 \text{ M}}{2.4 \times 10^{-8} [\text{NH}_3]^2}$$

$$[\text{NH}_3] = \sqrt{\frac{0.13}{2.4 \times 10^{-8} \times 1.6 \times 10^7}} = 0.58 \text{ M.}$$

If we combine this with the ammonia present in the complex ion, the total ammonia concentration is  $0.58 \text{ M} + (2 \times 0.13 \text{ M}) = 0.84 \text{ M}$ .

**12B** We use the solubility product constant expression to determine the maximum  $[\text{Ag}^+]$  that is possible in 0.010 M  $\text{Cl}^-$  without precipitation occurring.

$$K_{sp} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+](0.010 \text{ M}) \quad [\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.010} = 1.8 \times 10^{-8} \text{ M}$$

This is also the concentration of free silver ion in the  $K_f$  expression. Because of the large value of  $K_f$ , practically all of the silver ion in solution is present as the complex ion, and

$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ . We solve the expression for  $[\text{S}_2\text{O}_3^{2-}]$  and then add the  $[\text{S}_2\text{O}_3^{2-}]$  "tied up" in the complex ion.

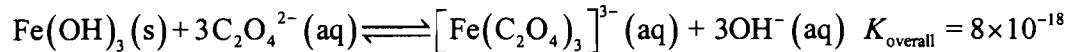
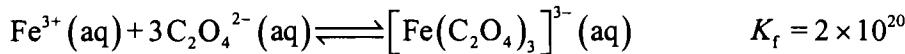
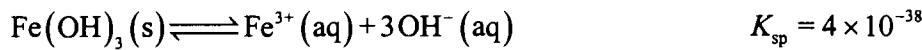
$$K_f = 1.7 \times 10^{13} = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2} = \frac{0.10 \text{ M}}{1.8 \times 10^{-8} \text{ M} [\text{S}_2\text{O}_3^{2-}]^2}$$

$$[\text{S}_2\text{O}_3^{2-}] = \sqrt{\frac{0.10}{1.8 \times 10^{-8} \times 1.7 \times 10^{13}}} = 5.7 \times 10^{-4} \text{ M} = \text{concentration of free } \text{S}_2\text{O}_3^{2-}$$

$$\text{total } [\text{S}_2\text{O}_3^{2-}] = 5.7 \times 10^{-4} \text{ M} + 0.10 \text{ M} [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} \times \frac{2 \text{ mol } \text{S}_2\text{O}_3^{2-}}{1 \text{ mol } [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}}$$

$$= 0.20 + 0.00057 \text{ M} = 0.20 \text{ M}$$

**13A** We combine the two equilibrium expressions, for  $K_f$  and for  $K_{sp}$ .



initial:	0.100 M	0 M	$\approx 0 \text{ M}$
changes:	$-3x \text{ M}$	$+x \text{ M}$	$+3x \text{ M}$
equil:	$(0.100 - 3x) \text{ M}$	$x \text{ M}$	$3x \text{ M}$

$$K_{\text{overall}} = \frac{[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} [\text{OH}^-]^3}{[\text{C}_2\text{O}_4^{2-}]^3} = \frac{(x)(3x)^3}{(0.100 - 3x)^3} = 8 \times 10^{-18} \approx \frac{27x^4}{(0.100)^3} \quad \text{assuming } 3x \ll 0.100$$

$$x = \sqrt[4]{\frac{(0.100)^3 8 \times 10^{-18}}{27}} = 4 \times 10^{-6} \text{ M} \quad \text{The assumption is valid.}$$

The solubility of  $\text{Fe(OH)}_3$  in 0.100 M  $\text{C}_2\text{O}_4^{2-}$  is  $4 \times 10^{-6} \text{ M}$ .

**13B** In Example 19-13 we saw that the expression for the solubility,  $s$ , of a silver halide in an aqueous ammonia solution, where  $[\text{NH}_3]$  is the concentration of aqueous ammonia, is given by:

$$K_{sp} \times K_f = \left( \frac{s}{[\text{NH}_3] - 2s} \right)^2 \quad \text{or} \quad \sqrt{K_{sp} \times K_f} = \frac{s}{[\text{NH}_3] - 2s}$$

We are comparing situations of constant  $[\text{NH}_3] = 0.100 \text{ M}$  and  $K_f = 1.6 \times 10^7$ .

We see that  $s$  will decrease as does  $K_{sp}$ . The values are:

$$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}, \quad K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}, \quad K_{sp}(\text{AgI}) = 8.5 \times 10^{-17}.$$

**14A** For FeS, we know that  $K_{\text{spa}} = 6 \times 10^2$ ; for  $\text{Ag}_2\text{S}$ ,  $K_{\text{spa}} = 6 \times 10^{-30}$ .

We compute the value of  $Q_{\text{spa}}$  in each case, with  $[\text{H}_2\text{S}] = 0.10\text{ M}$  and  $[\text{H}_3\text{O}^+] = 0.30\text{ M}$ .

For FeS,  $Q_{\text{spa}} = \frac{0.020 \times 0.10}{(0.30)^2} = 0.022 < 6 \times 10^2 = K_{\text{spa}}$ ; Precipitation of FeS should not occur.

For  $\text{Ag}_2\text{S}$ ,  $Q_{\text{spa}} = \frac{(0.010)^2 \times 0.10}{(0.30)^2} = 1.1 \times 10^{-4}$

$Q_{\text{spa}} > 6 \times 10^{-30} = K_{\text{spa}}$ ; Precipitation of  $\text{Ag}_2\text{S}$  should occur.

**14B** The  $[\text{H}_3\text{O}^+]$  needed to just form a precipitate can be obtained by direct substitution into the  $K_{\text{spa}}$  expression. When that expression is satisfied, a precipitate will just form.

$$K_{\text{spa}} = \frac{[\text{Fe}^{2+}][\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]^2} = 6 \times 10^2 = \frac{(0.015\text{ M Fe}^{2+})(0.10\text{ M H}_2\text{S})}{[\text{H}_3\text{O}^+]^2}, [\text{H}_3\text{O}^+] = \sqrt{\frac{0.015 \times 0.10}{6 \times 10^2}} = 0.002\text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.002) = 2.7$$

## REVIEW QUESTIONS

- $K_{\text{sp}}$  is the symbol for the solubility product constant, representing the equilibrium constant for the dissolution of a sparingly soluble (ionic) compound in water.
  - $K_f$  is the symbol for the formation constant of a complex ion: the complex ion is formed (the product) from combination of a simple cation with the appropriate set of ligands.
  - $Q_{\text{sp}}$ , or ion product, is reaction quotient for the dissolution of an ionic solid in water. The ion product has the same format as the solubility product expression, but it involves initial rather than equilibrium concentrations.
  - A complex ion is charged species consisting of a central metal ion attached to one or more groups of neutral molecules or ions called ligands.
- The common-ion effect refers to the phenomenon whereby less of a sparingly soluble ionic compound will dissolve in solution because of the presence of one of its constituent ions in solution.
  - Fractional precipitation refers to adding a precipitating agent (such as an anion) to a solution containing two other ions (such as cations) gradually so that only one compound precipitates.
  - Ion-pair formation refers to the result of the attraction between solvated ions of unlike charges in solution. These solvated ions cluster together and behave to some extent as one particle.

- (d) Qualitative cation analysis is a scheme of alternating selective precipitation and dissolution, with the goal of isolating each type of cation into its own sample, where a definitive test for it can be performed.
3. (a) The solubility of a compound refers to the concentration of that compound in solution, either as a molarity or as a mass per unit volume. The solubility product constant is the equilibrium constant in terms of concentrations of ions, for the dissolution equilibrium, raised to their appropriate coefficients.
- (b) The common-ion effect describes the lowering of the solubility of a compound in a solution due to the presence of one of the ions of that compound in the solution. The salt effect describes the enhancement of the solubility of a compound in a solution due to the presence of a different type of ion in solution.
- (c) An ion pair is a close association of a cation and an anion in solution, whereas the ion product is the value obtained when the initial concentrations for the dissolved ions involved in the solubility equilibrium are inserted into the equilibrium constant expression.
4. (a)  $\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)$   $K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$
- (b)  $\text{Ra}(\text{IO}_3)_2(s) \rightleftharpoons \text{Ra}^{2+}(aq) + 2\text{IO}_3^-(aq)$   $K_{sp} = [\text{Ra}^{2+}] [\text{IO}_3^-]^2$
- (c)  $\text{Ni}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ni}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$   $K_{sp} = [\text{Ni}^{2+}]^3 [\text{PO}_4^{3-}]^2$
- (d)  $\text{PuO}_2\text{CO}_3(s) \rightleftharpoons \text{PuO}_2^{2+}(aq) + \text{CO}_3^{2-}(aq)$   $K_{sp} = [\text{PuO}_2^{2+}] [\text{CO}_3^{2-}]$
5. (a)  $K_{sp} = [\text{Fe}^{3+}] [\text{OH}^-]^3$   $\text{Fe}(\text{OH})_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq)$
- (b)  $K_{sp} = [\text{BiO}^+] [\text{OH}^-]$   $\text{BiOOH}(s) \rightleftharpoons \text{BiO}^+(aq) + \text{OH}^-(aq)$
- (c)  $K_{sp} = [\text{Hg}_2^{2+}] [\text{I}^-]^2$   $\text{Hg}_2\text{I}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{I}^-(aq)$
- (d)  $K_{sp} = [\text{Pb}^{2+}]^3 [\text{AsO}_4^{3-}]^2$   $\text{Pb}_3(\text{AsO}_4)_2(s) \rightleftharpoons 3\text{Pb}^{2+}(aq) + 2\text{AsO}_4^{3-}(aq)$
6. (a)  $\text{CrF}_3(s) \rightleftharpoons \text{Cr}^{3+}(aq) + 3\text{F}^-(aq)$   $K_{sp} = [\text{Cr}^{3+}] [\text{F}^-]^3 = 6.6 \times 10^{-11}$
- (b)  $\text{Au}_2(\text{C}_2\text{O}_4)_3(s) \rightleftharpoons 2\text{Au}^{3+}(aq) + 3\text{C}_2\text{O}_4^{2-}(aq)$   $K_{sp} = [\text{Au}^{3+}]^2 [\text{C}_2\text{O}_4^{2-}]^3 = 1 \times 10^{-10}$
- (c)  $\text{Cd}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Cd}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$   $K_{sp} = [\text{Cd}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 2.1 \times 10^{-33}$
- (d)  $\text{SrF}_2(s) \rightleftharpoons \text{Sr}^{2+}(aq) + 2\text{F}^-(aq)$   $K_{sp} = [\text{Sr}^{2+}] [\text{F}^-]^2 = 2.5 \times 10^{-9}$

7. Let  $s$  = solubility of each compound in moles of compound per liter of solution.

(a)  $K_{sp} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = (s)(s) = s^2 = 1.2 \times 10^{-10}$   $s = 1.1 \times 10^{-5} \text{ M}$

(b)  $K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2 = (s)(2s)^2 = 4s^3 = 4.0 \times 10^{-5}$   $s = 2.2 \times 10^{-2} \text{ M}$

(c)  $K_{sp} = [\text{Ce}^{3+}][\text{F}^-]^3 = (s)(3s)^3 = 27s^4 = 8 \times 10^{-16}$   $s = 7 \times 10^{-5} \text{ M}$

(d)  $K_{sp} = [\text{Mg}^{2+}]^3[\text{AsO}_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5 = 2.1 \times 10^{-20}$   $s = 4.5 \times 10^{-5} \text{ M}$

8. Again, let  $s$  = solubility of each compound in moles of solute per liter of solution.

(a)  $K_{sp} = [\text{Cs}^+][\text{MnO}_4^-] = (s)(s) = s^2 = (3.8 \times 10^{-3})^2 = 1.4 \times 10^{-5}$

(b)  $K_{sp} = [\text{Pb}^{2+}][\text{ClO}_2^-]^2 = (s)(2s)^2 = 4s^3 = 4(2.8 \times 10^{-3})^3 = 8.8 \times 10^{-8}$

(c)  $K_{sp} = [\text{In}^{3+}][\text{IO}_3^-]^3 = (s)(3s)^3 = 27s^4 = 27(1.0 \times 10^{-3})^4 = 2.7 \times 10^{-11}$

9. Statement (d) is correct. Consider the solubility equation:  $\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq})$ .

The stoichiometry of the dissolving reaction indicates that two  $\text{I}^-$  ions are formed for each  $\text{Pb}^{2+}$  ion, thus,  $[\text{Pb}^{2+}] = 0.5[\text{I}^-]$ . The relationship between  $K_{sp}$  and  $[\text{Pb}^{2+}]$  is  $[\text{Pb}^{2+}] = \sqrt[3]{K_{sp}/4}$ .

10. We let  $s$  = molar solubility of  $\text{Mg}(\text{OH})_2$  in moles solute per liter of solution.

(a)  $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (s)(2s)^2 = 4s^3 = 1.8 \times 10^{-11}$   $s = 1.7 \times 10^{-4} \text{ M}$

(b) Equation:  $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

Initial:  $0.0862 \text{ M}$   $\approx 0 \text{ M}$

Changes:  $+s \text{ M}$   $+2s \text{ M}$

Equil:  $(0.0862 + s) \text{ M}$   $2s \text{ M}$

$$K_{sp} = (0.0862 + s)(2s)^2 = 1.8 \times 10^{-11} \approx (0.0862)(2s)^2 = 0.34s^2 \quad s = 7.3 \times 10^{-6} \text{ M}$$

(c)  $[\text{OH}^-] = [\text{KOH}] = 0.0355 \text{ M}$

Equation:  $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

Initial:  $0 \text{ M}$   $0.0355 \text{ M}$

Changes:  $+s \text{ M}$   $+2s \text{ M}$

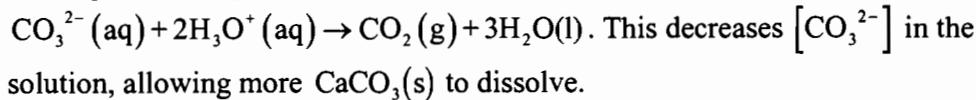
Equil:  $s \text{ M}$   $(0.0355 + 2s) \text{ M}$

$$K_{sp} = (s)(0.0355 + 2s)^2 = 1.8 \times 10^{-11} \approx (s)(0.0355)^2 = 0.0013s \quad s = 1.4 \times 10^{-8} \text{ M}$$

11. The solubility equilibrium is  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

(a) The addition of  $\text{Na}_2\text{CO}_3(\text{aq})$  produces  $\text{CO}_3^{2-}(\text{aq})$  in solution. This common ion suppresses the solubility of  $\text{CaCO}_3(\text{s})$ .

(b)  $\text{HCl}(\text{aq})$  is a strong acid that reacts with carbonate ion:



(c)  $\text{HSO}_4^-(\text{aq})$  is a moderately weak acid. It is strong enough to protonate carbonate ion, decreasing  $[\text{CO}_3^{2-}]$  and enhancing the solubility of  $\text{CaCO}_3(\text{s})$ , as the value of  $K_c$  indicates.



$$K_c = \frac{K_a(\text{HSO}_4^-)}{K_a(\text{HCO}_3^-)} = \frac{0.011}{4.7 \times 10^{-11}} = 2.3 \times 10^8$$

12. In each case, compute  $Q_{\text{sp}}$  and compare its value with the value of  $K_{\text{sp}}$ . If  $Q_{\text{sp}} > K_{\text{sp}}$ , a precipitate should form.

(a)  $Q_{\text{sp}} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = (0.0037)(0.0068) = 2.5 \times 10^{-5} > 3.5 \times 10^{-8} = K_{\text{sp}}$   
Precipitation should occur.

(b)  $Q_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (0.018)^2(0.0062) = 2.0 \times 10^{-6} < 1.4 \times 10^{-5} = K_{\text{sp}}$   
Precipitation is not expected to occur.

(c)  $\text{pOH} = 14.00 - 3.20 = 10.80 \quad [\text{OH}^-] = 10^{-10.80} = 1.6 \times 10^{-11} \text{ M}$   
 $Q_{\text{sp}} = [\text{Cr}^{3+}][\text{OH}^-]^3 = (0.038)(1.6 \times 10^{-11})^3 = 1.6 \times 10^{-34} < 6.3 \times 10^{-31} = K_{\text{sp}}$   
Precipitation is not expected to occur.

13. We use the  $K_{\text{sp}}$  expression to determine  $[\text{Ca}^{2+}]$  that can coexist with  $[\text{SO}_4^{2-}] = 0.750 \text{ M}$ .

$$K_{\text{sp}} = 9.1 \times 10^{-6} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = [\text{Ca}^{2+}](0.750 \text{ M}) \quad [\text{Ca}^{2+}] = \frac{9.1 \times 10^{-6}}{0.750 \text{ M}} = 1.2 \times 10^{-5} \text{ M}$$

$$\% \text{ unprecipitated} = \frac{1.2 \times 10^{-5} \text{ M}}{0.103 \text{ M}} \times 100\% = 0.012\% \text{ unprecipitated}$$

which is essentially

complete precipitation. Of course,  $[\text{SO}_4^{2-}]$  actually does decrease because some is consumed in the precipitation reaction. One mole of sulfate ion is removed from solution for each mole of calcium ion that precipitates, which amounts to 0.103 moles from each liter of solution. So, in this case  $[\text{SO}_4^{2-}] = 0.750 \text{ M} - 0.103 \text{ M} = 0.647 \text{ M}$ . But this increases the final  $[\text{Ca}^{2+}]$  only very slightly, to  $1.4 \times 10^{-5} \text{ M}$ , or 0.014% unprecipitated.

14. (a) Determine  $[I^-]$  when  $AgI$  just begins to precipitate, and  $[I^-]$  when  $PbI_2$  just begins to precipitate.

$$K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17} = (0.10)[I^-] \quad [I^-] = 8.5 \times 10^{-16} M$$

$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9} = (0.10)[I^-]^2 \quad [I^-] = \sqrt{\frac{7.1 \times 10^{-9}}{0.10}} = 2.7 \times 10^{-4} M$$

Since  $8.5 \times 10^{-16} M$  is less than  $2.7 \times 10^{-4} M$ ,  $AgI$  will precipitate before  $PbI_2$ .

- (b)  $[I^-] = 2.7 \times 10^{-4} M$  before the second cation,  $Pb^{2+}$ , begins to precipitate.

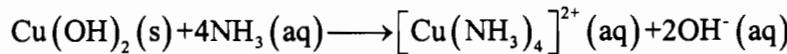
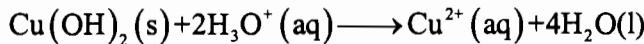
(c)  $K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17} = [Ag^+](2.7 \times 10^{-4}) \quad [Ag^+] = 3.1 \times 10^{-13} M$

- (d) Since  $[Ag^+]$  has decreased to much less than 0.1% of its initial value before  $PbI_2$  begins to precipitate, we conclude that  $Ag^+$  and  $Pb^{2+}$  can be separated by precipitation with iodide ion.

15.  $Mg(OH)_2(s)$  will be the most soluble in a solution of  $NH_4Cl(aq)$ .  $NH_4Cl$  will form an acidic solution, via the reaction  $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$  and this  $H_3O^+$  will react with  $OH^-$  ion:  $OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2H_2O(l)$  causing the solubility equilibrium to shift right.  $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ . Since  $NaOH$  has an ion in common with  $Mg(OH)_2$ , its use will actually decrease the solubility of  $Mg(OH)_2$ . Addition of  $Na_2CO_3$  will also decrease  $Mg(OH)_2$  solubility, through hydrolysis of the carbonate ion:  $H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$  followed by the common ion effect of  $OH^-$ .

16. (a)  $Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Br^-(aq) \rightarrow AgBr(s) + Na^+(aq) + NO_3^-(aq)$
- (b)  $Cu^{2+}(aq) + NO_3^-(aq) + H_3O^+(aq) + Cl^-(aq) \rightarrow$  no reaction
- (c)  $Fe^{2+}(aq) + H_2S$  (aq, in 0.3 M HCl)  $\rightarrow$  no reaction
- (d)  $Cu(OH)_2(s) + 4 NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 2 OH^-(aq)$
- (e)  $Fe^{3+}(aq) + 3 NH_3(aq) + 3 H_2O(l) \rightarrow Fe(OH)_3(s) + 3 NH_4^+(aq)$
- (f)  $Ag_2SO_4(s) + 4 NH_3(aq) \rightarrow 2[Ag(NH_3)_2]^+(aq) + SO_4^{2-}(aq)$
- (g)  $CaSO_3(s) + 2H_3O^+(aq) \rightarrow Ca^{2+}(aq) + 3H_2O(l) + SO_2(g)$

17.  $\text{Cu}(\text{OH})_2$  dissolves readily in acidic solutions  $[\text{HCl}(\text{aq}) \text{ and } \text{HNO}_3(\text{aq})]$  and ammoniacal solutions  $[\text{NH}_3(\text{aq})]$ . The net ionic equations for these two reactions are, respectively:



18. The best choice is  $\text{HCl}(\text{aq})$ .  $\text{AgCl}$  is insoluble in water, while  $\text{CuCl}_2$  is water soluble. On the other hand, both  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  form insoluble hydroxides and carbonates, so neither  $\text{NaOH}(\text{aq})$  nor  $(\text{NH}_4)_2\text{CO}_3(\text{aq})$  would be capable of separating these two cations.
19. Both  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$  form hydroxides, although  $\text{Cu}(\text{OH})_2 (K_{\text{sp}} = 2.2 \times 10^{-20})$  is much less soluble than  $\text{Mg}(\text{OH})_2 (K_{\text{sp}} = 1.8 \times 10^{-11})$ . Thus,  $\text{NaOH}(\text{aq})$  might be one choice to produce a precipitate of  $\text{Cu}(\text{OH})_2(\text{s})$  while leaving  $\text{Mg}^{2+}(\text{aq})$  in solution. A better choice, however, seems to be  $\text{NH}_3(\text{aq})$  in which  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  forms, ( $K_f = 1.1 \times 10^{13}$ ), while simultaneously creating an alkaline solution from which  $\text{Mg}(\text{OH})_2(\text{s})$  precipitates.

20. First we determine  $[\text{OH}^-]$  in this buffer solution.

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \frac{0.35\text{M}}{0.45\text{M}} = 4.63 \quad \text{pOH} = 14.00 - 4.63 = 9.37$$

$[\text{OH}^-] = 10^{-9.37} = 4.3 \times 10^{-10}\text{M}$ . Now, we compute the value of  $Q_{\text{sp}}$  for  $\text{Al}(\text{OH})_3$ .

$$Q_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^-]^3 = (0.275)(4.3 \times 10^{-10})^3 = 2.2 \times 10^{-29}$$

$Q_{\text{sp}} > 1.3 \times 10^{-33} = K_{\text{sp}}$  Precipitation should occur from this solution.

21. We first find the concentration of free metal ion. Then we determine the value of  $Q_{\text{sp}}$  for the precipitation reaction, and compare that value with the value of  $K_{\text{sp}}$  to determine whether precipitation will occur.



Initial:  $0\text{M}$   $1.05\text{M}$   $0.012\text{M}$

Changes:  $+x\text{M}$   $+2x\text{M}$   $-x\text{M}$

Equil:  $x\text{M}$   $(1.05 + 2x)\text{M}$   $(0.012 - x)\text{M}$

$$K_f = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 5.6 \times 10^{18} = \frac{0.012 - x}{x(1.05 + 2x)^2} \approx \frac{0.012}{(1.05)^2 x} \quad x = 1.9 \times 10^{-21}\text{M} = [\text{Ag}^+]$$

$$Q_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = (1.9 \times 10^{-21})(2.0) = 3.8 \times 10^{-21}$$

$Q_{\text{sp}} < 8.5 \times 10^{-17} = K_{\text{sp}}$  Precipitation should not occur.

22. We use the  $K_f$  expression to determine the concentration of free silver ion,  $[\text{Ag}^+]$ .

$$K_f = 1.6 \times 10^7 = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{1.6 \text{ M}}{[\text{Ag}^+](1.25 \text{ M})^2}; [\text{Ag}^+] = \frac{1.6}{1.6 \times 10^7 (1.25)^2} = 6.4 \times 10^{-8} \text{ M}$$

The  $K_{\text{sp}}$  expression is used to find the maximum  $[\text{Cl}^-]$  that can coexist with this  $[\text{Ag}^+]$ .

$$K_{\text{sp}} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = (6.4 \times 10^{-8} \text{ M})[\text{Cl}^-]; [\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{6.4 \times 10^{-8}} = 2.8 \times 10^{-3} \text{ M}.$$

## EXERCISES

### $K_{\text{sp}}$ and Solubility

23. We use the value of  $K_{\text{sp}}$  for each compound in determining the molar solubility in a saturated solution. In each case,  $s$  represents the molar solubility of the compound.

$$\text{AgCN} \quad K_{\text{sp}} = [\text{Ag}^+][\text{CN}^-] = (s)(s) = s^2 = 1.2 \times 10^{-16} \quad s = 1.1 \times 10^{-8} \text{ M}$$

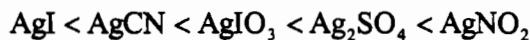
$$\text{AgIO}_3 \quad K_{\text{sp}} = [\text{Ag}^+][\text{IO}_3^-] = (s)(s) = s^2 = 3.0 \times 10^{-8} \quad s = 1.7 \times 10^{-4} \text{ M}$$

$$\text{AgI} \quad K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = (s)(s) = s^2 = 8.5 \times 10^{-17} \quad s = 9.2 \times 10^{-9} \text{ M}$$

$$\text{AgNO}_2 \quad K_{\text{sp}} = [\text{Ag}^+][\text{NO}_2^-] = (s)(s) = s^2 = 6.0 \times 10^{-4} \quad s = 2.4 \times 10^{-2} \text{ M}$$

$$\text{Ag}_2\text{SO}_4 \quad K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2(s) = 4s^3 = 1.4 \times 10^{-5} \quad s = 1.5 \times 10^{-2} \text{ M}$$

In order of increasing molar solubility, smallest to largest:



25. We determine  $[\text{F}^-]$  in saturated  $\text{CaF}_2$ , and from that value the concentration of  $\text{F}^-$  in ppm.

$$\text{For } \text{CaF}_2 \quad K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = (s)(2s)^2 = 4s^3 = 5.3 \times 10^{-9} \quad s = 1.1 \times 10^{-3} \text{ M}$$

The solubility in ppm is the number of grams of  $\text{CaF}_2$  in  $10^6$  g of solution. We assume a solution density of 1.00 g/mL.

$$\begin{aligned} \text{mass of F}^- &= 10^6 \text{ g soln} \times \frac{1 \text{ mL}}{1.00 \text{ g soln}} \times \frac{1 \text{ L soln}}{1000 \text{ mL}} \times \frac{1.1 \times 10^{-3} \text{ mol CaF}_2}{1 \text{ L soln}} \\ &\quad \times \frac{2 \text{ mol F}^-}{1 \text{ mol CaF}_2} \times \frac{19.0 \text{ g F}^-}{1 \text{ mol F}^-} = 42 \text{ g F}^- \end{aligned}$$

This is 42 times more concentrated than the optimum concentration of fluoride ion.  $\text{CaF}_2$  is, in fact, more soluble than is necessary. Its uncontrolled use might lead to excessive  $\text{F}^-$  in solution.

27. We first assume that the volume of the solution does not change appreciably when its temperature is lowered. Then we determine the mass of  $Mg(C_{16}H_{31}O_2)_2$  dissolved in each solution, recognizing that the molar solubility of  $Mg(C_{16}H_{31}O_2)_2$  equals the cube root of one fourth of its solubility product constant, since it is the only solute in the solution.

$$K_{sp} = 4s^3 \quad s = \sqrt[3]{K_{sp}/4}$$

$$\text{At } 50^\circ\text{C: } s = \sqrt[3]{4.8 \times 10^{-12}/4} = 1.1 \times 10^{-4} \text{ M; At } 25^\circ\text{C: } s = \sqrt[3]{3.3 \times 10^{-12}/4} = 9.4 \times 10^{-5} \text{ M}$$

$$\text{amount of } Mg(C_{16}H_{31}O_2)_2 (50^\circ\text{C}) = 0.965 \text{ L} \times \frac{1.1 \times 10^{-4} \text{ mol } Mg(C_{16}H_{31}O_2)_2}{1 \text{ L soln}} = 1.1 \times 10^{-4} \text{ mol}$$

$$\text{amount of } Mg(C_{16}H_{31}O_2)_2 (25^\circ\text{C}) = 0.965 \text{ L} \times \frac{9.4 \times 10^{-5} \text{ mol } Mg(C_{16}H_{31}O_2)_2}{1 \text{ L soln}} = 0.91 \times 10^{-4} \text{ mol}$$

mass of  $Mg(C_{16}H_{31}O_2)_2$  precipitated:

$$= (1.1 - 0.91) \times 10^{-4} \text{ mol} \times \frac{535.15 \text{ g } Mg(C_{16}H_{31}O_2)_2}{1 \text{ mol } Mg(C_{16}H_{31}O_2)_2} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 11 \text{ mg}$$

29. First we determine  $[I^-]$  in the saturated solution.

$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9} = (s)(2s)^2 = 4s^3 \quad s = 1.2 \times 10^{-3} \text{ M}$$

The  $AgNO_3$  reacts with the  $I^-$  in this saturated solution in the titration.

$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$  We determine the amount of  $Ag^+$  needed for this titration, and then  $[AgNO_3]$  in the titrant.

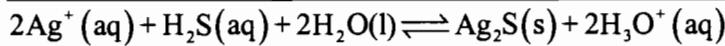
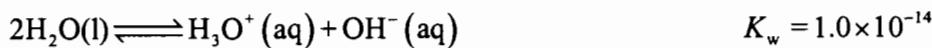
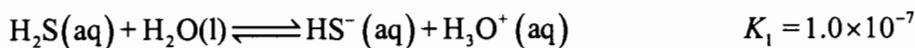
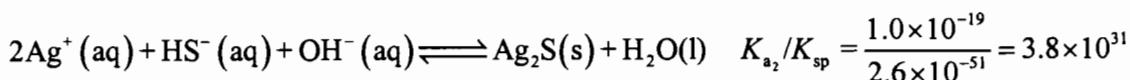
$$\text{moles } Ag^+ = 0.02500 \text{ L} \times \frac{1.2 \times 10^{-3} \text{ mol } PbI_2}{1 \text{ L soln}} \times \frac{2 \text{ mol } I^-}{1 \text{ mol } PbI_2} \times \frac{1 \text{ mol } Ag^+}{1 \text{ mol } I^-} = 6.0 \times 10^{-5} \text{ mol } Ag^+$$

$$AgNO_3 \text{ molarity} = \frac{6.0 \times 10^{-5} \text{ mol } Ag^+}{0.0133 \text{ L soln}} \times \frac{1 \text{ mol } AgNO_3}{1 \text{ mol } Ag^+} = 4.5 \times 10^{-3} \text{ M}$$

31. We use the ideal gas law to determine the moles of  $H_2S$  gas used.

$$n = \frac{PV}{RT} = \frac{\left(748 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) \times \left(30.4 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right)}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times (23 + 273) \text{ K}} = 1.23 \times 10^{-3} \text{ moles}$$

If we assume that all the  $H_2S$  is consumed in forming  $Ag_2S$ , we can compute the  $[Ag^+]$  in the  $AgBrO_3$  solution. This assumption is valid if the equilibrium constant for the cited reaction is large, which is the case, as shown below:



$$K_{\text{overall}} = (K_{\text{a}_2}/K_{\text{sp}})(K_1)(K_w) = (3.8 \times 10^{31})(1.0 \times 10^{-7})(1.0 \times 10^{-14}) = 3.8 \times 10^{10}$$

$$[\text{Ag}^+] = \frac{1.23 \times 10^{-3} \text{ mol H}_2\text{S}}{338 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \times \frac{2 \text{ mol Ag}^+}{1 \text{ mol H}_2\text{S}} = 7.28 \times 10^{-3} \text{ M}$$

$$\text{Then, for AgBrO}_3, \quad K_{\text{sp}} = [\text{Ag}^+][\text{BrO}_3^-] = (7.28 \times 10^{-3})^2 = 5.30 \times 10^{-5}$$

## The Common-Ion Effect

33. The presence of KI in a solution produces a significant  $[\text{I}^-]$  in the solution. Not as much AgI can dissolve in such a solution as in pure water, since the ion product,  $[\text{Ag}^+][\text{I}^-]$ , cannot exceed the value of  $K_{\text{sp}}$  (i.e. the  $\text{I}^-$  from the KI that dissolves represses the dissociation of AgI(s). In similar fashion, AgNO<sub>3</sub> produces a significant  $[\text{Ag}^+]$  in solution, again influencing the value of the ion product; not as much AgI can dissolve as in pure water.

35. Equation:  $\text{Ag}_2\text{SO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

$$\text{Original:} \quad 0 \text{ M} \quad 0.150 \text{ M}$$

$$\text{Add solid:} \quad +x \text{ M} \quad +x/2 \text{ M}$$

$$\text{Equil:} \quad x \text{ M} \quad (0.150 + x/2) \text{ M}$$

$$x = [\text{Ag}^+] = 9.7 \times 10^{-3} \text{ M}; \quad K_{\text{sp}} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (9.7 \times 10^{-3})^2 (0.150 + 0.0049) = 1.5 \times 10^{-5}$$

37. For PbI<sub>2</sub>,  $K_{\text{sp}} = 7.1 \times 10^{-9} = [\text{Pb}^{2+}][\text{I}^-]^2$

In a solution where  $1.5 \times 10^{-4}$  mol PbI<sub>2</sub> is dissolved,  $[\text{Pb}^{2+}] = 1.5 \times 10^{-4}$  M, and

$$[\text{I}^-] = 2[\text{Pb}^{2+}] = 3.0 \times 10^{-4} \text{ M}$$

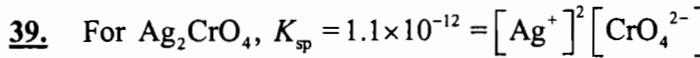
- Equation:  $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq})$

$$\text{Initial:} \quad 1.5 \times 10^{-4} \text{ M} \quad 3.0 \times 10^{-4} \text{ M}$$

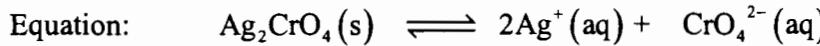
$$\text{Add lead(II):} \quad +x \text{ M}$$

$$\text{Equil:} \quad (0.00015 + x) \text{ M} \quad 0.00030 \text{ M}$$

$$K_{\text{sp}} = 7.1 \times 10^{-9} = (0.00015 + x)(0.00030)^2; (0.00015 + x) = 0.079; x = 0.079 \text{ M} = [\text{Pb}^{2+}]$$



In a solution where  $5.0 \times 10^{-8}$  mol  $\text{Ag}_2\text{CrO}_4$ /L is dissolved,  $[\text{CrO}_4^{2-}] = 5.0 \times 10^{-8}$  M and  $[\text{Ag}^+] = 1.0 \times 10^{-7}$  M



Initial:  $1.0 \times 10^{-7}$  M  $5.0 \times 10^{-8}$  M

Add chromate:  $+x$  M

Equil:  $1.0 \times 10^{-7}$  M  $(5.0 \times 10^{-8} + x)$  M

$$K_{\text{sp}} = 1.1 \times 10^{-12} = (1.0 \times 10^{-7})^2 (5.0 \times 10^{-8} + x); (5.0 \times 10^{-8} + x) = 1.1 \times 10^2$$

$$x = 1.1 \times 10^2 \text{ M} = [\text{CrO}_4^{2-}].$$

This is an impossibly high concentration to reach; we cannot lower the solubility of  $\text{Ag}_2\text{CrO}_4$  to  $5.0 \times 10^{-8}$  mol  $\text{Ag}_2\text{CrO}_4$ /L with  $\text{CrO}_4^{2-}$  as the common ion.

Let's consider using  $\text{Ag}^+$  as the common ion.



Initial:  $1.0 \times 10^{-7}$  M  $5.0 \times 10^{-8}$  M

Add silver(I) ion:  $+x$  M

Equil:  $(1.0 \times 10^{-7} + x)$  M  $5.0 \times 10^{-8}$  M

$$K_{\text{sp}} = 1.1 \times 10^{-12} = (1.0 \times 10^{-7} + x)^2 (5.0 \times 10^{-8}) \quad (1.0 \times 10^{-7} + x) = \sqrt{\frac{1.1 \times 10^{-12}}{5.0 \times 10^{-8}}} = 4.7 \times 10^{-3}$$

$$x = 4.7 \times 10^{-3} - 1.0 \times 10^{-7} = 4.7 \times 10^{-3} \text{ M} = [\text{I}^-]; \text{ This is an easy-to-reach concentration.}$$

41.  $[\text{Ca}^{2+}] = \frac{115 \text{ g Ca}^{2+}}{10^6 \text{ g soln}} \times \frac{1 \text{ mol Ca}^{2+}}{40.08 \text{ g Ca}^{2+}} \times \frac{1000 \text{ g soln}}{1 \text{ L soln}} = 2.87 \times 10^{-3} \text{ M}$

$$[\text{Ca}^{2+}][\text{F}^-]^2 = K_{\text{sp}} = 5.3 \times 10^{-9} = (2.87 \times 10^{-3})[\text{F}^-]^2 \quad [\text{F}^-] = 1.4 \times 10^{-3} \text{ M}$$

$$\text{ppm F}^- = \frac{1.4 \times 10^{-3} \text{ mol F}^-}{1 \text{ L soln}} \times \frac{19.00 \text{ g F}^-}{1 \text{ mol F}^-} \times \frac{1 \text{ L soln}}{1000 \text{ g}} \times 10^6 \text{ g soln} = 27 \text{ ppm}$$

## Criterion for Precipitation from Solution

43. We first determine  $[\text{Mg}^{2+}]$ , and then determine the value of  $Q_{\text{sp}}$  in order to compare it to the value of  $K_{\text{sp}}$ . We express molarity in millimoles per milliliter, entirely equivalent to moles per liter.

$$[\text{Mg}^{2+}] = \frac{22.5 \text{ mg MgCl}_2}{325 \text{ mL soln}} \times \frac{1 \text{ mmol MgCl}_2 \cdot 6\text{H}_2\text{O}}{203.3 \text{ mg MgCl}_2 \cdot 6\text{H}_2\text{O}} \times \frac{1 \text{ mmol Mg}^{2+}}{1 \text{ mmol MgCl}_2} = 3.41 \times 10^{-4} \text{ M}$$

$$Q_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2 = (3.41 \times 10^{-4})(0.035)^2 = 4.1 \times 10^{-7} > 3.7 \times 10^{-8} = K_{\text{sp}}$$

Thus, precipitation of  $\text{MgF}_2(\text{s})$  should occur from this solution.

45. We determine the  $[\text{OH}^-]$  needed to just initiate precipitation of  $\text{Cd}(\text{OH})_2$

$$K_{\text{sp}} = [\text{Cd}^{2+}][\text{OH}^-]^2 = 2.5 \times 10^{-14} = (0.0055 \text{ M})[\text{OH}^-]^2 \quad [\text{OH}^-] = \sqrt{\frac{2.5 \times 10^{-14}}{0.0055}} = 2.1 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(2.1 \times 10^{-6}) = 5.68 \quad \text{pH} = 14.00 - 5.68 = 8.32$$

$\text{Cd}(\text{OH})_2$  will precipitate from a solution with  $\text{pH} > 8.32$ .

47. (a) First we determine  $[\text{Cl}^-]$  due to the added  $\text{NaCl}$ .

$$[\text{Cl}^-] = \frac{0.10 \text{ mg NaCl}}{1.0 \text{ L soln}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} = 1.7 \times 10^{-6} \text{ M}$$

Then we determine the value of the ion product and compare it to the solubility product constant value.

$$Q_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (0.10)(1.7 \times 10^{-6}) = 1.7 \times 10^{-7} > 1.8 \times 10^{-10} = K_{\text{sp}}$$
 for  $\text{AgCl}$

Precipitation of  $\text{AgCl}(\text{s})$  should occur.

- (b) The  $\text{KBr}(\text{aq})$  is diluted on mixing, but the  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  are barely affected by dilution.

$$[\text{Br}^-] = 0.10 \text{ M} \times \frac{0.05 \text{ mL}}{0.05 \text{ mL} + 250 \text{ mL}} = 2 \times 10^{-5} \text{ M}$$

Now we determine  $[\text{Ag}^+]$  in a saturated  $\text{AgCl}$  solution.

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (s)(s) = s^2 = 1.8 \times 10^{-10} \quad s = 1.3 \times 10^{-5} \text{ M}$$

Then we determine the value of the ion product for  $\text{AgBr}$  and compare it to the solubility product constant value.

$$Q_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = (1.3 \times 10^{-5})(2 \times 10^{-5}) = 3 \times 10^{-10} > 5.0 \times 10^{-13} = K_{\text{sp}}$$
 for  $\text{AgBr}$

Precipitation of  $\text{AgBr}(\text{s})$  should occur.

- (c) The hydroxide ion is diluted by mixing the two solutions.

$$[\text{OH}^-] = 0.0150 \text{ M} \times \frac{0.05 \text{ mL}}{0.05 \text{ mL} + 3000 \text{ mL}} = 2 \times 10^{-7} \text{ M}$$

But the  $[\text{Mg}^{2+}]$  does not change significantly.

$$[\text{Mg}^{2+}] = \frac{2.0 \text{ mg Mg}^{2+}}{1.0 \text{ L soln}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Mg}^{2+}}{24.3 \text{ g Mg}} = 8.2 \times 10^{-5} \text{ M}$$

Then we determine the value of the ion product and compare it to the solubility product constant value.

$$Q_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (3 \times 10^{-7})(8.2 \times 10^{-5})^2 = 2 \times 10^{-15}$$

$Q_{\text{sp}} < 1.8 \times 10^{-11} = K_{\text{sp}}$  for  $\text{Mg}(\text{OH})_2$ . Thus, no precipitate forms.

49. We determine  $[\text{C}_2\text{O}_4^{2-}]$  in this solution. From key idea 3 in Section 17-6,

$$[\text{C}_2\text{O}_4^{2-}] = K_{\text{a}_2} = 5.4 \times 10^{-5}$$

$$Q_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (0.150)(5.4 \times 10^{-5}) = 8.1 \times 10^{-6} > 4 \times 10^{-9} = K_{\text{sp}}$$

Thus,  $\text{CaC}_2\text{O}_4$  should precipitate from this solution.

## Completeness of Precipitation

51. First determine that a precipitate forms. The solutions mutually dilute each other.

$$[\text{CrO}_4^{2-}] = 0.350 \text{ M} \times \frac{200.0 \text{ mL}}{200.0 \text{ mL} + 200.0 \text{ mL}} = 0.175 \text{ M}$$

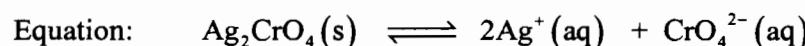
$$[\text{Ag}^+] = 0.0100 \text{ M} \times \frac{200.0 \text{ mL}}{200.0 \text{ mL} + 200.0 \text{ mL}} = 0.00500 \text{ M}$$

We determine the value of the ion product and compare it to the solubility product constant value.

$$Q_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (0.00500)^2 (0.175) = 4.4 \times 10^{-6} > 1.1 \times 10^{-12} = K_{\text{sp}}$$

$\text{Ag}_2\text{CrO}_4$  should precipitate.

Now, we assume that as much solid forms as possible, and then we approach equilibrium by dissolving that solid in a solution that contains the ion in excess.



Orig. soln:  $0.00500 \text{ M}$   $0.175 \text{ M}$

Form solid:  $-0.00500 \text{ M}$   $-0.00250 \text{ M}$

Not at equilibrium  $0 \text{ M}$   $0.173 \text{ M}$

Changes:	$+2x \text{ M}$	$+x \text{ M}$
Equil:	$2x \text{ M}$	$(0.173 + x) \text{ M}$

$$K_{sp} = [\text{Ag}^+]^+ [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12} = (2x)(0.173 + x) \approx (4x^2)(0.173)$$

$$x = \sqrt{\frac{1.1 \times 10^{-12}}{4 \times 0.173}} = 1.3 \times 10^{-6} \text{ M} \quad [\text{Ag}^+] = 2x = 2.6 \times 10^{-6} \text{ M}$$

$$\% \text{ Ag}^+ \text{ unprecipitated} = \frac{2.6 \times 10^{-6} \text{ M final}}{0.00500 \text{ M initial}} \times 100\% = 0.052\% \text{ unprecipitated}$$

- 53.** We first use the solubility product constant expression to determine  $[\text{Pb}^{2+}]$  in a solution with  $0.100 \text{ M Cl}^-$ .

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.6 \times 10^{-5} = [\text{Pb}^{2+}](0.100)^2 \quad [\text{Pb}^{2+}] = \frac{1.6 \times 10^{-5}}{(0.100)^2} = 1.6 \times 10^{-3} \text{ M}$$

$$\% \text{ unprecipitated} = \frac{1.6 \times 10^{-3} \text{ M}}{0.065 \text{ M}} \times 100\% = 2.5\%$$

Now, we want to determine what  $[\text{Cl}^-]$  must be maintained to keep  $[\text{Pb}^{2+}]_{\text{final}} = 1\%$ ;

$$[\text{Pb}^{2+}]_{\text{initial}} = 0.010 \times 0.065 \text{ M} = 6.5 \times 10^{-4} \text{ M}$$

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.6 \times 10^{-5} = (6.5 \times 10^{-4})[\text{Cl}^-]^2 \quad [\text{Cl}^-] = \sqrt{\frac{6 \times 10^{-5}}{6.5 \times 10^{-4}}} = 0.16 \text{ M}$$

## Fractional Precipitation

- 55.** The concentrations of silver ion that are cited in Example 19-7 range from  $5.0 \times 10^{-11} \text{ M}$  to  $1.0 \times 10^{-5} \text{ M}$ . These are incredibly small concentrations, especially the first. Virtually any  $\text{AgNO}_3(\text{aq})$  solution that we would prepare by usual means would have at least these concentrations. However, there is the matter of dilution to be considered. If one drop (0.05 mL) of  $\text{AgNO}_3(\text{aq})$  is added to 500.0 mL of solution, the  $[\text{Ag}^+]$  will decrease by a factor of  $10^4$ . Thus, we would have to begin with  $0.15 \text{ M AgNO}_3$  for this dilution to produce  $1.5 \times 10^{-5} \text{ M}$ . So we cannot be too careless and use extremely dilute  $\text{AgNO}_3(\text{aq})$ .

- 57.** Normally we would worry about the mutual dilution of the two solutions, but the values of the solubility product constants are so small that only a very small volume of  $0.50 \text{ M Pb}(\text{NO}_3)_2$  solution needs to be added, as we shall see.

- (a)** Since the two anions are present at the same concentration and they have the same type of formula (one anion per cation), the one forming the compound with the smallest  $K_{sp}$  value will precipitate first. Thus,  $\text{CrO}_4^{2-}$  is the first anion to precipitate.

- (b) At the point where  $\text{SO}_4^{2-}$  begins to precipitate, we have

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.6 \times 10^{-8} = [\text{Pb}^{2+}](0.010\text{M}); [\text{Pb}^{2+}] = \frac{1.6 \times 10^{-8}}{0.010} = 1.6 \times 10^{-6} \text{M}$$

Now we can test our original assumption, that only a very small volume of 0.50 M  $\text{Pb}(\text{NO}_3)_2$  solution has been added. We assume that we have 1.00 L of the original solution, the one with the two anions dissolved in it, and compute the volume of 0.50 M  $\text{Pb}(\text{NO}_3)_2$  that has to be added to achieve  $[\text{Pb}^{2+}] = 1.6 \times 10^{-6} \text{M}$

$$V_{\text{added}} = 1.00 \text{ L} \times \frac{1.6 \times 10^{-6} \text{ mol Pb}^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{1 \text{ mol Pb}^{2+}} \times \frac{1 \text{ L Pb}^{2+} \text{ soln}}{0.50 \text{ mol Pb}(\text{NO}_3)_2}$$

$$V_{\text{added}} = 3.2 \times 10^{-5} \text{ L Pb}^{2+} \text{ soln} = 0.0032 \text{ mL Pb}^{2+} \text{ soln}$$

This is less than one drop (0.05 mL) of the  $\text{Pb}^{2+}$  solution, clearly a very small volume.

- (c) The two anions are effectively separated if  $[\text{Pb}^{2+}]$  has not reached  $1.6 \times 10^{-6} \text{ M}$  when  $[\text{CrO}_4^{2-}]$  is reduced to 0.1% of its original value, that is, to

$$0.010 \times 10^{-3} \text{ M} = 1.0 \times 10^{-5} \text{ M} = [\text{CrO}_4^{2-}]$$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 2.8 \times 10^{-13} = [\text{Pb}^{2+}](1.0 \times 10^{-5})$$

$$[\text{Pb}^{2+}] = \frac{2.8 \times 10^{-13}}{1.0 \times 10^{-5}} = 2.8 \times 10^{-8} \text{ M}$$

Thus, the two anions can be effectively separated by fractional precipitation.

## Solubility and pH

- 59.** In each case we indicate whether the compound is more soluble in acid than in water. We write the net ionic equation for the reaction in which the solid dissolves in acid. Substances are more soluble in acid if either (1) an acid-base reaction occurs [as in (b-d)] or (2) a gas is produced, since escape of the gas from the reaction mixture causes the reaction to shift to the right.

- (a) Same:  $\text{KCl}$

- (b) Acid:  $\text{MgCO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

- (c) Acid:  $\text{FeS}(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{S}(\text{g})$

- (d) Acid:  $\text{Ca}(\text{OH})_2(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

- (e) Water:  $\text{C}_6\text{H}_5\text{COOH}$  is less soluble in acid, because of the  $\text{H}_3\text{O}^+$  common ion.

**61.** We determine  $[\text{Mg}^{2+}]$  in the solution.

$$[\text{Mg}^{2+}] = \frac{0.65 \text{ g Mg(OH)}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol Mg(OH)}_2}{58.3 \text{ g Mg(OH)}_2} \times \frac{1 \text{ mol Mg}^{2+}}{1 \text{ mol Mg(OH)}_2} = 0.011 \text{ M}$$

Then we determine  $[\text{OH}^-]$  in the solution, and its pH.

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.8 \times 10^{-11} = (0.011)[\text{OH}^-]^2; [\text{OH}^-] = \sqrt{\frac{1.8 \times 10^{-11}}{0.011}} = 4.0 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(4.0 \times 10^{-5}) = 4.40$$

$$\text{pH} = 14.00 - 4.40 = 9.60$$

**63. (a)** We calculate  $[\text{OH}^-]$  needed for precipitation.

$$K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^-]^3 = 1.3 \times 10^{-33} = (0.075 \text{ M})[\text{OH}^-]^3$$

$$[\text{OH}^-] = \sqrt[3]{\frac{1.3 \times 10^{-33}}{0.075}} = 2.6 \times 10^{-11} \text{ M} \quad \text{pOH} = -\log(2.6 \times 10^{-11}) = 10.59$$

$$\text{pH} = 14.00 - 10.59 = 3.41$$

**(b)** We use the Henderson–Hasselbalch equation to determine  $[\text{C}_2\text{H}_3\text{O}_2^-]$ .

$$\text{pH} = 3.41 = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{1.00 \text{ M}}$$

$$\log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{1.00 \text{ M}} = 3.41 - 4.74 = -1.33; \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{1.00 \text{ M}} = 10^{-1.33} = 0.047; [\text{C}_2\text{H}_3\text{O}_2^-] = 0.047 \text{ M}$$

This situation does not quite obey the guideline that the ratio of concentrations must fall in the range 0.10 to 10.0, but the resulting error is a small one in this circumstance.

$$\begin{aligned} \text{mass NaC}_2\text{H}_3\text{O}_2 &= 0.2500 \text{ L} \times \frac{0.047 \text{ mol C}_2\text{H}_3\text{O}_2^-}{1 \text{ L soln}} \times \frac{1 \text{ mol NaC}_2\text{H}_3\text{O}_2}{1 \text{ mol C}_2\text{H}_3\text{O}_2^-} \times \frac{82.03 \text{ g NaC}_2\text{H}_3\text{O}_2}{1 \text{ mol NaC}_2\text{H}_3\text{O}_2} \\ &= 0.96 \text{ g NaC}_2\text{H}_3\text{O}_2 \end{aligned}$$

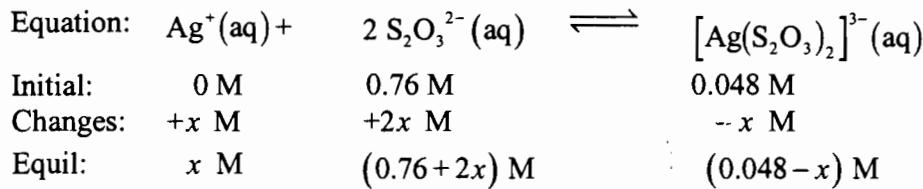
## Complex-Ion Equilibria

**65.** Lead(II) ion forms a complex ion with chloride ion. It forms no such complex ion with nitrate ion. The formation of this complex ion decreases the concentrations of free  $\text{Pb}^{2+}(\text{aq})$  and free  $\text{Cl}^-(\text{aq})$ . Thus, addition of  $\text{PbCl}_2$  will dissolve in the  $\text{HCl}(\text{aq})$  up until the value of the solubility product is exceeded.  $\text{Pb}^{2+}(\text{aq}) + 3\text{Cl}^-(\text{aq}) \rightleftharpoons [\text{PbCl}_3]^- (\text{aq})$

**67.** We substitute the given concentrations directly into the  $K_f$  expression.

$$K_f = \frac{[[\text{Cu}(\text{CN})_4]^{3-}]}{[\text{Cu}^+][\text{CN}^-]^4} = \frac{0.0500}{(6.1 \times 10^{-32})(0.80)^4} = 2.0 \times 10^{30}$$

**69.** We first find the concentration of free metal ion. Then we determine the value of  $Q_{sp}$  for the precipitation reaction, and compare its value with the value of  $K_{sp}$  to determine whether precipitation should occur.

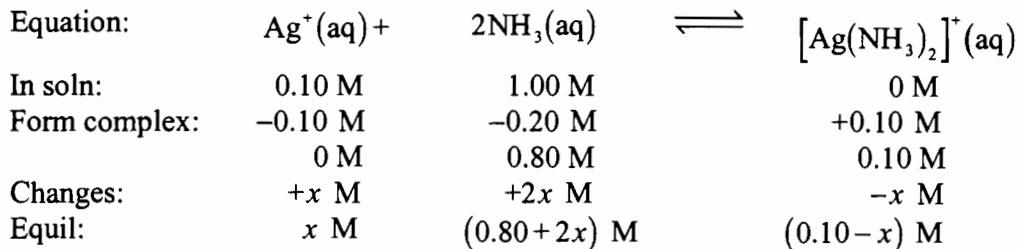


$$K_f = \frac{[[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2} = 1.7 \times 10^{13} = \frac{0.048-x}{x(0.76+2x)^2} \approx \frac{0.048}{(0.76)^2 x}; x = 4.9 \times 10^{-15} \text{ M} = [\text{Ag}^+]$$

$$Q_{sp} = [\text{Ag}^+][\text{I}^-] = (4.9 \times 10^{-15})(2.0) = 9.8 \times 10^{-15} > 8.5 \times 10^{-17} = K_{sp}.$$

Because  $Q_{sp} > K_{sp}$ , precipitation of  $\text{AgI}(\text{s})$  should occur.

**71.** We first compute the free  $[\text{Ag}^+]$  in the original solution. The size of the complex ion formation equilibrium constant indicates that the reaction lies to the far right, so we form as much complex ion as possible stoichiometrically.



$$K_f = 1.6 \times 10^7 = \frac{[[\text{Ag}(\text{NH}_3)_2]^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{0.10-x}{x(0.80+2x)^2} \approx \frac{0.10}{x(0.80)^2}; x = \frac{0.10}{1.6 \times 10^7 (0.80)^2} = 9.8 \times 10^{-9} \text{ M}.$$

Thus,  $[\text{Ag}^+] = 9.8 \times 10^{-9} \text{ M}$ . We next determine the  $[\text{I}^-]$  that can coexist in this solution without precipitation.

$$K_{sp} = [\text{Ag}^+][\text{I}^-] = 8.5 \times 10^{-17} = (9.8 \times 10^{-9})[\text{I}^-]; [\text{I}^-] = \frac{8.5 \times 10^{-17}}{9.8 \times 10^{-9}} = 8.7 \times 10^{-9} \text{ M}$$

Finally, we determine the mass of KI needed to produce this  $[I^-]$

$$\text{mass KI} = 1.00 \text{ L soln} \times \frac{8.7 \times 10^{-9} \text{ mol } I^-}{1 \text{ L soln}} \times \frac{1 \text{ mol KI}}{1 \text{ mol } I^-} \times \frac{166.0 \text{ g KI}}{1 \text{ mol KI}} = 1.4 \times 10^{-6} \text{ g KI}$$

## Precipitation and Solubilities of Metal Sulfides

**73.** We know that  $K_{\text{spa}} = 3 \times 10^7$  for MnS and  $K_{\text{spa}} = 6 \times 10^2$  for FeS. The metal sulfide will begin to precipitate when  $Q_{\text{spa}} = K_{\text{spa}}$ . Let us determine  $[H_3O^+]$  just necessary to form each precipitate. We assume that the solution is saturated with  $H_2S$ ,  $[H_2S] = 0.10 \text{ M}$ .

$$K_{\text{spa}} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2} \quad [H_3O^+] = \sqrt{\frac{[M^{2+}][H_2S]}{K_{\text{spa}}}} = \sqrt{\frac{(0.10 \text{ M})(0.10 \text{ M})}{3 \times 10^7}} = 1.8 \times 10^{-5} \text{ M for MnS}$$

$$[H_3O^+] = \sqrt{\frac{(0.10 \text{ M})(0.10 \text{ M})}{6 \times 10^2}} = 4.1 \times 10^{-3} \text{ M for FeS}$$

Thus, if the  $[H_3O^+]$  is maintained just a bit higher than  $1.8 \times 10^{-5} \text{ M}$ , FeS will precipitate and  $Mn^{2+}(\text{aq})$  will remain in solution. To determine if the separation is complete, we see whether  $[Fe^{2+}]$  has decreased to 0.1% or less of its original value when the solution is held at the aforementioned acidity. Let  $[H_3O^+] = 2.0 \times 10^{-5} \text{ M}$  and calculate  $[Fe^{2+}]$ .

$$K_{\text{spa}} = \frac{[Fe^{2+}][H_2S]}{[H_3O^+]^2} = 6 \times 10^2 = \frac{[Fe^{2+}](0.10 \text{ M})}{(2.0 \times 10^{-5} \text{ M})^2}; [Fe^{2+}] = \frac{(6 \times 10^2)(2.0 \times 10^{-5})^2}{0.10} = 2.4 \times 10^{-6} \text{ M}$$

$$\% Fe^{2+}(\text{aq}) \text{ remaining} = \frac{2.4 \times 10^{-6} \text{ M}}{0.10 \text{ M}} \times 100\% = 0.0024\% \quad \therefore \text{Separation is complete.}$$

**75. (a)** Calculate  $[H_3O^+]$  in the buffer solution with the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.74 + \log \frac{0.15 \text{ M}}{0.25 \text{ M}} = 4.52 \quad [H_3O^+] = 10^{-4.52} = 3.0 \times 10^{-5} \text{ M}$$

We use this information to calculate a value of  $Q_{\text{spa}}$  for MnS in this solution and then comparison of  $Q_{\text{spa}}$  with  $K_{\text{spa}}$  will allow us to decide if a precipitate will form.

$$Q_{\text{spa}} = \frac{[Mn^{2+}][H_2S]}{[H_3O^+]^2} = \frac{(0.15)(0.10)}{(3.0 \times 10^{-5})^2} = 1.7 \times 10^7 < 3 \times 10^7 = K_{\text{spa}} \text{ for MnS}$$

Precipitation of MnS(s) will not occur.

**(b)** We need to change  $[H_3O^+]$  so that

$$Q_{\text{spa}} = 3 \times 10^7 = \frac{(0.15)(0.10)}{[\text{H}_3\text{O}^+]^2}; \quad [\text{H}_3\text{O}^+] = \sqrt{\frac{(0.15)(0.10)}{3 \times 10^7}}$$

$$[\text{H}_3\text{O}^+] = 2.2 \times 10^{-5} \text{ M} \quad \text{pH} = 4.66$$

This is a more basic solution, which we can achieve by increasing the basic component of the buffer solution, the acetate ion. We find out the new acetate ion concentration with the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.66 = 4.74 + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{0.25 \text{ M}}$$

$$\log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{0.25 \text{ M}} = 4.66 - 4.74 = -0.08$$

$$\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{0.25 \text{ M}} = 10^{-0.08} = 0.83 \quad [\text{C}_2\text{H}_3\text{O}_2^-] = 0.83 \times 0.25 \text{ M} = 0.21 \text{ M}$$

## Qualitative Analysis

77. The purpose of adding hot water is to separate  $\text{Pb}^{2+}$  from  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ . Thus, the most important consequence of the absence of a valid test for the presence or absence of  $\text{Pb}^{2+}$ . In addition, if we add  $\text{NH}_3$  first,  $\text{PbCl}_2$  may form  $\text{Pb}(\text{OH})_2$ . If  $\text{Pb}(\text{OH})_2$  does form, it will be present with  $\text{Hg}_2\text{Cl}_2$  in the solid, although  $\text{Pb}(\text{OH})_2$  will not darken with added  $\text{NH}_3$ . Thus, we might falsely conclude that  $\text{Ag}^+$  is present, but not falsely conclude that  $\text{Hg}_2^{2+}$  is present.
79. (a)  $\text{Ag}^+$  and/or  $\text{Hg}_2^{2+}$  are probably present. Both of these cations form precipitates from an acidic solution of chloride ion.
- (b) We cannot tell whether  $\text{Mg}^{2+}$  is present or not. Both  $\text{MgS}$  and  $\text{MgCl}_2$  are water soluble.
- (c)  $\text{Pb}^{2+}$  possibly is absent; it is the only cation of those given which forms a precipitate in an acidic solution that is treated with  $\text{H}_2\text{S}$ , and no sulfide precipitate was formed.
- (d) We cannot tell whether  $\text{Fe}^{2+}$  is present or not.  $\text{FeS}$  will not precipitate from an acidic solution that is treated with  $\text{H}_2\text{S}$ ; the solution must be alkaline for a  $\text{FeS}$  precipitate to form.
- (a) and (c) are the valid conclusions.

## Feature Problems

- 100.**  $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$  in the saturated solution. Let us first determine the amount of  $\text{H}_3\text{O}^+$  in the 100.0 mL diluted effluent.  $\text{H}_3\text{O}^+(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{Na}^+(\text{aq})$

$$\begin{aligned} \text{mmol H}_3\text{O}^+ &= 100.0 \text{ mL} \times \frac{8.25 \text{ mL base}}{10.00 \text{ mL sample}} \times \frac{0.0105 \text{ mmol NaOH}}{1 \text{ mL base}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol NaOH}} \\ &= 0.866 \text{ mmol H}_3\text{O}^+(\text{aq}) \end{aligned}$$

Now we determine  $[\text{Ca}^{2+}]$  in the original 25.00 mL sample, remembering that  $2\text{H}_3\text{O}^+$  were produced for each  $\text{Ca}^{2+}$ .

$$[\text{Ca}^{2+}] = \frac{0.866 \text{ mmol H}_3\text{O}^+(\text{aq}) \times \frac{1 \text{ mmol Ca}^{2+}}{2 \text{ mmol H}_3\text{O}^+}}{25.00 \text{ mL}} = 0.0173 \text{ M}$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (0.0173)^2 = 3.0 \times 10^{-6}; \text{ Compared with } 9.1 \times 10^{-6} \text{ in Appendix D.}$$

- 101. (a)** We assume that there is little of each ion present in solution at equilibrium; that this is a simple stoichiometric calculation. This is true because we are titrating: we stop when just enough silver ion has been added.  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$

$$\begin{aligned} V &= 100.0 \text{ mL} \times \frac{29.5 \text{ mg Cl}^-}{1000 \text{ mL}} \times \frac{1 \text{ mmol Cl}^-}{35.45 \text{ mg Cl}^-} \times \frac{1 \text{ mmol Ag}^+}{1 \text{ mmol Cl}^-} \times \frac{1 \text{ mL}}{0.01000 \text{ mmol AgNO}_3} \\ &= 8.32 \text{ mL} \end{aligned}$$

- (b)** We first calculate the concentration of each ion as the consequence of dilution. Then we determine the  $[\text{Ag}^+]$  from the value of  $K_{\text{sp}}$

$$\text{initial } [\text{Ag}^+] = 0.01000 \text{ M} \times \frac{8.32 \text{ mL added}}{108.3 \text{ mL final volume}} = 7.68 \times 10^{-4} \text{ M}$$

$$\text{initial } [\text{Cl}^-] = \frac{29.5 \text{ mg Cl}^- \times \frac{1 \text{ mmol Cl}^-}{35.45 \text{ mg Cl}^-}}{1000 \text{ mL}} \times \frac{100.0 \text{ mL taken}}{108.3 \text{ mL final volume}} = 7.68 \times 10^{-4} \text{ M}$$

The slight excess of each ion will precipitate until the solubility constant is satisfied.

$$[\text{Ag}^+] = [\text{Cl}^-] = \sqrt{K_{\text{sp}}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

- (c) If we want  $\text{Ag}_2\text{CrO}_4$  to appear just when  $\text{AgCl}$  has completed precipitation,

$[\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M}$ . We determine  $[\text{CrO}_4^{2-}]$  from the  $K_{\text{sp}}$  expression.

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12} = (1.3 \times 10^{-5})^2 [\text{CrO}_4^{2-}];$$

$$[\text{CrO}_4^{2-}] = \frac{1.1 \times 10^{-12}}{(1.3 \times 10^{-5})^2} = 0.0065 \text{ M}$$

- (d) If  $[\text{CrO}_4^{2-}]$  were greater than just computed,  $\text{Ag}_2\text{CrO}_4$  would appear before all  $\text{Cl}^-$  had precipitated, leading to a false early endpoint. We would calculate a falsely low  $[\text{Cl}^-]$  of the original solution.

If  $[\text{CrO}_4^{2-}]$  were less than computed in part 3,  $\text{Ag}_2\text{CrO}_4$  would appear somewhat after all  $\text{Cl}^-$  had precipitated, leading one to conclude there was more  $\text{Cl}^-$  in solution than actually was the case.

- (e) If  $\text{Ag}^+$  were in the sample being titrated, it would react immediately with the  $\text{CrO}_4^{2-}$  in that sample, forming a red-orange precipitate. This precipitate would not be likely to dissolve so that  $\text{AgCl}$  could form. There would be no visual indication of the endpoint.

102. (a) We need to calculate the  $[\text{Mg}^{2+}]$  in a solution that is saturated with  $\text{Mg}(\text{OH})_2$ .

$$K_{\text{sp}} = 1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (s)(2s)^2 = 4s^3$$

$$s = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 1.7 \times 10^{-4} \text{ M} = [\text{Mg}^{2+}]$$

- (b) Even though water has been added to the original solution, it still is saturated (it is in equilibrium with the undissolved solid  $\text{Mg}(\text{OH})_2$ ).  $[\text{Mg}^{2+}] = 1.7 \times 10^{-4} \text{ M}$ .

- (c) Although  $\text{HCl}(\text{aq})$  reacts with  $\text{OH}^-$ , it will not react with  $\text{Mg}^{2+}$ . The solution simply is diluted.  $[\text{Mg}^{2+}] = 1.7 \times 10^{-4} \text{ M} \times \frac{100.0 \text{ mL initial volume}}{(100.0 + 500.0) \text{ mL final volume}} = 2.8 \times 10^{-5} \text{ M}$

- (d) In this instance, we have a dual dilution to a 275.0 mL total volume, followed by a common-ion problem.

$$\text{initial } [\text{Mg}^{2+}] = \frac{\left(25.00 \text{ mL} \times \frac{1.7 \times 10^{-4} \text{ mmol Mg}^{2+}}{1 \text{ mL}}\right) + \left(250.0 \text{ mL} \times \frac{0.065 \text{ mmol Mg}^{2+}}{1 \text{ mL}}\right)}{275.0 \text{ mL total volume}} \\ = 0.059 \text{ M}$$

$$\text{initial } [\text{OH}^-] = \frac{25.00 \text{ mL} \times \frac{1.7 \times 10^{-4} \text{ mmol Mg}^{2+}}{1 \text{ mL}} \times \frac{2 \text{ mmol OH}^-}{1 \text{ mmol Mg}^{2+}}}{275.0 \text{ mL total volume}} = 3.1 \times 10^{-5} \text{ M}$$

Let's see if precipitation occurs.

$$Q_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.059)(3.1 \times 10^{-5})^2 = 5.7 \times 10^{-11} > 1.8 \times 10^{-11} = K_{\text{sp}}$$

Precipitation barely occurs. If  $[\text{OH}^-]$  goes down by  $1.4 \times 10^{-5} \text{ M}$  (which means that  $[\text{Mg}^{2+}]$  drops by  $0.7 \times 10^{-5} \text{ M}$ ) then  $[\text{OH}^-] = 1.7 \times 10^{-5} \text{ M}$  and

$[\text{Mg}^{2+}] = (0.059 \text{ M} - 0.7 \times 10^{-5} \text{ M}) = 0.059 \text{ M}$ , then  $Q_{\text{sp}} < K_{\text{sp}}$  and precipitation will stop. Thus,  $[\text{Mg}^{2+}] = 0.059 \text{ M}$ .

- (e) Again we have a dual dilution, now to a 200.0 mL final volume, followed by a common-ion problem.

$$\text{initial } [\text{Mg}^{2+}] = \frac{50.00 \text{ mL} \times \frac{1.7 \times 10^{-4} \text{ mmol Mg}^{2+}}{1 \text{ mL}}}{200.0 \text{ mL total volume}} = 4.3 \times 10^{-5} \text{ M}$$

$$\text{initial } [\text{OH}^-] = 0.150 \text{ M} \times \frac{150.0 \text{ mL initial volume}}{200.0 \text{ mL total volume}} = 0.113 \text{ M}$$

Now it is evident that precipitation will occur. We determine the  $[\text{Mg}^{2+}]$  that can exist in solution with 0.113 M  $\text{OH}^-$ . It is clear that  $[\text{Mg}^{2+}]$  will drop dramatically to satisfy the  $K_{\text{sp}}$  expression but the larger value of  $[\text{OH}^-]$  will scarcely be affected.

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.8 \times 10^{-11} = [\text{Mg}^{2+}](0.0113 \text{ M})^2$$

$$[\text{Mg}^{2+}] = \frac{1.8 \times 10^{-11}}{(0.0113)^2} = 1.4 \times 10^{-9} \text{ M}$$

# CHAPTER 20

## SPONTANEOUS CHANGE: ENTROPY AND FREE ENERGY

### PRACTICE EXAMPLES

- 1A** In general,  $\Delta S > 0$  if  $\Delta n_{\text{gas}} > 0$ . This is because gases are very disordered compared to liquids or solids; (gases possess large entropies). Recall that  $\Delta n_{\text{gas}}$  is the difference between the sum of the stoichiometric coefficients of the gaseous products and a similar sum for the reactants.
- (a)  $\Delta n_{\text{gas}} = 2 + 0 - (2 + 1) = -1$ . One mole of gas is consumed here. We predict  $\Delta S < 0$ .
- (b)  $\Delta n_{\text{gas}} = 1 + 0 - 0 = +1$ . Since one mole of gas is produced, we predict  $\Delta S > 0$ .
- 1B** (a) The outcome is uncertain in the reaction between  $\text{ZnS(s)}$  and  $\text{Ag}_2\text{O(s)}$ . We have used  $\Delta n_{\text{gas}}$  to estimate the sign of entropy change. There is no gas involved in this reaction and thus our prediction is uncertain.
- (b) In the chlor-alkali process we are confident that entropy increases because two moles of gas have formed where none were originally present.

- 2A** For a vaporization,  $\Delta G_{\text{vap}}^\circ = 0 = \Delta H_{\text{vap}}^\circ - T\Delta S_{\text{vap}}^\circ$ . Thus,  $\Delta S_{\text{vap}}^\circ = \Delta H_{\text{vap}}^\circ / T_{\text{vap}}$ . We substitute the given values.  $\Delta S_{\text{vap}}^\circ = \frac{\Delta H_{\text{vap}}^\circ}{T_{\text{vap}}} = \frac{20.2 \text{ kJ mol}^{-1}}{(-29.79 + 273.15) \text{ K}} = 83.0 \text{ J mol}^{-1} \text{ K}^{-1}$
- 2B** For a phase change,  $\Delta G_{\text{tr}}^\circ = 0 = \Delta H_{\text{tr}}^\circ - T\Delta S_{\text{tr}}^\circ$ . Thus,  $\Delta H_{\text{tr}}^\circ = T\Delta S_{\text{tr}}^\circ$ . We substitute the given values.  $\Delta H_{\text{tr}}^\circ = T\Delta S_{\text{tr}}^\circ = (95.5 + 273.2) \text{ K} \times 1.09 \text{ J mol}^{-1} \text{ K}^{-1} = 402 \text{ J / mol}$
- 3A** The entropy change for the reaction is expressed in terms of the standard entropies of the reagents.

$$\begin{aligned}\Delta S^\circ &= 2S^\circ[\text{NH}_3(\text{g})] - S^\circ[\text{N}_2(\text{g})] - 3S^\circ[\text{H}_2(\text{g})] \\ &= 2 \times 192.5 \text{ J mol}^{-1} \text{ K}^{-1} - 191.6 \text{ J mol}^{-1} \text{ K}^{-1} - 3 \times 130.7 \text{ J mol}^{-1} \text{ K}^{-1} = -198.7 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

To form *one* mole of  $\text{NH}_3(\text{g})$ , the standard entropy change is  $-99.4 \text{ J mol}^{-1} \text{ K}^{-1}$

- 3B** The entropy change for the reaction is expressed in terms of the standard entropies of the reagents.

$$\Delta S^\circ = S^\circ[\text{NO(g)}] + S^\circ[\text{NO}_2\text{(g)}] - S^\circ[\text{N}_2\text{O}_3\text{(g)}]$$

$$\begin{aligned} 138.5 \text{ J mol}^{-1} \text{ K}^{-1} &= 210.8 \text{ J mol}^{-1} \text{ K}^{-1} + 240.1 \text{ J mol}^{-1} \text{ K}^{-1} - S^\circ[\text{N}_2\text{O}_3\text{(g)}] \\ &= 450.9 \text{ J mol}^{-1} \text{ K}^{-1} - S^\circ[\text{N}_2\text{O}_3\text{(g)}] \end{aligned}$$

$$S^\circ[\text{N}_2\text{O}_3\text{(g)}] = 450.9 \text{ J mol}^{-1} \text{ K}^{-1} - 138.5 \text{ J mol}^{-1} \text{ K}^{-1} = 312.4 \text{ J mol}^{-1} \text{ K}$$

- 4A** (a) Because  $\Delta n_{\text{gas}} = 2 - (1 + 3) = -2$  for the synthesis of ammonia, we would predict  $\Delta S < 0$  for the reaction. We already know that  $\Delta H < 0$ . Thus, the reaction falls into case 2, spontaneous at low temperatures and nonspontaneous at high temperatures.
- (b) For the formation of ethylene  $\Delta n_{\text{gas}} = 1 - (2 + 0) = -1$  and thus  $\Delta S < 0$ . We are given that  $\Delta H > 0$  and, thus, this reaction corresponds to case 4, a reaction that is nonspontaneous at all temperatures.
- 4B** (a) Because  $\Delta n_{\text{gas}} = +1$  for the decomposition of calcium carbonate, we would predict  $\Delta S > 0$  for the reaction, favoring the reaction at high temperatures. High temperatures also favor this endothermic ( $\Delta H^\circ > 0$ ) reaction.
- (b) Roasting ZnS(s) has  $\Delta n_{\text{gas}} = 2 - 3 = -1$  and, thus,  $\Delta S < 0$ . We are given that  $\Delta H < 0$ ; thus, this reaction corresponds to case 2, a reaction spontaneous at low temperatures, and nonspontaneous at high ones.

- 5A** The expression  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  is used with  $T = 298.15 \text{ K}$ .

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -1648 \text{ kJ} - 298.15 \text{ K} \times (-549.3 \text{ J K}^{-1}) \times (1 \text{ kJ} / 1000 \text{ J}) \\ &= -1648 \text{ kJ} + 163.8 \text{ kJ} = -1484 \text{ kJ} \end{aligned}$$

- 5B** We just need to substitute values from Appendix D into the supplied expression.

$$\begin{aligned} \Delta G^\circ &= 2\Delta G_f^\circ[\text{NO}_2\text{(g)}] - 2\Delta G_f^\circ[\text{NO(g)}] - \Delta G_f^\circ[\text{O}_2\text{(g)}] \\ &= 2 \times 51.31 \text{ kJ mol}^{-1} - 2 \times 86.55 \text{ kJ mol}^{-1} - 0.00 \text{ kJ mol}^{-1} = -70.48 \text{ kJ mol}^{-1} \end{aligned}$$

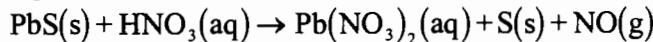
- 6A** Pressures of gases and molarities of solutes in aqueous solution appear in thermodynamic equilibrium constant expressions. Pure solids and liquids (including solvents) do not appear.

$$(a) \quad K_{\text{eq}} = \frac{P\{\text{SiCl}_4\}}{P\{\text{Cl}_2\}^2} = K_p$$

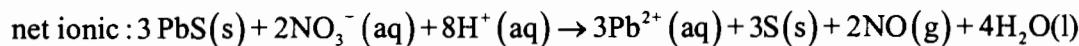
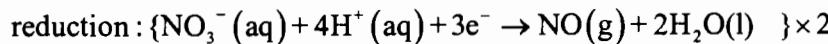
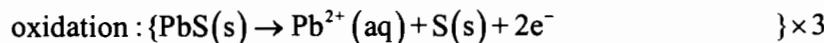
$$(b) \quad K_{\text{eq}} = \frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{P\{\text{Cl}_2\}}$$

$K_{\text{eq}} = K_p$  for (a) because all factors in the  $K_{\text{eq}}$  expression are gas pressures.

- 6B** We need the balanced chemical equation in order to write the equilibrium constant expression. We start by translating names into formulas.



The equation then is balanced with the ion-electron method.



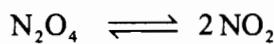
In writing the thermodynamic equilibrium constant, recall that

neither pure solids (PbS(s) and S(s)) nor pure liquids (H<sub>2</sub>O(l))

appear in the thermodynamic equilibrium constant expression. Note also that we have written H<sup>+</sup>(aq) here for brevity even though we understand that H<sub>3</sub>O<sup>+</sup>(aq) is the acidic species in aqueous solution.

$$K = \frac{[\text{Pb}^{2+}]^3 P\{\text{NO}\}^2}{[\text{NO}_3^-]^2 [\text{H}^+]^8}$$

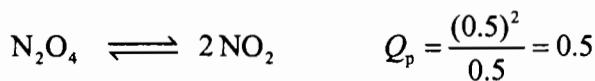
- 7A** Since the reaction is taking place at 298.15 K, we can use standard free energies of formation to calculate the standard free energy change for the reaction:



$$\Delta G^\circ = 2\Delta G_f^\circ[\text{NO}_2\text{(g)}] - \Delta G_f^\circ[\text{N}_2\text{O}_4\text{(g)}] = 2 \times 51.31 \text{ kJ/mol} - 97.89 \text{ kJ/mol} = +4.73 \text{ kJ}$$

$\Delta G_{\text{rxn}}^\circ = +4.73 \text{ kJ}$ . Thus, the reaction is non-spontaneous as written at 298.15 K.

- 7B** In order to answer this question we must calculate the reaction quotient and compare it to the  $K_p$  value for the reaction:



0.5 bar      0.5 bar

$$\Delta G_{\text{rxn}}^\circ = +4.73 \text{ kJ} = -RT\ln K_p; \quad 4.73 \text{ kJ/mol} = -(8.3145 \times 10^{-3} \text{ kJ/K}\cdot\text{mol})(298.15 \text{ K})\ln K_p$$

Therefore,  $K_p = 0.148$ . Since  $Q_p$  is greater than  $K_p$ , we can conclude that the reverse reaction will proceed spontaneously, i.e. NO<sub>2</sub> will spontaneously convert into N<sub>2</sub>O<sub>4</sub>.

- 8A** We first determine the value of  $\Delta G^\circ$  and then set  $\Delta G^\circ = -RT\ln K_{\text{eq}}$  to determine  $K_{\text{eq}}$ .

$$\Delta G = \Delta G_f^\circ[\text{Ag}^+\text{(aq)}] + \Delta G_f^\circ[\text{I}^-\text{(aq)}] - \Delta G_f^\circ[\text{AgI(s)}]$$

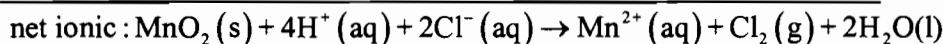
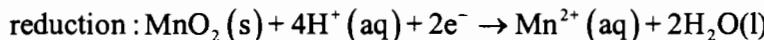
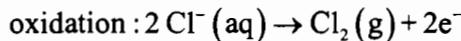
$$= [(77.11 - 51.57) - (-66.19)] \text{ kJ/mol} = +91.73$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = -\frac{-91.73 \text{ kJ/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -37.00$$

$$K_{\text{eq}} = e^{-37.00} = 8.5 \times 10^{-17}$$

This is precisely equal to the value for the  $K_{\text{sp}}$  listed in Appendix D.

**8B** We begin by translating names into formulas.  $\text{MnO}_2(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Cl}_2(\text{aq})$   
Then we produce a balanced net ionic equation with the ion-electron method.



Next we determine the value of  $\Delta G^\circ$  for the reaction and then the value of the equilibrium constant

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{Mn}^{2+}(\text{aq})] + \Delta G_f^\circ[\text{Cl}_2(\text{g})] + 2\Delta G_f^\circ[\text{H}_2\text{O}(\text{l})] \\ &\quad - \Delta G_f^\circ[\text{MnO}_2(\text{s})] - 4\Delta G_f^\circ[\text{H}^+(\text{aq})] - 2\Delta G_f^\circ[\text{Cl}^-(\text{aq})] \\ &= -228.1 \text{ kJ} + 0.0 \text{ kJ} + 2 \times (-237.1 \text{ kJ}) \\ &\quad - (-465.1 \text{ kJ}) - 4 \times 0.0 \text{ kJ} - 2 \times (-131.2 \text{ kJ}) = +25.2 \text{ kJ}\end{aligned}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{-(+25.2 \times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -10.17 \quad K_{\text{eq}} = e^{-10.17} = 4 \times 10^{-5}$$

Because the value of  $K_{\text{eq}}$  is so much smaller than unity, we do not expect an appreciable reaction.

**9A** We set equal the two expressions for  $\Delta G^\circ$  and solve for the absolute temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_{\text{eq}} \quad \Delta H^\circ = T\Delta S^\circ - RT\ln K_{\text{eq}} = T(\Delta S^\circ - R\ln K_{\text{eq}})$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K_{\text{eq}}} = \frac{-114.1 \times 10^3 \text{ J/mol}}{[-146.4 - 8.3145 \ln(150)] \text{ J mol}^{-1} \text{ K}^{-1}} = 607 \text{ K}$$

**9B** We expect the value of the equilibrium constant to increase as temperature decreases since this is an exothermic reaction and it should become more spontaneous (shift right) at lower temperatures. Thus, we expect  $K_{\text{eq}}$  to be larger than 1000, which is its value at  $4.3 \times 10^2 \text{ K}$ .

**(a)** The value of the equilibrium constant at  $25^\circ \text{C}$  is obtained directly from the value of  $\Delta G^\circ$ , since that value is also for  $25^\circ \text{C}$ . Note:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -77.1 \text{ kJ/mol} - 298.15 \text{ K}(-0.1213 \text{ kJ/mol} \cdot \text{K}) = -40.9 \text{ kJ/mol}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{-(40.9 \times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = 16.5 \quad K_{\text{eq}} = e^{16.5} = 1.5 \times 10^7$$

**(b)** First, we solve for  $\Delta G^\circ$  at  $75^\circ \text{C} = 348 \text{ K}$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -77.1 \frac{\text{kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} - \left( 348.15 \text{ K} \times \left( -121.3 \frac{\text{J}}{\text{mol K}} \right) \right) \\ &= -34.87 \times 10^3 \text{ J/mol}\end{aligned}$$

Then we use this value to obtain the value of the equilibrium constant, as in part (a).

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{-(-34.87 \times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 348.15 \text{ K}} = 12.05 \quad K_{\text{eq}} = e^{+12.05} = 1.7 \times 10^5$$

**10A** We use the value of  $K_p = 9.1 \times 10^2$  at 800 K and  $\Delta H^\circ = -1.8 \times 10^5 \text{ J / mol}$  in the van't Hoff equation.

$$\ln \frac{5.8 \times 10^{-2}}{9.1 \times 10^2} = \frac{-1.8 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{800 \text{ K}} - \frac{1}{T \text{ K}} \right) = -9.66; \quad \frac{1}{T} = \frac{1}{800} - \frac{9.66 \times 8.3145}{1.8 \times 10^5}$$

$$1/T = 1.25 \times 10^{-3} - 4.5 \times 10^{-4} = 8.0 \times 10^{-4} \quad T = 1240 \text{ K} \approx 970^\circ\text{C}$$

This temperature is an estimate because it is an extrapolated point beyond the range of the data supplied.

**10B** The temperature we are considering is  $235^\circ\text{C} = 508 \text{ K}$ . We use the value of  $K_p = 9.1 \times 10^2$  at 800 K and  $\Delta H^\circ = -1.8 \times 10^5 \text{ J/mol}$  in the van't Hoff equation.

$$\ln \frac{K_p}{9.1 \times 10^2} = \frac{-1.8 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{800 \text{ K}} - \frac{1}{508 \text{ K}} \right) = +15.6; \quad \frac{K_p}{9.1 \times 10^2} = e^{+15.6} = 6 \times 10^6$$

$$K_p = 6 \times 10^6 \times 9.1 \times 10^2 = 5 \times 10^9$$

## REVIEW QUESTIONS

- $\Delta S_{\text{univ}}$  is the symbol for the entropy change of the universe. If this quantity is positive, the associated process is spontaneous.
  - $\Delta G_f^\circ$  is the symbol for the standard free energy of formation, the free energy change of the standard state reaction when one mole of a substance is produced from stable forms of its elements.
  - $K_{\text{eq}}$  is the symbol for the thermodynamic equilibrium constant; in this expression gases are represented by pressures and solutes in aqueous solution by molarities.
- Absolute* molar entropy refers to the entropy of a substance relative to pure perfect crystals at 0 K, which have zero entropy.
  - A reversible process is one occurring in a state of dynamic equilibrium, one that can be made to reverse its direction when an infinitesimal change is made to some property of the system.
  - Trouton's rule states that the entropy change of vaporization approximates  $87 \text{ J mol}^{-1} \text{ K}^{-1}$ . It works well for nonpolar liquids.
  - An equilibrium constant is evaluated from tabulated thermodynamic data by combining values of  $\Delta G_f^\circ$  to obtain  $\Delta G_{\text{rxn}}^\circ$  and then using  $\Delta G_{\text{rxn}}^\circ = -RT \ln K_{\text{eq}}$ .

3. (a) A spontaneous process is one that occurs without (or sometimes in spite of) external intervention. A nonspontaneous process will only occur when some external agency operates on it.
- (b) The second law of thermodynamics places limitations on converting heat into work and on the spontaneous directions of processes. The third law of thermodynamics establishes a zero point for entropy.
- (c)  $\Delta G$  refers to the free energy change for any process, while  $\Delta G^\circ$  requires that both the initial and final states of the process are standard ones: gases at 1 atm pressure, aqueous solutes at 1 molar concentration, solids and liquids are pure and the temperature is 298 K.
4. (a) Increase in entropy because a gas has been created from a liquid, a condensed phase.
- (b) Decrease in entropy as a condensed phase, a solid, is created from a solid and a gas.
- (c) For this reaction we cannot be certain of the entropy change; even though the number of moles of gas produced is the same as the number that reacted, we cannot conclude that the entropy change is zero because not all gases have the same molar entropy.
- (d)  $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$  Decrease in entropy since five moles of gas with high entropy become only four moles of gas, with about the same quantity of entropy per mole.
5. (a) At 75° C, 1 mol  $\text{H}_2\text{O}$  (g, 1 atm) has a greater entropy than 1 mol  $\text{H}_2\text{O}$  (1iq., 1 atm) since a gas is much more disordered than a liquid.
- (b)  $50.0 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.8 \text{ g Fe}} = 0.896 \text{ mol Fe}$  has a higher entropy than 0.80 mol Fe, both (s) at 1 atm and 5° C, because entropy is an extensive property that depends on the amount of substance present.
- (c) 1 mol  $\text{Br}_2$  (1iq., 1 atm, 8° C) has a higher entropy than 1 mol  $\text{Br}_2$  (s, 1 atm, -8° C) because solids are more ordered substances than are liquids, and the temperature is higher.
- (d) 0.312 mol  $\text{SO}_2$  (g, 0.110 atm, 32.5° C) has a higher entropy than 0.284 mol  $\text{O}_2$  (g, 15.0 atm, 22.3° C) for at least three reasons. First, entropy is an extensive property that depends on the amount of substance present. Second, entropy increases with temperature. Third, entropy is greater at lower pressures. Furthermore, entropy generally is higher per mole for more complicated molecules.

**6.** We predict the sign of  $\Delta S$  based on the number of moles of gas in the balanced chemical equation; if  $\Delta n_{\text{gas}} < 0$ ,  $\Delta S$  is smaller than zero. If  $\Delta n_{\text{gas}} > 0$ ,  $\Delta S$  is greater than zero.

- (a)  $\Delta S > 0$  and  $\Delta H > 0$  This is case 3 in Table 20-1.
- (b)  $\Delta S < 0$  and  $\Delta H < 0$  This is case 2 in Table 20-1.
- (c)  $\Delta S > 0$  and  $\Delta H < 0$  This is case 1 in Table 20-1.
- (d)  $\Delta S < 0$  and  $\Delta H > 0$  This is case 4 in Table 20-1.

**7.** Answer (b) is correct. Br—Br bonds are broken in this reaction, meaning that it is endothermic, with  $\Delta H > 0$ . Since the number of moles of gas increases during the reaction,  $\Delta S > 0$ . And, because  $\Delta G = \Delta H - T \Delta S$ , this reaction is nonspontaneous at low temperatures where the  $\Delta H$  term predominates, with  $\Delta G > 0$ , and spontaneous at high temperatures where the  $T \Delta S$  term predominates, with  $\Delta G < 0$ .

**8.** Answer (d) is correct. A reaction that proceeds only through electrolysis is a reaction that is nonspontaneous. Such a reaction has  $\Delta G > 0$ .

**9.** Answer (d) is correct. Because  $\Delta G^\circ = -RT \ln K_{\text{eq}}$ , if  $\Delta G^\circ = 0$ ,  $\ln K_{\text{eq}} = 0$ , which means that  $K_{\text{eq}} = 1$ .

**10.**

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ [\text{NH}_4\text{Cl}(\text{s})] - \Delta H_f^\circ [\text{NH}_3(\text{g})] - \Delta H_f^\circ [\text{HCl}(\text{g})] \\ &= -314.4 \text{ kJ/mol} - (-46.11 \text{ kJ/mol} - 92.31 \text{ kJ/mol}) = -176.0 \text{ kJ/mol} \\ \Delta G^\circ &= \Delta G_f^\circ [\text{NH}_4\text{Cl}(\text{s})] - \Delta G_f^\circ [\text{NH}_3(\text{g})] - \Delta G_f^\circ [\text{HCl}(\text{g})] \\ &= -202.9 \text{ kJ/mol} - (-16.48 \text{ kJ/mol} - 95.30 \text{ kJ/mol}) = -91.1 \text{ kJ/mol} \\ \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-176.0 \text{ kJ/mol} + 91.1 \text{ kJ/mol}}{298 \text{ K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -285 \text{ J mol}^{-1}\end{aligned}$$

**11. (a)**

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ [\text{C}_2\text{H}_6(\text{g})] - \Delta G_f^\circ [\text{C}_2\text{H}_2(\text{g})] - 2\Delta G_f^\circ [\text{H}_2(\text{g})] \\ &= -32.82 \text{ kJ/mol} - 209.2 \text{ kJ/mol} - 2(0.00 \text{ kJ/mol}) = -242.0 \text{ kJ/mol}\end{aligned}$$

**(b)**

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ [\text{SO}_2(\text{g})] + \Delta G_f^\circ [\text{O}_2(\text{g})] - 2\Delta G_f^\circ [\text{SO}_3(\text{g})] \\ &= 2(-300.2 \text{ kJ/mol}) + 0.00 \text{ kJ/mol} - 2(-371.1 \text{ kJ/mol}) = +141.8 \text{ kJ/mol}\end{aligned}$$

**(c)**

$$\begin{aligned}\Delta G^\circ &= 3\Delta G_f^\circ [\text{Fe}(\text{s})] + 4\Delta G_f^\circ [\text{H}_2\text{O}(\text{g})] - \Delta G_f^\circ [\text{Fe}_3\text{O}_4(\text{s})] - 4\Delta G_f^\circ [\text{H}_2(\text{g})] \\ &= 3(0.00 \text{ kJ/mol}) + 4(-228.6 \text{ kJ/mol}) - (-1015 \text{ kJ/mol}) - 4(0.00 \text{ kJ/mol}) \\ &= 101 \text{ kJ/mol}\end{aligned}$$

**(d)**

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ [\text{Al}^{3+}(\text{aq})] + 3\Delta G_f^\circ [\text{H}_2(\text{g})] - 2\Delta G_f^\circ [\text{Al}(\text{s})] - 6\Delta G_f^\circ [\text{H}^+(\text{aq})] \\ &= 2(-485 \text{ kJ/mol}) + 3(0.00 \text{ kJ/mol}) - 2(0.00 \text{ kJ/mol}) - 6(0.00 \text{ kJ/mol}) \\ &= -970. \text{ kJ/mol}\end{aligned}$$

12. (a) This temperature is the melting point of  $I_2(s)$  at 1 atm pressure. From the phase diagram for iodine, we see that this process occurs at  $113.6^\circ C$ .
- (b)  $\Delta G^\circ = 0$  for  $I_2(s, 1 \text{ atm}) \rightleftharpoons I_2(l, 1 \text{ atm})$ . The point of the crossing of the lines in Figure 20-9 is the point where  $\Delta G^\circ = 0$ . In addition the melting point of a substance is the temperature where liquid and solid have the same free energy.

13. (a)  $\Delta H_{\text{vap}}^\circ = \frac{\Delta H_{\text{vap}}^\circ}{T_{\text{vap}}} = \frac{3.86 \text{ kcal/mol}}{-85.05^\circ C + 273.15 \text{ K}} \times \frac{1000 \text{ cal}}{1 \text{ kcal}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 85.9 \text{ J mol}^{-1} \text{ K}^{-1}$

(b)  $\Delta S_{\text{fus}}^\circ = \frac{\Delta H_{\text{fus}}^\circ}{T_{\text{fus}}} = \frac{27.05 \text{ cal/g}}{97.82^\circ C + 273.15 \text{ K}} \times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 7.014 \text{ J mol}^{-1} \text{ K}^{-1}$

14. (a)  $K_{\text{eq}} = \frac{P\{\text{NO}_2(g)\}^2}{P\{\text{NO}(g)\}^2 P\{\text{O}_2\}} = K_p$  (c)  $K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K_c$

(b)  $K_{\text{eq}} = P\{\text{SO}_2(g)\} = K_p$  (d)  $K_{\text{eq}} = P\{\text{H}_2\text{O}(g)\} P\{\text{CO}_2(g)\} = K_p$

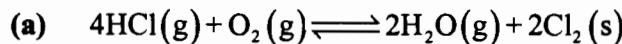
(e)  $K_{\text{eq}} = \frac{[\text{Mn}^{2+}(\text{aq})]P\{\text{Cl}_2(g)\}}{[\text{H}^+]^4 [\text{Cl}^-]^2}$ , neither  $K_p$  nor  $K_c$

15.  $\Delta G^\circ = -RT \ln K_p = -(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(1000 \text{ K}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \ln(2.45 \times 10^{-7}) = 127 \text{ kJ/mol}$

16. 
$$\begin{aligned} \Delta G^\circ &= 2\Delta G_f^\circ[\text{NO}(g)] - \Delta G_f^\circ[\text{N}_2\text{O}(g)] - 0.5\Delta G_f^\circ[\text{O}_2(g)] \\ &= 2(86.55 \text{ kJ/mol}) - (104.2 \text{ kJ/mol}) - 0.5(0.00 \text{ kJ/mol}) = 68.9 \text{ kJ/mol} \\ &= -RT \ln K_p = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln K_p \end{aligned}$$

$$\ln K_p = -\frac{68.9 \text{ kJ/mol}}{8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = -27.8 \quad K_p = e^{-27.8} = 8 \times 10^{-13}$$

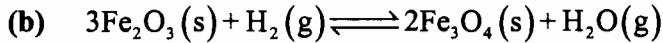
17. We first balance the chemical equation and then calculate the value of  $\Delta G^\circ$  with data from Appendix D, and finally calculate the value of  $K_{\text{eq}}$  with the use of  $\Delta G^\circ = -RT \ln K$ .



$$\begin{aligned} \Delta G^\circ &= 2\Delta G_f^\circ[\text{H}_2\text{O}(g)] + 2\Delta G_f^\circ[\text{Cl}_2(g)] - 4\Delta G_f^\circ[\text{HCl}(g)] - \Delta G_f^\circ[\text{O}_2(g)] \\ &= 2 \times (-228.6 \text{ kJ/mol}) + 2 \times 0 \text{ kJ/mol} - 4 \times (-95.30 \text{ kJ/mol}) - 0 \text{ kJ/mol} \end{aligned}$$

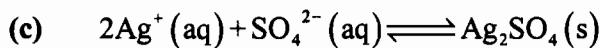
$$\Delta G^\circ = -76.0 \text{ kJ/mol}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{+76.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = +30.7 \quad K_{\text{eq}} = e^{+30.7} = 2 \times 10^{13}$$



$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ[\text{Fe}_3\text{O}_4(\text{s})] + \Delta G_f^\circ[\text{H}_2\text{O}(\text{g})] - 3\Delta G_f^\circ[\text{Fe}_2\text{O}_3(\text{s})] - \Delta G_f^\circ[\text{H}_2(\text{g})] \\ &= 2 \times (-1015 \text{ kJ/mol}) - 228.6 \text{ kJ/mol} - 3 \times (-742.2 \text{ kJ/mol}) - 0.00 \text{ kJ/mol} \\ &= -32 \text{ kJ/mol}\end{aligned}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{32 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 13; \quad K_{\text{eq}} = e^{+13} = 4 \times 10^5$$



$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{Ag}_2\text{SO}_4(\text{s})] - 2\Delta G_f^\circ[\text{Ag}^+(\text{aq})] - \Delta G_f^\circ[\text{SO}_4^{2-}(\text{aq})] \\ &= -618.4 \text{ kJ/mol} - 2 \times 77.11 \text{ kJ/mol} - (-744.5 \text{ kJ/mol}) = -28.1 \text{ kJ/mol}\end{aligned}$$

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT} = \frac{28.1 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 11.3; \quad K_{\text{eq}} = e^{+11.3} = 8 \times 10^4$$

18.  $\Delta S^\circ = S^\circ\{\text{CO}_2(\text{g})\} + S^\circ\{\text{H}_2(\text{g})\} - S^\circ\{\text{CO}(\text{g})\} - S^\circ\{\text{H}_2\text{O}(\text{g})\}$   
 $= 213.7 \text{ J mol}^{-1} \text{ K}^{-1} + 130.7 \text{ J mol}^{-1} \text{ K}^{-1} - 197.7 \text{ J mol}^{-1} \text{ K}^{-1} - 188.8 \text{ J mol}^{-1} \text{ K}^{-1}$   
 $= -42.1 \text{ J mol}^{-1} \text{ K}^{-1}$

19. We only compute a value of  $\Delta G^\circ$  for each reaction. If this value is significantly less than zero, we conclude that the reaction is expected to occur to some extent at 298.15 K.

(a)  $\Delta G^\circ = 2\Delta G_f^\circ[\text{O}_3(\text{g})] - 3\Delta G_f^\circ[\text{O}_2(\text{g})] = 2(163.2 \text{ kJ/mol}) - 3(0.00 \text{ kJ/mol})$   
 $= 326.4 \text{ kJ/mol}$  Does not occur to a significant extent.

(b)  $\Delta G^\circ = 2\Delta G_f^\circ[\text{NO}_2(\text{g})] - \Delta G_f^\circ[\text{N}_2\text{O}_4(\text{g})] = 2(51.31 \text{ kJ/mol}) - 97.89 \text{ kJ/mol}$   
 $= 4.73 \text{ kJ/mol}$  Occurs only to a very small extent.

(c)  $\Delta G^\circ = 2\Delta G_f^\circ[\text{BrCl}(\text{g})] - \Delta G_f^\circ[\text{Cl}_2(\text{g})] - \Delta G_f^\circ[\text{Br}_2(\text{l})]$   
 $= 2(-0.98 \text{ kJ/mol}) - 0.00 \text{ kJ/mol} - 0.00 \text{ kJ/mol}$   
 $= -2.0 \text{ kJ/mol}$  Occurs to some small extent.

We could have predicted the first and last result by simply looking at the free energy of formation of product. The small size of the result in the other case indicates that some calculation is necessary.

$$20. \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ \quad T = \frac{\Delta H^\circ - \Delta G^\circ}{\Delta S^\circ}$$

$$T = \frac{-24.8 \times 10^3 \text{ J} - (-45.5 \times 10^3 \text{ J})}{15.2 \text{ J/K}} = 1.36 \times 10^3 \text{ K}$$

$$21. \quad (a) \quad \Delta G^\circ = 2\Delta G_f^\circ [\text{N}_2\text{O}_5(\text{g})] - 2\Delta G_f^\circ [\text{N}_2\text{O}_4(\text{g})] - \Delta G_f^\circ [\text{O}_2(\text{g})] \\ = 2(115.1 \text{ kJ/mol}) - 2(97.89 \text{ kJ/mol}) - (0.00 \text{ kJ/mol}) = 34.4 \text{ kJ/mol}$$

$$(b) \quad \Delta G^\circ = -RT \ln K_p \quad \ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{34.4 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = -13.9 \\ K_p = e^{-13.9} = 9 \times 10^{-7}$$

$$22. \quad (a) \quad \Delta S^\circ = S^\circ [\text{Na}_2\text{CO}_3(\text{s})] + S^\circ [\text{H}_2\text{O}(\text{l})] + S^\circ [\text{CO}_2(\text{g})] - 2S^\circ [\text{NaHCO}_3(\text{s})] \\ = 135.0 \frac{\text{J}}{\text{K mol}} + 69.91 \frac{\text{J}}{\text{K mol}} + 213.7 \frac{\text{J}}{\text{K mol}} - 2 \left( 101.7 \frac{\text{J}}{\text{K mol}} \right) = 215.2 \frac{\text{J}}{\text{K mol}}$$

$$(b) \quad \Delta H^\circ = \Delta H_f^\circ [\text{Na}_2\text{CO}_3(\text{s})] + \Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] + \Delta H_f^\circ [\text{CO}_2(\text{g})] - 2\Delta H_f^\circ [\text{NaHCO}_3(\text{s})] \\ = -1131 \frac{\text{kJ}}{\text{mol}} - 285.8 \frac{\text{kJ}}{\text{mol}} - 393.5 \frac{\text{kJ}}{\text{mol}} - 2 \left( -950.8 \frac{\text{kJ}}{\text{mol}} \right) = +91 \frac{\text{kJ}}{\text{mol}}$$

$$(c) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 91 \text{ kJ/mol} - (298 \text{ K})(215.2 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ = 91 \text{ kJ/mol} - 64.13 \text{ kJ/mol} = 27 \text{ kJ/mol}$$

$$(d) \quad \Delta G^\circ = -RT \ln K_{\text{eq}} \quad \ln K_{\text{eq}} = -\frac{\Delta G^\circ}{RT} = -\frac{27 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = -10.9 \\ K_{\text{eq}} = e^{-10.9} = 2 \times 10^{-5}$$

$$23. \quad (a) \quad \Delta S^\circ = S^\circ [\text{CH}_3\text{CH}_2\text{OH}(\text{g})] + S^\circ [\text{H}_2\text{O}(\text{g})] - S^\circ [\text{CO}(\text{g})] - 2S^\circ [\text{H}_2(\text{g})] - S^\circ [\text{CH}_3\text{OH}(\text{g})] \\ = 282.7 \frac{\text{J}}{\text{K mol}} + 188.8 \frac{\text{J}}{\text{K mol}} - 197.7 \frac{\text{J}}{\text{K mol}} - 2 \left( 130.7 \frac{\text{J}}{\text{K mol}} \right) - 239.8 \frac{\text{J}}{\text{K mol}} \\ = -227.4 \frac{\text{J}}{\text{K mol}}$$

$$\Delta H^\circ = \Delta H_f^\circ [\text{CH}_3\text{CH}_2\text{OH}(\text{g})] + \Delta H_f^\circ [\text{H}_2\text{O}(\text{g})] - \Delta H_f^\circ [\text{CO}(\text{g})] - 2\Delta H_f^\circ [\text{H}_2(\text{g})] - \Delta H_f^\circ [\text{CH}_3\text{OH}(\text{g})] \\ = -235.1 \frac{\text{kJ}}{\text{mol}} - 241.8 \frac{\text{kJ}}{\text{mol}} - \left( -110.5 \frac{\text{kJ}}{\text{mol}} \right) - 2 \left( 0.00 \frac{\text{kJ}}{\text{mol}} \right) - \left( -200.7 \frac{\text{kJ}}{\text{mol}} \right) = -165.7 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G^\circ = -165.7 \frac{\text{kJ}}{\text{mol}} - (298 \text{ K}) \left( -227.4 \times 10^{-3} \frac{\text{kJ}}{\text{K mol}} \right) = -165.4 \frac{\text{kJ}}{\text{mol}} + 67.8 \frac{\text{kJ}}{\text{mol}} = -97.9 \frac{\text{kJ}}{\text{mol}}$$

- (b)  $\Delta H^\circ < 0$  for this reaction; it is favored at low temperatures. And because  $\Delta n_{\text{gas}} = +2 - 4 = -2$ , which is less than zero, the reaction is favored at high pressures.
- (c) We assume that neither  $\Delta S^\circ$  nor  $\Delta H^\circ$  varies significantly with temperature. Then we compute a value for  $\Delta G^\circ$  at 750 K. From this value of  $\Delta G^\circ$ , we compute a value for  $K_p$ .

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -165.7 \text{ kJ/mol} - (750. \text{ K})(-227.4 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ &= -165.7 \text{ kJ/mol} + 170.6 \text{ kJ/mol} = +4.9 \text{ kJ/mol} = -RT \ln K_p\end{aligned}$$

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{4.9 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 750. \text{ K}} = -0.79, \quad K_p = e^{-0.79} = 0.5$$

24. We use the van't Hoff equation with  $\Delta H^\circ = -1.8 \times 10^5 \text{ J/mol}$ ,  $T_1 = 800. \text{ K}$ ,  $T_2 = 100.^\circ \text{ C} = 373 \text{ K}$ , and  $K_1 = 9.1 \times 10^2$ .

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{-1.8 \times 10^5 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{800 \text{ K}} - \frac{1}{373 \text{ K}} \right) = 31$$

$$\frac{K_2}{K_1} = e^{31} = 2.9 \times 10^{13} = \frac{K_2}{9.1 \times 10^2} \quad K_2 = (2.9 \times 10^{13})(9.1 \times 10^2) = 3 \times 10^{16}$$

## EXERCISES

### Spontaneous Change, Entropy, and Disorder

25. (a) The freezing of ethanol involves a *decrease* in the entropy of the system, since solids are more ordered than liquids, in general.
- (b) The sublimation of dry ice involves converting a quite ordered solid into a very disordered vapor. Thus, the entropy of the system *increases* substantially.
- (c) The burning of rocket fuel involves converting a somewhat ordered liquid fuel into the highly disordered mixture of the gaseous combustion products. The entropy of the system *increases* substantially.
27. The first law of thermodynamics states that energy is neither created nor destroyed (thus, "The energy of the universe is constant"). A consequence of the second law of thermodynamics is that entropy of the universe increases for all spontaneous, that is, naturally occurring, processes (and therefore, "the entropy of the universe increases toward a maximum").

- 29.** (a) Negative; A liquid (moderate entropy) combines with a solid to form another solid.  
 (b) Positive; One mole of high entropy gas forms where no gas was present before.  
 (c) Positive; One mole of high entropy gas forms where no gas was present before.  
 (d) Uncertain; Same number of moles of gaseous products as of gaseous reactants.  
 (e) Negative; Two moles of gas (and a solid) combine to form just one mole of gas.

## Phase Transitions

**31.** (a)  $\Delta H_{\text{vap}}^{\circ} = \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(\text{g})] - \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(\text{l})] = -241.8 \text{ kJ/mol} - (-285.8 \text{ kJ/mol})$   
 $= +44.0 \text{ kJ/mol}$

$$\Delta S_{\text{vap}}^{\circ} = S^{\circ}[\text{H}_2\text{O}(\text{g})] - S^{\circ}[\text{H}_2\text{O}(\text{l})] = 188.8 \text{ J mol}^{-1} \text{ K}^{-1} - 69.91 \text{ J mol}^{-1} \text{ K}^{-1}$$
 $= 118.9 \text{ J mol}^{-1} \text{ K}^{-1}$

There is an alternate, but incorrect, method of obtaining  $\Delta S_{\text{vap}}^{\circ}$ .

$$\Delta S_{\text{vap}}^{\circ} = \frac{\Delta H_{\text{vap}}^{\circ}}{T} = \frac{44.0 \times 10^3 \text{ J/mol}}{298.15 \text{ K}} = 148 \text{ J mol}^{-1} \text{ K}^{-1}$$

This method is invalid because the temperature in the denominator of the equation must be the temperature at which the liquid-vapor transition is at equilibrium. Liquid water and water vapor at 1 atm pressure (standard state, indicated by  $^{\circ}$ ) are in equilibrium only at  $100^{\circ} \text{ C} = 373 \text{ K}$ .

- (b) The reason why  $\Delta H_{\text{vap}}^{\circ}$  is different from its value at  $100^{\circ} \text{ C}$  has to do with the heat required to bring the reactants and products down to 298 K from 373 K. The specific heat of liquid water is higher than the heat capacity of steam. Thus, more heat is given off (this is negative heat, an exothermic process) by lowering the temperature of the liquid water from  $100^{\circ} \text{ C}$  to  $25^{\circ} \text{ C}$  than is given off by lowering the temperature of the same amount of steam. Another way to think of this is that hydrogen bonding is more disrupted in water at  $100^{\circ} \text{ C}$  than at  $25^{\circ} \text{ C}$  (because the molecules are in rapid—thermal—motion), and hence, there is not as much energy needed to convert liquid to vapor.

The reason why  $\Delta S_{\text{vap}}^{\circ}$  has a larger value at  $25^{\circ} \text{ C}$  than at  $100^{\circ} \text{ C}$  has to do with disorder. A vapor at 1 atm pressure (the case at both temperatures) has about the same entropy. On the other hand, liquid water is more disordered at higher temperatures since more of the hydrogen bonds are disrupted by thermal motion. (The hydrogen bonds are totally disrupted in the two vapors).

- 33.** Trouton's rule is obeyed most closely by liquids that do not have a high degree of order within the liquid. In both HF and  $\text{CH}_3\text{OH}$ , hydrogen bonds create considerable order within the liquid. In  $\text{C}_6\text{H}_5\text{CH}_3$ , the only attractive forces are non-directional London forces, which cause the molecules to attract each other, but have no preferred orientation as

hydrogen bonds do. Thus, of the three choices, liquid  $C_6H_5CH_3$  would most closely follow Trouton's rule.

35. The liquid water-gaseous water equilibrium  $H_2O(l, 0.50 \text{ atm}) \rightleftharpoons H_2O(g, 0.50 \text{ atm})$  can only be established at one temperature, namely the boiling point for water under 0.50 atm external pressure. We can estimate the boiling point for water under 0.50 atm external pressure by using the Clausius-Clapeyron equation:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}^{\circ}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

We know that at 373 K, the pressure of water vapor is 1.00 atm. Let's make  $P_1 = 1.00 \text{ atm}$ ,  $P_2 = 0.50 \text{ atm}$  and  $T_1 = 373 \text{ K}$ . Thus, the boiling point under 0.50 atm pressure is  $T_2$ . To find  $T_2$  we simply insert the appropriate information into the Clausius-Clapeyron equation:

$$\ln \frac{0.50 \text{ atm}}{1.00 \text{ atm}} = \frac{40.7 \text{ kJ mol}^{-1}}{8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{373 \text{ K}} - \frac{1}{T_2} \right)$$

$$-1.416 \times 10^{-4} \text{ K} = \left( \frac{1}{373 \text{ K}} - \frac{1}{T_2} \right)$$

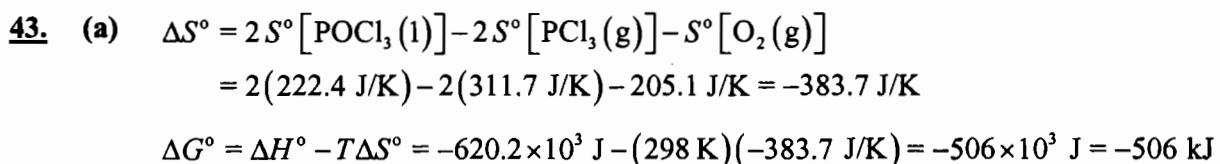
Solving for  $T_2$  we find a temperature of 354 K or 81°C. Consequently, to achieve an equilibrium between gaseous and liquid water under 0.50 atm pressure, the temperature must be set at 354 K.

## Free Energy and Spontaneous Change

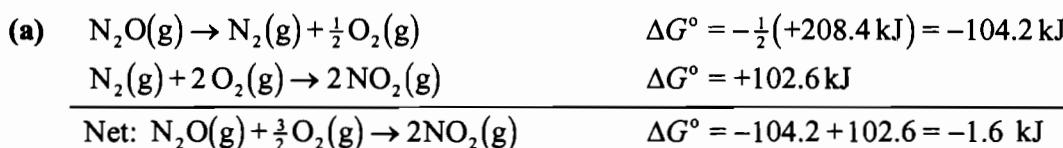
37. (a)  $\Delta H^{\circ} < 0$  and  $\Delta S^{\circ} < 0$  (since  $\Delta n_{\text{gas}} < 0$ ) for this reaction. Thus, this reaction is case 2 of Table 20-1. It is spontaneous at low temperatures and nonspontaneous at high temperatures.
- (b) We are unable to predict the sign of  $\Delta S^{\circ}$  for this reaction, since  $\Delta n_{\text{gas}} = 0$ . Thus, no strong prediction as to the temperature behavior of this reaction can be made. Since  $\Delta H^{\circ} > 0$ , we can, however, conclude that the reaction will be non-spontaneous at low temperatures.
- (c)  $\Delta H^{\circ} > 0$  and  $\Delta S^{\circ} > 0$  (since  $\Delta n_{\text{gas}} > 0$ ) for this reaction. This is case 3 of Table 20-1. It is nonspontaneous at low temperatures, but spontaneous at high temperatures.
39. First of all, the process is clearly spontaneous, and therefore  $\Delta G < 0$ . In addition, the gases are more disordered when they are at a lower pressure and therefore  $\Delta S > 0$ . We also conclude that  $\Delta H = 0$ , because the gases are ideal and thus there are no forces of attraction or repulsion between them, producing no energy of interaction.

- 41.** (a) An exothermic reaction (one that gives off heat) may not occur spontaneously if, at the same time, the system becomes more ordered, that is,  $\Delta S^\circ < 0$ . This is particularly true at a high temperature, where the  $T\Delta S$  term dominates the  $\Delta G$  expression. An example of such a process is freezing water (clearly exothermic because the reverse process, melting ice, is endothermic) at temperatures above 0 °C.
- (b) A reaction in which  $\Delta S > 0$  need not be spontaneous if that process also is endothermic. This is particularly true at low temperatures, where the  $\Delta H$  term dominates the  $\Delta G$  expression. An example is the vaporization of water (clearly an endothermic process, one that requires heat, and one that produces a gas, so  $\Delta S > 0$ ) at low temperatures, that is, below 100 °C.

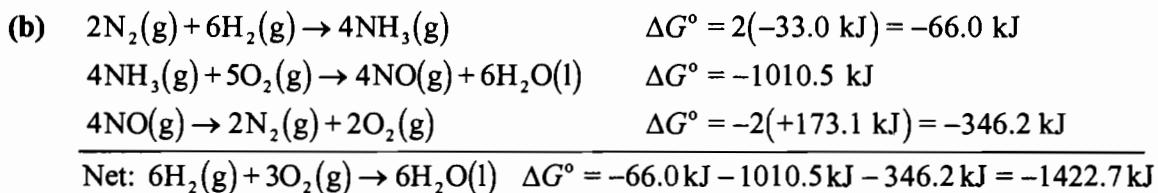
### Standard Free Energy Change



- (b) The reaction proceeds spontaneously in the forward direction when reactants and products are in their standard states, because the value of  $\Delta G^\circ$  is less than zero.
- 45.** We combine the reactions in the same way as for Hess's law calculations.



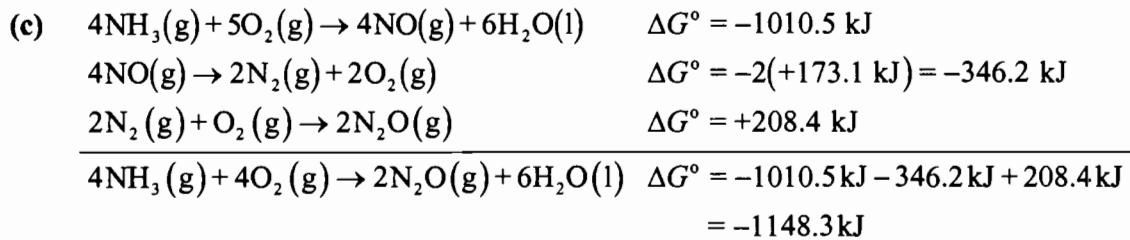
This reaction reaches an equilibrium condition, a conclusion we reach based on the relatively small absolute value of  $\Delta G^\circ$ .



This reaction is three times the desired reaction, which therefore has

$$\Delta G^\circ = -1422.7 \text{ kJ} \div 3 = -474.3 \text{ kJ}.$$

The large negative  $\Delta G^\circ$  value indicates that this reaction would tend to go to completion at 25 °C.



This reaction is twice the desired reaction, which, therefore, has

$$\Delta G^\circ = -1148.3 \text{ kJ} \div 2 = -574.2 \text{ kJ}.$$

The very large negative value of  $\Delta G^\circ$  for this reaction indicates that it will go to completion.

**47.** The combustion reaction is:  $\text{C}_6\text{H}_6(\text{l}) + \frac{15}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g or l})$

$$\begin{aligned}
 \text{(a)} \quad \Delta G^\circ &= 6\Delta G_f^\circ[\text{CO}_2(\text{g})] + 3\Delta G_f^\circ[\text{H}_2\text{O}(\text{l})] - \Delta G_f^\circ[\text{C}_6\text{H}_6(\text{l})] - \frac{15}{2}\Delta G_f^\circ[\text{O}_2(\text{g})] \\
 &= 6(-394.4 \text{ kJ}) + 3(-237.1 \text{ kJ}) - (+124.5 \text{ kJ}) - \frac{15}{2}(0.00 \text{ kJ}) = -3202 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \Delta G^\circ &= 6\Delta G_f^\circ[\text{CO}_2(\text{g})] + 3\Delta G_f^\circ[\text{H}_2\text{O}(\text{g})] - \Delta G_f^\circ[\text{C}_6\text{H}_6(\text{l})] - \frac{15}{2}\Delta G_f^\circ[\text{O}_2(\text{g})] \\
 &= 6(-394.4 \text{ kJ}) + 3(-228.6 \text{ kJ}) - (+124.5 \text{ kJ}) - \frac{15}{2}(0.00 \text{ kJ}) = -3177 \text{ kJ}
 \end{aligned}$$

We could determine the difference between the two values of  $\Delta G^\circ$  by noting the difference between the two products:  $3\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{H}_2\text{O}(\text{g})$  and determining the value of  $\Delta G^\circ$  for this difference:

$$\Delta G^\circ = 3\Delta G_f^\circ[\text{H}_2\text{O}(\text{g})] - 3\Delta G_f^\circ[\text{H}_2\text{O}(\text{l})] = 3[-228.6 - (-237.1)] \text{ kJ} = 25.5 \text{ kJ}$$

$$\begin{aligned}
 \text{49. (a)} \quad \Delta S^\circ_{\text{rxn}} &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\
 &= [1 \text{ mol} \times 301.2 \text{ J K}^{-1}\text{mol}^{-1} + 2 \text{ mol} \times 188.8 \text{ J K}^{-1}\text{mol}^{-1}] - [2 \text{ mol} \times 247.4 \text{ J K}^{-1}\text{mol}^{-1} \\
 &\quad + 1 \text{ mol} \times 238.5 \text{ J K}^{-1}\text{mol}^{-1}] = -54.5 \text{ J K}^{-1}
 \end{aligned}$$

$$\Delta S^\circ_{\text{rxn}} = -0.0545 \text{ kJ K}^{-1}$$

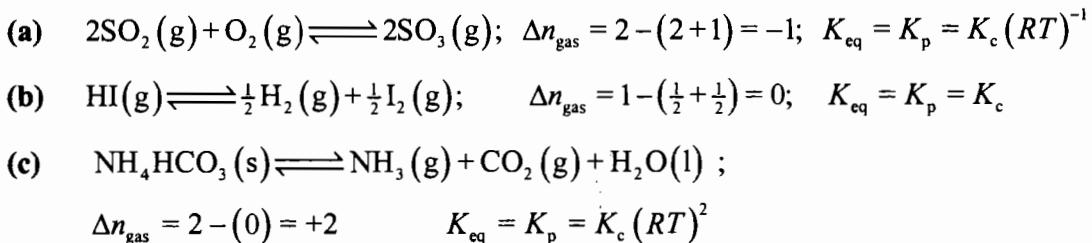
$$\begin{aligned}
 \text{(b)} \quad \Delta H^\circ_{\text{rxn}} &= \sum(\text{bonds broken in reactants (kJ/mol)}) - \sum(\text{bonds broken in products (kJ/mol)}) \\
 &= [4 \text{ mol} \times (389 \text{ kJ mol}^{-1})_{\text{N-H}} + 4 \text{ mol} \times (222 \text{ kJ mol}^{-1})_{\text{O-F}}] - \\
 &\quad [4 \text{ mol} \times (301 \text{ kJ mol}^{-1})_{\text{N-F}} + 4 \text{ mol} \times (464 \text{ kJ mol}^{-1})_{\text{O-H}}]
 \end{aligned}$$

$$\Delta H^\circ_{\text{rxn}} = -616 \text{ kJ}$$

$$\begin{aligned}
 \text{(c)} \quad \Delta G^\circ_{\text{rxn}} &= \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} = -616 \text{ kJ} - 298 \text{ K}(-0.0545 \text{ kJ K}^{-1}) = -600 \text{ kJ} \\
 \text{Since the } \Delta G^\circ_{\text{rxn}} \text{ is negative, the reaction is spontaneous, and hence feasible} \\
 \text{at } 25^\circ\text{C. Because both the entropy and enthalpy changes are negative, this} \\
 \text{reaction will be more highly favored at low temperatures (i.e., the reaction is} \\
 \text{enthalpy driven)}
 \end{aligned}$$

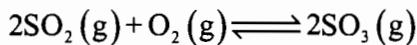
## The Thermodynamic Equilibrium Constant

- 51.** In all three cases,  $K_{\text{eq}} = K_p$  because only gases, solids, and liquids are present in the chemical equations. There are no factors for solids and liquids in  $K_{\text{eq}}$  expressions, and gases appear as partial pressures in atmospheres. That makes  $K_{\text{eq}}$  the same as  $K_p$  for these three reactions. We now recall that  $K_p = K_c (RT)^{\Delta n}$ . Hence, in these three cases we have:



## Relationships Involving $\Delta G$ , $\Delta G^\circ$ , $Q$ and $K$

- 53.** First we need to determine the standard free energy change for the reaction:



$$\begin{aligned} \Delta G^\circ &= 2\Delta G_f^\circ[\text{SO}_3(\text{g})] - 2\Delta G_f^\circ[\text{SO}_2(\text{g})] - \Delta G_f^\circ[\text{O}_2(\text{g})] \\ &= 2 \times (-371.1 \text{ kJ/mol}) - 2 \times (-300.2 \text{ kJ/mol}) - 0.0 \text{ kJ/mol} = -141.8 \text{ kJ} \end{aligned}$$

Now we can calculate  $\Delta G$  by employing the equation  $\Delta G = \Delta G^\circ + RT \ln Q_p$ , where

$$Q_p = \frac{P\{\text{SO}_3(\text{g})\}^2}{P\{\text{O}_2(\text{g})\}P\{\text{SO}_2(\text{g})\}^2}; Q_p = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})(1.0 \times 10^{-4} \text{ atm})^2} = 5.0 \times 10^6$$

$$\Delta G = -141.8 \text{ kJ} + (8.3145 \times 10^{-3} \text{ kJ/K} \cdot \text{mol})(298 \text{ K}) \ln(5.0 \times 10^6)$$

$$\Delta G = -141.8 \text{ kJ} + 38.2 \text{ kJ} = -104 \text{ kJ}$$

Since  $\Delta G$  is negative, the reaction is spontaneous in the forward direction.

- 55.** In order to determine in which direction the reaction is spontaneous, we need to calculate the non-standard free energy change for the reaction. To accomplish this, we will employ the equation  $\Delta G = \Delta G^\circ + RT \ln Q_c$ , where

$$Q_c = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{CO}_2^-(\text{aq})]}{[\text{CH}_3\text{CO}_2\text{H}(\text{aq})]}; Q_c = \frac{(1.0 \times 10^{-3} \text{ M})^2}{(0.10 \text{ M})} = 1.0 \times 10^{-5}$$

$$\Delta G = 27.07 \text{ kJ} + (8.3145 \times 10^{-3} \text{ kJ/K} \cdot \text{mol})(298 \text{ K}) \ln(1.0 \times 10^{-5})$$

$$\Delta G = 27.07 \text{ kJ} + (-28.53 \text{ kJ}) = -1.46 \text{ kJ}$$

Since  $\Delta G$  is negative, the reaction is spontaneous in the forward direction.

Since  $\Delta G$  is negative, the reaction is spontaneous in the forward direction.

57. The relationship  $\Delta S^\circ = (\Delta G^\circ - \Delta H^\circ)/T$  (Equation (b)) is incorrect. Rearranging this equation to put  $\Delta G^\circ$  on one side by itself gives  $\Delta G^\circ = \Delta H^\circ + T\Delta S^\circ$ . This equation is not valid. The  $\Delta H^\circ$  term should be subtracted from the  $T\Delta S^\circ$  term, not added to it.
59. (a) To determine  $K_p$  we need the equilibrium partial pressures. In the ideal gas law, each partial pressure is defined by  $P = nRT/V$ . Because  $R$ ,  $T$ , and  $V$  are the same for each gas, and because there are the same number of partial pressure factors in the numerator as in the denominator of the  $K_p$  expression, we can use the ratio of amounts to determine  $K_p$ .

$$K_p = \frac{P\{\text{CO(g)}\} P\{\text{H}_2\text{O(g)}\}}{P\{\text{CO}_2\text{(g)}\} P\{\text{H}_2\text{(g)}\}} = \frac{n\{\text{CO(g)}\} n\{\text{H}_2\text{O(g)}\}}{n\{\text{CO}_2\text{(g)}\} n\{\text{H}_2\text{(g)}\}}$$

$$= \frac{0.224 \text{ mol CO} \times 0.224 \text{ mol H}_2\text{O}}{0.276 \text{ mol CO}_2 \times 0.276 \text{ mol H}_2} = 0.659$$

$$\begin{aligned} \text{(b)} \quad \Delta G^\circ_{1000\text{K}} &= -RT \ln K_p \\ &= -8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 1000. \text{ K} \times \ln(0.659) \\ &= 3.467 \times 10^3 \text{ J/mol} = 3.467 \text{ kJ/mol} \end{aligned}$$

$$Q_p = \frac{0.0340 \text{ mol CO} \times 0.0650 \text{ mol H}_2\text{O}}{0.0750 \text{ mol CO}_2 \times 0.095 \text{ mol H}_2} = 0.31 < 0.659 = K_p$$

Since  $Q_p$  is smaller than  $K_p$ , the reaction will proceed to the right, forming products, to attain equilibrium, i.e.,  $\Delta G = 0$ .

61. (a)  $K_{\text{eq}} = K_c$
- $$\Delta G^\circ = -RT \ln K_{\text{eq}} = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(445 + 273) \text{ K} \ln 50.2 = -23.4 \text{ kJ}$$
- (b)  $K_{\text{eq}} = K_p = K_c (RT)^{\Delta n} = 1.7 \times 10^{-13} (0.0821 \times 298)^{1/2} = 8.4 \times 10^{-13}$
- $$\Delta G^\circ = -RT \ln K_p = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln (8.4 \times 10^{-13})$$
- $$\Delta G^\circ = +68.9 \text{ kJ/mol}$$
- (c)  $K_{\text{eq}} = K_p = K_c (RT)^{\Delta n} = 4.61 \times 10^{-3} (0.08206 \times 298)^{+1} = 0.113$
- $$\Delta G^\circ = -RT \ln K_p = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln (0.113) = +5.40 \text{ kJ/mol}$$
- (d)  $K_{\text{eq}} = K_c = 9.14 \times 10^{-6}$
- $$\Delta G^\circ = -RT \ln K_c = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln (9.14 \times 10^{-6})$$
- $$\Delta G^\circ = +28.7 \text{ kJ/mol}$$

63.  $\Delta G^\circ = -RT \ln K_p = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})(298\text{K}) \ln(6.5 \times 10^{11}) = -67.4 \text{ kJ/mol}$



$\Delta G_f^\circ$  of  $\text{COCl}_2\text{(g)}$  given in Appendix D is  $-204.6 \text{ kJ/mol}$ , (excellent agreement.).

65. (a) We can determine the equilibrium partial pressure from the value of the equilibrium constant.

$$\Delta G^\circ = -RT \ln K_p \quad \ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{58.54 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K}} = -23.63$$

$$K_p = P\{\text{O}_2\text{(g)}\}^{1/2} = e^{-23.63} = 5.5 \times 10^{-11} \quad P\{\text{O}_2\text{(g)}\} = (5.5 \times 10^{-11})^2 = 3.0 \times 10^{-21} \text{ atm}$$

- (b) Lavoisier did two things to increase the quantity of oxygen that he obtained. First, he ran the reaction at a high temperature, which favors the products (i.e., the side with molecular oxygen.) Second, the molecular oxygen was removed immediately after it was formed, which causes the equilibrium to shift to the right continuously (the shift towards products as result of the removal of the  $\text{O}_2$  is an example of Le Châtelier's principle).

### $\Delta G^\circ$ and $K_{\text{eq}}$ as a Function of Temperature

67. We first determine the value of  $\Delta G^\circ$  at  $400^\circ\text{C}$ , from the values of  $\Delta H^\circ$  and  $\Delta S^\circ$ , which are determined from information listed in Appendix D.

$$\begin{aligned} \Delta H^\circ &= 2\Delta H_f^\circ[\text{NH}_3\text{(g)}] - \Delta H_f^\circ[\text{N}_2\text{(g)}] - 3\Delta H_f^\circ[\text{H}_2\text{(g)}] \\ &= 2(-46.11 \text{ kJ/mol}) - (0.00 \text{ kJ/mol}) - 3(0.00 \text{ kJ/mol}) = -92.22 \text{ kJ/mol N}_2 \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= 2S^\circ[\text{NH}_3\text{(g)}] - S^\circ[\text{N}_2\text{(g)}] - 3S^\circ[\text{H}_2\text{(g)}] \\ &= 2(192.5 \text{ J mol}^{-1}\text{K}^{-1}) - (191.6 \text{ J mol}^{-1}\text{K}^{-1}) - 3(130.7 \text{ J mol}^{-1}\text{K}^{-1}) = -198.7 \text{ J mol}^{-1}\text{K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = -92.22 \text{ kJ/mol} - 673 \text{ K} \times (-0.1987 \text{ kJ mol}^{-1}\text{K}^{-1}) \\ &= +41.51 \text{ kJ/mol} = -RT \ln K_p \end{aligned}$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-41.51 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 673 \text{ K}} = -7.42; \quad K_p = e^{-7.42} = 6.0 \times 10^{-4}$$

**69.** We assume that both  $\Delta H^\circ$  and  $\Delta S^\circ$  are constant with temperature.

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ[\text{SO}_3(\text{g})] - 2\Delta H_f^\circ[\text{SO}_2(\text{g})] - \Delta H_f^\circ[\text{O}_2(\text{g})] \\ &= 2(-395.7 \text{ kJ/mol}) - 2(-296.8 \text{ kJ/mol}) - (0.00 \text{ kJ/mol}) = -197.8 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 2S^\circ[\text{SO}_3(\text{g})] - 2S^\circ[\text{SO}_2(\text{g})] - S^\circ[\text{O}_2(\text{g})] \\ &= 2(256.8 \text{ J mol}^{-1} \text{ K}^{-1}) - 2(248.2 \text{ J mol}^{-1} \text{ K}^{-1}) - (205.1 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -187.9 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_{\text{eq}} \quad \Delta H^\circ = T\Delta S^\circ - RT\ln K_{\text{eq}} \quad T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K_{\text{eq}}}$$

$$T = \frac{-197.8 \times 10^3 \text{ J/mol}}{-187.9 \text{ J mol}^{-1} \text{ K}^{-1} - 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \ln(1.0 \times 10^6)} \approx 650 \text{ K}$$

This value compares very favorably with the value of  $T = 6.37 \times 10^2$  that was obtained in Example 20-10.

**71. (a)**  $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{57.2 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{273 \text{ K}} \right) = -2.11$

$$\frac{K_2}{K_1} = e^{-2.11} = 0.121 \quad K_2 = 0.121 \times 0.113 = 0.014 \text{ at } 273 \text{ K}$$

**(b)**  $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{57.2 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{T_1} - \frac{1}{298 \text{ K}} \right) = \ln \frac{0.113}{1.00} = -2.180$

$$\left( \frac{1}{T_1} - \frac{1}{298 \text{ K}} \right) = \frac{-2.180 \times 8.3145}{57.2 \times 10^3} \text{ K}^{-1} = -3.17 \times 10^{-4} \text{ K}^{-1}$$

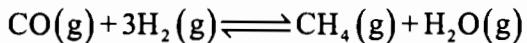
$$\frac{1}{T_1} = \frac{1}{298} - 3.17 \times 10^{-4} = 3.36 \times 10^{-3} - 3.17 \times 10^{-4} = 3.04 \times 10^{-3} \text{ K}^{-1}; \quad T_1 = 329 \text{ K}$$

**73.** First, the van't Hoff equation is used to obtain a value of  $\Delta H^\circ$ .  $200^\circ\text{C} = 473\text{K}$  and  $260^\circ\text{C} = 533\text{K}$ .

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \ln \frac{2.15 \times 10^{11}}{4.56 \times 10^8} = 6.156 = \frac{\Delta H^\circ}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{533 \text{ K}} - \frac{1}{473 \text{ K}} \right)$$

$$6.156 = -2.9 \times 10^{-5} \Delta H^\circ \quad \Delta H^\circ = \frac{6.156}{-2.9 \times 10^{-5}} = -2.1 \times 10^5 \text{ J/mol} = -2.1 \times 10^2 \text{ kJ/mol}$$

Another route to  $\Delta H^\circ$  is the combination of standard enthalpies of formation.



$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{CH}_4\text{(g)}] + \Delta H_f^\circ[\text{H}_2\text{O(g)}] - \Delta H_f^\circ[\text{CO(g)}] - 3\Delta H_f^\circ[\text{H}_2\text{(g)}] \\ &= -74.81 \text{ kJ/mol} - 241.8 \text{ kJ/mol} - (-110.5) - 3 \times 0.00 \text{ kJ/mol} = -206.1 \text{ kJ/mol}\end{aligned}$$

Within the precision of the data supplied, the results are in agreement.

## Coupled Reactions

**75. (a)** We compute  $\Delta G^\circ$  for the given reaction in the following manner

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{TiCl}_4\text{(l)}] + \Delta H_f^\circ[\text{O}_2\text{(g)}] - \Delta H_f^\circ[\text{TiO}_2\text{(s)}] - 2\Delta H_f^\circ[\text{Cl}_2\text{(g)}] \\ &= -804.2 \text{ kJ/mol} + 0.00 \text{ kJ/mol} - (-944.7 \text{ kJ/mol}) - 2(0.00 \text{ kJ/mol}) \\ &= +140.5 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{TiCl}_4\text{(l)}] + S^\circ[\text{O}_2\text{(g)}] - S^\circ[\text{TiO}_2\text{(s)}] - 2S^\circ[\text{Cl}_2\text{(g)}] \\ &= 252.3 \text{ J mol}^{-1} \text{ K}^{-1} + 205.1 \text{ J mol}^{-1} \text{ K}^{-1} - (50.33 \text{ J mol}^{-1} \text{ K}^{-1}) - 2(223.1 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -39.1 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

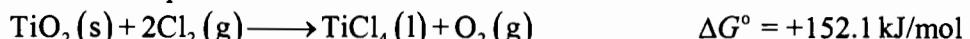
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = +140.5 \text{ kJ/mol} - (298 \text{ K})(-39.1 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ &= +140.5 \text{ kJ/mol} + 11.6 \text{ kJ/mol} = +152.1 \text{ kJ/mol}\end{aligned}$$

This reaction is nonspontaneous at 25° C. (We also could have used values of  $\Delta G_f^\circ$  to calculate  $\Delta G^\circ$ .)

**(b)** For the cited reaction,  $\Delta G^\circ = 2\Delta G_f^\circ[\text{CO}_2\text{(g)}] - 2\Delta G_f^\circ[\text{CO(g)}] - \Delta G_f^\circ[\text{O}_2\text{(g)}]$

$$\Delta G^\circ = 2(-394.4 \text{ kJ/mol}) - 2(-137.2 \text{ kJ/mol}) - 0.00 \text{ kJ/mol} = -514.4 \text{ kJ/mol}$$

Then we couple the two reactions.



The coupled reaction has  $\Delta G^\circ < 0$ , and, therefore, is spontaneous.

## FEATURE PROBLEMS

- 98. (a)** The first method involves combining the values of  $\Delta G_f^\circ$ . The second uses

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ [\text{H}_2\text{O}(g)] - \Delta G_f^\circ [\text{H}_2\text{O}(l)] \\ &= -228.572 \text{ kJ/mol} - (-237.129 \text{ kJ/mol}) = +8.557 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ [\text{H}_2\text{O}(g)] - \Delta H_f^\circ [\text{H}_2\text{O}(l)] \\ &= -241.818 \text{ kJ/mol} - (-285.830 \text{ kJ/mol}) = +44.012 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ [\text{H}_2\text{O}(g)] - S^\circ [\text{H}_2\text{O}(l)] \\ &= 188.825 \text{ J mol}^{-1} \text{ K}^{-1} - 69.91 \text{ J mol}^{-1} \text{ K}^{-1} = +118.92 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.012 \text{ kJ/mol} - 298.15 \text{ K} \times 118.92 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} = +8.556 \text{ kJ/mol}\end{aligned}$$

- (b)** We use the average value:  $\Delta G^\circ = +8.558 \times 10^3 \text{ J / mol} = -RT \ln K_{\text{eq}}$

$$\ln K_{\text{eq}} = -\frac{8558 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -3.452; \quad K_{\text{eq}} = e^{-3.452} = 0.0317 \text{ bar}$$

$$\text{(c)} \quad P\{\text{H}_2\text{O}\} = 0.0317 \text{ bar} \times \frac{1 \text{ atm}}{1.01325 \text{ bar}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 23.8 \text{ mmHg}$$

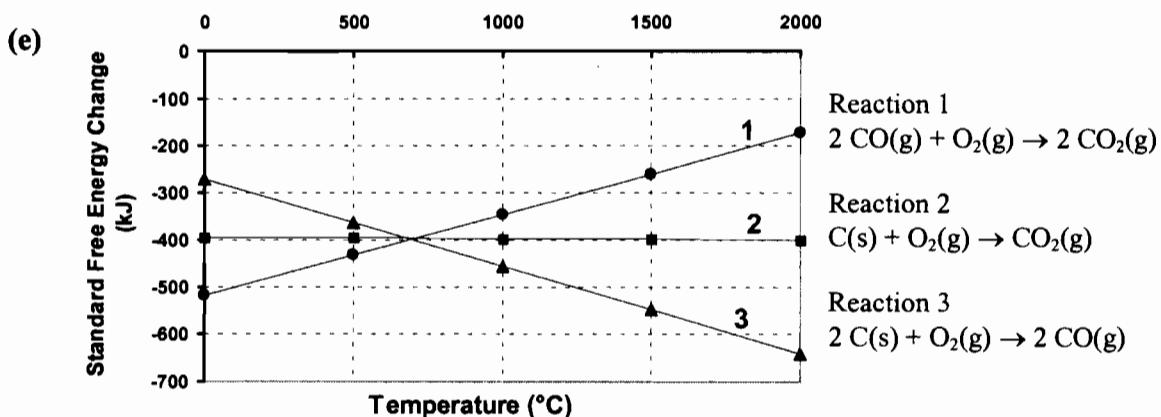
$$\text{(d)} \quad \ln K_{\text{eq}} = -\frac{8590 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -3.465;$$

$$K_{\text{eq}} = e^{-3.465} = 0.0312, \text{ atm};$$

$$P\{\text{H}_2\text{O}\} = 0.0313 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 23.8 \text{ mmHg}$$

- 99. (a)** When we combine two reactions and obtain the overall value of  $\Delta G^\circ$ , we subtract the value on the plot of the reaction that becomes a reduction from the value on the plot of the reaction that is an oxidation. Thus, to reduce  $\text{ZnO}$  with elemental  $\text{Mg}$ , we subtract the values on the line labeled " $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$ " from those on the line labeled " $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ ". The result for the overall  $\Delta G^\circ$  will always be negative because every point on the "zinc" line is above the corresponding point on the "magnesium" line

- (b) In contrast, the “carbon” line is only below the “zinc” line at temperatures above about  $1000^{\circ}\text{C}$ . Only at these elevated temperatures can  $\text{ZnO}$  be reduced by carbon.
- (c) The decomposition of zinc oxide to its elements is the reverse of the plotted reaction, the value of  $\Delta G^{\circ}$  for the decomposition becomes negative, and the reaction becomes spontaneous, where the value of  $\Delta G^{\circ}$  for the plotted reaction becomes positive. This occurs above about  $1850^{\circ}\text{C}$ .
- (d) The “carbon” line has a negative slope, indicating that carbon monoxide becomes more stable as temperature rises. The point where  $\text{CO(g)}$  would become less stable than  $2\text{C(s)}$  and  $\text{O}_2\text{(g)}$  looks to be below  $-1000^{\circ}\text{C}$  (by extrapolating the line to lower temperatures). Based on this plot, it is not possible to decompose  $\text{CO(g)}$  to  $\text{C(s)}$  and  $\text{O}_2\text{(g)}$  in a spontaneous reaction.



All three lines are straight-line plots of  $\Delta G^{\circ}$  vs.  $T$  following the equation  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ .

The general equation for a straight line is given below with the slightly modified Gibbs Free-Energy equation as a reference:  $\Delta G^{\circ} = -\Delta S^{\circ}T + \Delta H^{\circ}$  (here  $\Delta H^{\circ}$  is assumed to be constant)

$$y = mx + b \quad (m = -\Delta S^{\circ} = \text{slope of the line})$$

Thus, the slope of each line multiplied by minus one is equal to the  $\Delta S^{\circ}$  for the oxide formation reaction. It is hardly surprising, therefore, that the slopes for these lines differ so markedly because these three reactions have quite different  $\Delta S^{\circ}$  values ( $\Delta S^{\circ}$  for Reaction 1 =  $-173.1 \text{ J K}^{-1}$ ,  $\Delta S^{\circ}$  for Reaction 2 =  $2.86 \text{ J K}^{-1}$ ,  $\Delta S^{\circ}$  for Reaction 3 =  $178.8 \text{ J K}^{-1}$ )

- (f) Since other metal oxides apparently have positive slopes similar to Mg and Zn, we can conclude that in general, the stability of metal oxides decreases as the temperature increases. Put another way, the decomposition of metal oxides to their elements becomes more spontaneous as the temperature is increased. By contrast, the two reactions involving elemental carbon, namely Reaction 2 and Reaction 3,

have negative slopes, indicating that the formation of  $\text{CO}_2(\text{g})$  and  $\text{CO}(\text{g})$  from graphite becomes more favorable as the temperature rises, respectively. This means that the  $\Delta G^\circ$  for the reduction of metal oxides by carbon becomes more and more negative with increasing temperature. Moreover, there must exist a threshold temperature for each metal oxide above which the reaction with carbon will occur spontaneously. Carbon would appear to be an excellent reducing agent, therefore, because it will reduce virtually any metal oxide to its corresponding metal as long as the temperature chosen for the reaction is higher than the threshold temperature (the threshold temperature is commonly referred to as the transition temperature).

Consider for instance the reaction of  $\text{MgO}(\text{s})$  with graphite to give  $\text{CO}_2(\text{g})$  and  $\text{Mg}$  metal:



$$T_{\text{transition}} = \frac{\Delta H^\circ_{\text{rxn}}}{\Delta S^\circ_{\text{rxn}}} = \frac{809.9 \text{ kJ}}{0.2194 \text{ kJ K}^{-1}} = 3693 \text{ K} = T_{\text{threshold}}$$

Consequently, above 3691 K, carbon will spontaneously reduce  $\text{MgO}$  to  $\text{Mg}$  metal.

- 100. (a)** With a 36% efficiency and a condenser temperature ( $T_1$ ) of  $41^\circ\text{C} = 314 \text{ K}$ ,

$$\text{efficiency} = \frac{T_h - T_1}{T_h} \times 100\% = 36\%$$

$$\frac{T_h - 314}{T_h} = 0.36; \quad T_h = (0.36 \times T_h) + 314 \text{ K}; \quad 0.64 T_h = 314 \text{ K}; \quad T_h = 4.9 \times 10^2 \text{ K}$$

- (b)** The overall efficiency of the power plant is affected by factors in other than the thermodynamic efficiency. For example, a portion of the heat of combustion of the fuel is lost to parts of the surroundings other than the steam boiler; there are frictional losses of energy in moving parts in the engine; and so on. To compensate for these losses, the thermodynamic efficiency must be greater than 36%. To obtain this higher thermodynamic efficiency,  $T_h$  must be greater than  $4.9 \times 10^2 \text{ K}$ .
- (c)** The steam pressure we are seeking is the vapor pressure of water at  $4.9 \times 10^2 \text{ K}$ . We also know that the vapor pressure of water at  $373 \text{ K}$  ( $100^\circ\text{C}$ ) is 1 atm. The enthalpy of vaporization of water at  $298 \text{ K}$  is  $\Delta H^\circ = \Delta H_f^\circ[\text{H}_2\text{O}(\text{g})] - \Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -241.8 \text{ kJ/mol} - (-285.8 \text{ kJ/mol}) = 44.0 \text{ kJ/mol}$ . Although the enthalpy of vaporization is somewhat temperature dependent, we will assume that this value holds from  $298 \text{ K}$  to  $4.9 \times 10^2 \text{ K}$ , and make appropriate substitutions into the Clausius-Clapeyron equation.

$$\ln\left(\frac{P_2}{1 \text{ atm}}\right) = \frac{44.0 \text{ kJ mol}^{-1}}{8.3145 \times 10^{-3} \text{ kJ mol}^{-1}} \left( \frac{1}{373 \text{ K}} - \frac{1}{490 \text{ K}} \right) = 5.29 \times 10^{-3} (2.68 \times 10^{-3} - 2.04 \times 10^{-3})$$

$$\ln\left(\frac{P_2}{1 \text{ atm}}\right) = 3.39; \quad \left(\frac{P_2}{1 \text{ atm}}\right) = 29.7; \quad P_2 \approx 30 \text{ atm}$$

The answer cannot be given with greater certainty because of the weakness of the assumption of a constant  $H^\circ_{\text{vapn}}$ .

- (d) It is not possible to devise a heat engine with 100% efficiency or greater. For 100% efficiency,  $T_1 = 0 \text{ K}$ , which is unattainable. To have an efficiency greater than 100 % would require a *negative*  $T_1$ , which is also unattainable.

101. (a) Under biological standard conditions (see page 813)



If all of the energy of combustion of 1 mole of glucose is employed in the conversion of ADP to ATP, then the maximum number of moles ATP produced is

$$\text{Maximum number} = \frac{2870 \text{ kJ mol}^{-1}}{32.4 \text{ kJ mol}^{-1}} = 88.6 \text{ moles ATP}$$

- (b) In an actual cell the number of ATP moles produced is 38, so that the efficiency is:

$$\text{Efficiency} = \frac{\text{number of ATP's actually produced}}{\text{Maximum number of ATP's that can be produced}} = \frac{38}{88.6} = 0.43$$

Thus, the cell's efficiency is about 43%.

- (c) The previously calculated efficiency is based upon the biological standard state. We now calculate the Gibbs energies involved under the actual conditions in the cell. To do this we require the relationship between  $\Delta G$  and  $\Delta G'$  for the two coupled reactions. For the combustion of glucose we have

$$\Delta G = \Delta G' + RT \ln\left(\frac{a_{\text{CO}_2}^6 a_{\text{H}_2\text{O}}^6}{a_{\text{glu}}^6 a_{\text{O}_2}^6}\right)$$

For the conversion of ADP to ATP we have

$$\Delta G = \Delta G' + RT \ln\left(\frac{a_{\text{ATP}} a_{\text{H}_2\text{O}}}{a_{\text{ADP}} a_{\text{P}_i} ([\text{H}^+]/10^{-7})}\right)$$

Using the concentrations and pressures provided we can calculate the Gibbs energy for the combustion of glucose under biological conditions. First, we need to replace the activities by the appropriate effective concentrations. That is,

$$\Delta G = \Delta G' + RT \ln\left(\frac{(p/p^\circ)_{\text{CO}_2}^6 a_{\text{H}_2\text{O}}^6}{[\text{glu}]/[\text{glu}]^\circ (p/p^\circ)_{\text{O}_2}^6}\right)$$

using  $\alpha_{H_2O} \approx 1$  for a dilute solution we obtain

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{(0.050 \text{ bar}/1 \text{ bar})^6 \times 1^6}{[\text{glu}]/1 \times (0.132 \text{ bar}/1 \text{ bar})^6} \right)$$

The concentration of glucose is given in mg/mL and this has to be converted to molarity as follows:

$$[\text{glu}] = \frac{1.0 \text{ mg}}{\text{mL}} \times \frac{\text{g}}{1000 \text{ mg}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1}{180.16 \text{ g mol}^{-1}} = 0.00555 \text{ mol L}^{-1},$$

where the molar mass of glucose is 180.16 g mol<sup>-1</sup>.

Assuming a temperature of 37 °C for a biological system we have, for one mole of glucose:

$$\Delta G = -2870 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times \ln \left( \frac{(0.050)^6 \times 1^6}{0.00555/1 \times (0.132)^6} \right)$$

$$\Delta G = -2870 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times \ln \left( \frac{(0.3788)^6}{0.00555} \right)$$

$$\Delta G = -2870 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times \ln(0.5323)$$

$$\Delta G = -2870 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times (-0.6305)$$

$$\Delta G = -2870 \times 10^3 \text{ J} - 1.637 \times 10^3 \text{ J}$$

$$\Delta G = -2872 \times 10^3 \text{ J}$$

In a similar manner we calculate the Gibbs free energy change for the conversion of ADP to ATP:

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{[\text{ATP}]/1 \times 1}{[\text{ADP}]/1 \times [\text{P}_i]/1 \times ([\text{H}^+]/10^{-7})} \right)$$

$$\Delta G = 32.4 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times \ln \left( \frac{0.0001}{0.0001 \times 0.0001 \times (10^{-7}/10^{-7})} \right)$$

$$\Delta G = 32.4 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times \ln(10^4)$$

$$\Delta G = 32.4 \times 10^3 \text{ J} + 8.314 \text{ JK}^{-1} \times 310 \text{ K} \times (9.2103)$$

$$\Delta G = 32.4 \times 10^3 \text{ J} + 23.738 \times 10^3 \text{ J}$$

$$\Delta G = 56.2 \times 10^3 \text{ J}$$

- (d) The efficiency under biological conditions is

$$\text{Efficiency} = \frac{\text{number of ATP's actually produced}}{\text{Maximum number of ATP's that can be produced}} = \frac{38}{2872/56.2} = 0.744$$

Thus, the cell's efficiency is about 74%.

The theoretical efficiency of the diesel engine is:

$$\text{Efficiency} = \frac{T_h - T_l}{T_h} \times 100\% = \frac{1923 - 873}{1923} \times 100\% = 55\%$$

Thus, the diesel's actual efficiency is  $0.78 \times 55\% = 43\%$ .

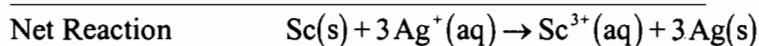
The cell's efficiency is 74% whereas that of the diesel engine is only 43 %. Why is there such a large discrepancy? The diesel engine supplies heat to the surroundings, which is at a lower temperature than the engine. This dissipation of energy raises the temperature of the surroundings and the entropy of the surroundings. A cell operates under isothermal conditions and the energy not used goes only towards changing the entropy of the cell's surroundings. The cell is more efficient since it does not heat the surroundings.

# CHAPTER 21

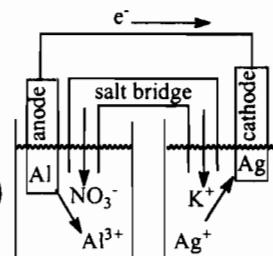
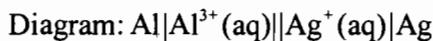
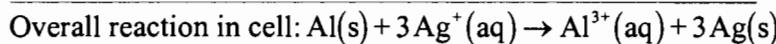
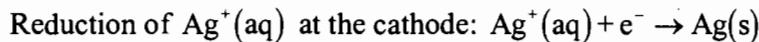
## ELECTROCHEMISTRY

### PRACTICE EXAMPLES

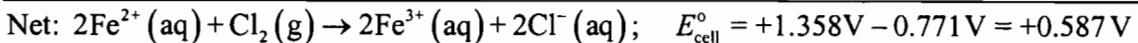
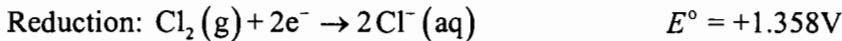
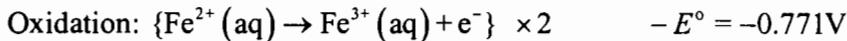
- 1A** The conventions state that the anode material is written first, and the cathode material is written last.



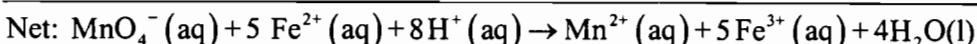
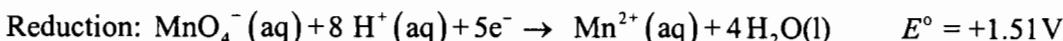
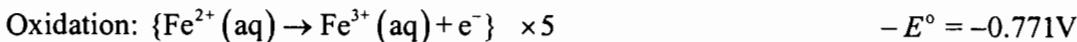
- 1B** Oxidation of  $\text{Al(s)}$  at the anode:  $\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$



- 2A** We obtain the two balanced half-equations and the half-cell potentials from Table 21-1.

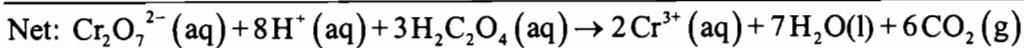
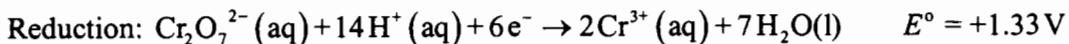
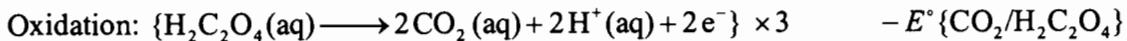


- 2B** Since we need to refer to Table 21-1 in any event, it is perhaps a bit easier to locate the two balanced half-equations in the table. There is only one half-equation involving both  $\text{Fe}^{2+}(\text{aq})$  and  $\text{Fe}^{3+}(\text{aq})$  ions. It is reversed and written as an oxidation below. The half-equation involving  $\text{MnO}_4^-(\text{aq})$  is also written below. [Actually, we need to know that in acidic solution  $\text{Mn}^{2+}(\text{aq})$  is the principal reduction product of  $\text{MnO}_4^-(\text{aq})$ .]



$E_{\text{cell}}^\circ = +1.51\text{V} - 0.771\text{V} = +0.74\text{V}$

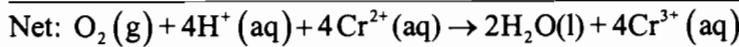
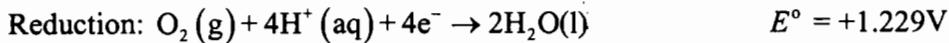
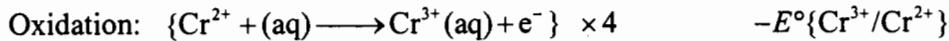
- 3A** We write down the oxidation half-equation with the method of Chapter 5, and obtain the reduction half-equation from Table 21-1, along with the reduction half-cell potential.



$$E_{cell}^\circ = +1.81V = +1.33V - E^\circ \{CO_2/H_2C_2O_4\};$$

$$E^\circ \{CO_2/H_2C_2O_4\} = 1.33V - 1.81V = -0.48V$$

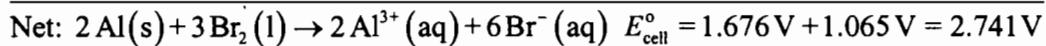
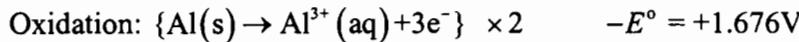
- 3B** The 2<sup>nd</sup> 1/2-reaction must have  $O_2(g)$  as reactant and  $H_2O(l)$  as product.



$$E_{cell}^\circ = +1.653V = +1.229V - E^\circ \{Cr^{3+}/Cr^{2+}\};$$

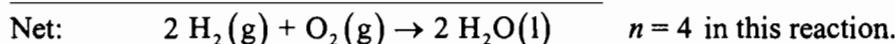
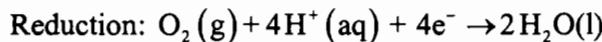
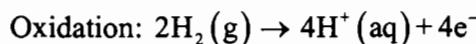
$$E^\circ \{Cr^{3+}/Cr^{2+}\} = 1.229V - 1.653V = -0.424V$$

- 4A** First we write down the two half-equations, obtain the half-cell potential for each, and then calculate  $E_{cell}^\circ$ . From that value, we determine  $\Delta G^\circ$



$$\Delta G^\circ = -nFE_{cell}^\circ = -6 \text{ mol } e^- \times \frac{96,485 \text{ C}}{1 \text{ mol } e^-} \times 2.741 \text{ V} = -1.587 \times 10^6 \text{ J} = -1587 \text{ kJ}$$

- 4B** First we write down the two half-equations, one of which is the reduction equation from the previous example. The other is the oxidation that occurs in the standard hydrogen electrode.

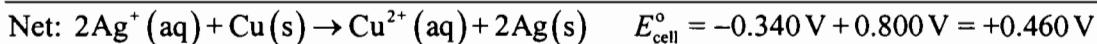
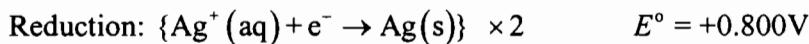


This net reaction is simply twice the formation reaction for  $H_2O(l)$  and, therefore,

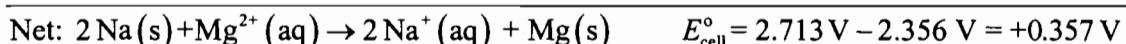
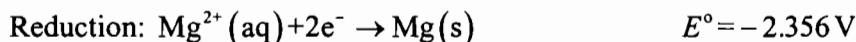
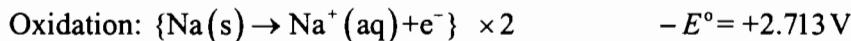
$$\Delta G^\circ = 2\Delta G_f^\circ [H_2O(l)] = 2 \times (-237.1 \text{ kJ}) = -474.2 \times 10^3 \text{ J} = -nFE_{cell}^\circ$$

$$E_{cell}^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-(-474.2 \times 10^3 \text{ J})}{4 \text{ mol } e^- \times \frac{96,485 \text{ C}}{\text{mole}^-}} = +1.229 \text{ V} = E^\circ, \text{ as we might expect.}$$

**5A** Cu(s) will displace metal ions of a metal less active than copper. Silver ion is one example.



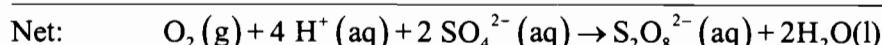
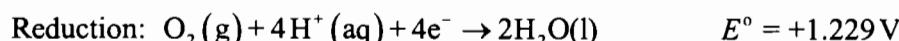
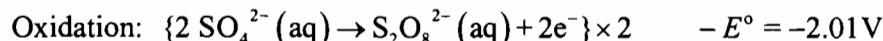
**5B** We determine the value for the hypothetical reaction's cell potential.



The method is not feasible because another reaction occurs that has an even larger cell potential, i.e., Na(s) reacts with water to form  $\text{H}_2(\text{g})$  and  $\text{NaOH}(\text{aq})$ , which has

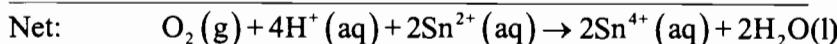
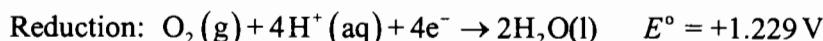
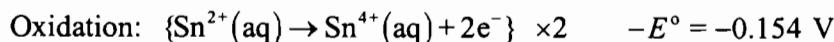
$$E_{\text{cell}}^\circ = 2.713\text{V} - 0.828\text{V} = +1.885\text{V}$$

**6A** The oxidation is that of  $\text{SO}_4^{2-}$  to  $\text{S}_2\text{O}_8^{2-}$ , the reduction is that of  $\text{O}_2$  to  $\text{H}_2\text{O}$ .



Because the standard cell potential is negative, we conclude that this cell reaction is nonspontaneous. This would not be a feasible method of producing peroxodisulfate ion.

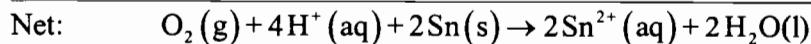
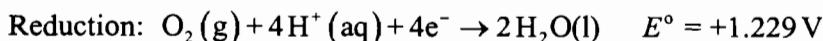
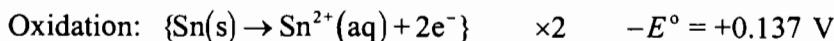
**6B (1)** The oxidation is that of  $\text{Sn}^{2+}(\text{aq})$  to  $\text{Sn}^{4+}(\text{aq})$ , the reduction is that of  $\text{O}_2$  to  $\text{H}_2\text{O}$ .



$$E_{\text{cell}}^\circ = -0.154\text{V} + 1.229\text{V} = +1.075\text{V}$$

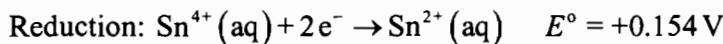
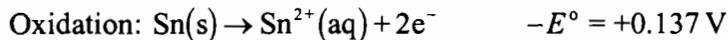
Since the standard cell potential is positive, this cell reaction is spontaneous.

**6B (2)** The oxidation is that of  $\text{Sn}(\text{s})$  to  $\text{Sn}^{2+}(\text{aq})$ , the reduction is still that of  $\text{O}_2$  to  $\text{H}_2\text{O}$ .



$$E_{\text{cell}}^\circ = 0.137\text{V} + 1.229\text{V} = +1.366\text{V}$$

The standard cell potential for this reaction is more positive than that for situation (1); reaction (2) should occur preferentially. Also, if  $\text{Sn}^{4+}(\text{aq})$  is formed, it should react with  $\text{Sn}(\text{s})$  to form  $\text{Sn}^{2+}(\text{aq})$ .



**7A** For the reaction  $2\text{Al}(\text{s}) + 3\text{Cu}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Cu}(\text{s})$  we know  $n = 6$  and

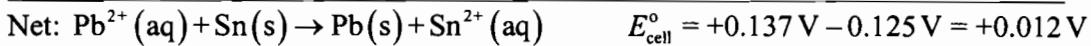
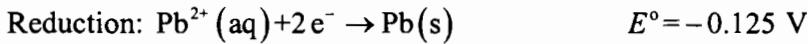
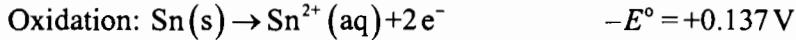
$$E_{\text{cell}}^\circ = +2.013 \text{ V}.$$

We calculate the value of  $K_{\text{eq}}$ .

$$E_{\text{cell}}^\circ = \frac{0.0257}{n} \ln K_{\text{eq}}; \quad \ln K_{\text{eq}} = \frac{nE_{\text{cell}}^\circ}{0.0257} = \frac{6 \times (+2.013)}{0.0257} = 470; \quad K_{\text{eq}} = e^{470} = 10^{204}$$

The huge size of the equilibrium constant indicates that this reaction indeed will go to completion.

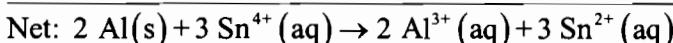
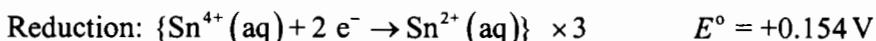
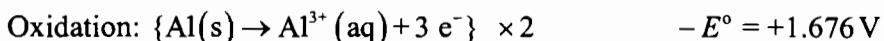
**7B** We first determine the value of  $E_{\text{cell}}^\circ$  from the half-cell potentials.



$$E_{\text{cell}}^\circ = \frac{0.0257}{n} \ln K_{\text{eq}} \quad \ln K_{\text{eq}} = \frac{nE_{\text{cell}}^\circ}{0.0257} = \frac{2 \times (+0.012)}{0.0257} = 0.93 \quad K_{\text{eq}} = e^{0.93} = 2.5$$

The equilibrium constant's small size indicates that this reaction will not go to completion.

**8A** We first need to determine the standard cell voltage and the cell reaction.



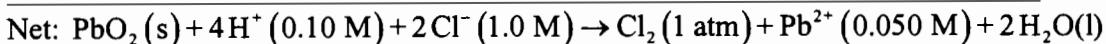
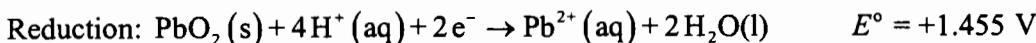
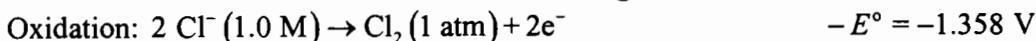
$$E_{\text{cell}}^\circ = +1.676 \text{ V} + 0.154 \text{ V} = +1.830 \text{ V}$$

Note that  $n = 6$ . We now set up and substitute into the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Al}^{3+}]^2 [\text{Sn}^{2+}]^3}{[\text{Sn}^{4+}]^3} = +1.830 - \frac{0.0592}{6} \log \frac{(0.36 \text{ M})^2 (0.54 \text{ M})^3}{(0.086 \text{ M})^3}$$

$$= +1.830 \text{ V} - 0.0149 \text{ V} = +1.815 \text{ V}$$

**8B** We first need to determine the standard cell voltage and the cell reaction.



$$E_{\text{cell}}^\circ = -1.358 \text{ V} + 1.455 \text{ V} = +0.097 \text{ V} \quad \text{Note that } n = 2. \text{ Substitute into Nernst equation.}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{P\{\text{Cl}_2\} [\text{Pb}^{2+}]}{[\text{H}^+]^4 [\text{Cl}^-]^2} = +0.097 - \frac{0.0592}{2} \log \frac{(1.0 \text{ atm})(0.050 \text{ M})}{(0.10 \text{ M})^4 (1.0 \text{ M})^2}$$

$$= +0.097 \text{ V} - 0.080 \text{ V} = +0.017 \text{ V}$$

**9A** The cell reaction is  $2 \text{Fe}^{3+} (0.35 \text{ M}) + \text{Cu} (\text{s}) \rightarrow 2 \text{Fe}^{2+} (0.25 \text{ M}) + \text{Cu}^{2+} (0.15 \text{ M})$  with  $n = 2$ , and  $E_{\text{cell}}^\circ = -0.337 \text{ V} + 0.771 \text{ V} = 0.434 \text{ V}$  Next, substitute this voltage into the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]^2 [\text{Cu}^{2+}]}{[\text{Fe}^{3+}]^2} = 0.434 - \frac{0.0592}{2} \log \frac{(0.25)^2 (0.15)}{(0.35)^2} = 0.434 + 0.033$$

$E_{\text{cell}} = +0.467 \text{ V}$  The reaction is spontaneous as written.

**9B** The reaction is not spontaneous in either direction when  $E_{\text{cell}} = 0.000 \text{ V}$ . We use the standard cell potential from Example 21-9.

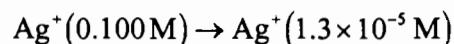
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}; \quad 0.000 \text{ V} = 0.012 \text{ V} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$$

$$\log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = \frac{0.012 \times 2}{0.0592} = 0.41; \quad \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = 10^{0.41} = 2.6$$

**10A** In this concentration cell  $E_{\text{cell}}^\circ = 0.000 \text{ V}$  because the same reaction occurs at anode and cathode, only the concentrations of the ions differ.  $[\text{Ag}^+] = 0.100 \text{ M}$  in the cathode compartment. The anode compartment contains a saturated solution of  $\text{AgCl}(\text{aq})$ .

$$K_{\text{sp}} = 1.8 \times 10^{-10} = [\text{Ag}^+] [\text{Cl}^-] = s^2; \quad s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

Now we apply the Nernst equation. The cell reaction is



$$E_{\text{cell}} = 0.000 - \frac{0.0592}{1} \log \frac{1.3 \times 10^{-5} \text{ M}}{0.100 \text{ M}} = +0.23 \text{ V}$$

**10B** For this cell because the electrodes are identical, the standard electrode potentials are numerically equal and subtracting one from the other leads to the value  $E_{\text{cell}}^{\circ} = 0.000 \text{ V}$ . However, because the ion concentrations differ, there is a potential difference between the two half cells (non-zero nonstandard voltage for the cell).  $[\text{Pb}^{2+}] = 0.100 \text{ M}$  in the cathode compartment. The anode compartment contains a saturated solution of  $\text{PbI}_2$ . We use the Nernst equation (with  $n = 2$ ) to determine  $[\text{Pb}^{2+}]$  in the saturated solution.

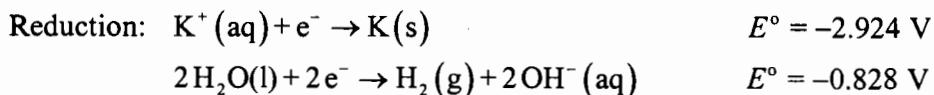
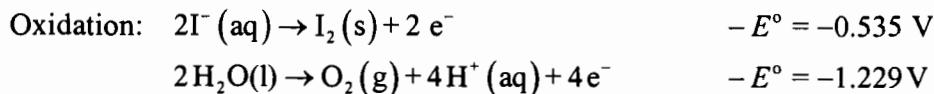
$$E_{\text{cell}} = +0.0567 \text{ V} = 0.000 - \frac{0.0592}{2} \log \frac{x \text{ M}}{0.100 \text{ M}}; \quad \log \frac{x \text{ M}}{0.100 \text{ M}} = \frac{2 \times 0.0567}{-0.0592} = -1.92$$

$$\frac{x \text{ M}}{0.100 \text{ M}} = 10^{-1.92} = 0.012; \quad [\text{Pb}^{2+}]_{\text{anode}} = x \text{ M} = 0.012 \times 0.100 \text{ M} = 0.0012 \text{ M};$$

$$[\text{I}^-] = 2 \times 0.0012 \text{ M} = 0.0024 \text{ M}$$

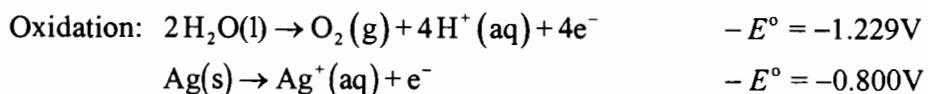
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2 = (0.0012)(0.0024)^2 = 6.9 \times 10^{-9} \text{ compared with } 7.1 \times 10^{-9} \text{ in Appendix D}$$

**11A** From Table 21-1 we choose one oxidations and one reductions reaction so as to get the least negative cell voltage. This will be the most likely pair of  $\frac{1}{2}$ -reactions to occur.

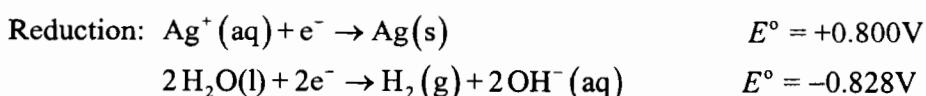


The least negative standard cell potential ( $-0.535 \text{ V} - 0.828 \text{ V} = -1.363 \text{ V}$ ) occurs when  $\text{I}_2 \text{ (s)}$  is produced by oxidation at the anode, and  $\text{H}_2 \text{ (g)}$  is produced by reduction at the cathode.

**11B** We obtain from Table 21-1 all the possible oxidations and reductions and choose one of each to get the least negative cell voltage. That pair is the most likely pair of half-reactions to occur.



[We cannot further oxidize  $\text{NO}_3^- \text{ (aq)}$  or  $\text{Ag}^+ \text{ (aq)}$ .]



Thus, we expect to form silver metal at the cathode and  $\text{Ag}^+ \text{ (aq)}$  at the anode.

- 12A** The half-cell equation is  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ , indicating that two moles of electrons are required for each mole of copper deposited. Current is measured in amperes, or coulombs per second. We convert the mass of copper to coulombs of electrons needed for the reduction and the time in hours to seconds.

$$\text{Current} = \frac{12.3 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mole}^-}{1 \text{ mol Cu}} \times \frac{96,485 \text{ C}}{1 \text{ mole}^-}}{5.50 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}}} = \frac{3.73 \times 10^4 \text{ C}}{1.98 \times 10^4 \text{ s}} = 1.89 \text{ amperes}$$

- 12B** We first determine the moles of  $\text{O}_2(\text{g})$  produced with the ideal gas equation.

$$\text{moles O}_2(\text{g}) = \frac{\left(738 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}}\right) \times 2.62 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times (26.2 + 273.2) \text{ K}} = 0.104 \text{ mol O}_2$$

Then we determine the time needed to produce this amount of  $\text{O}_2$ .

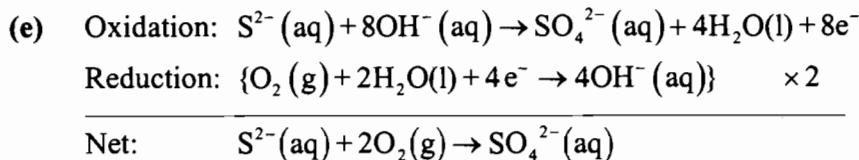
$$\text{elapsed time} = 0.104 \text{ mol O}_2 \times \frac{4 \text{ mol e}^-}{1 \text{ mol O}_2} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{2.13 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 5.23 \text{ h}$$

## REVIEW QUESTIONS

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- $E^\circ$  is the symbol for the standard cell potential, the voltage measured when no current is flowing and all cell reagents are in their standard states.
  - $F$  is the symbol for Faraday's constant, the charge on one mole of electrons, 96,485 coulombs.
  - The anode is the electrode where oxidation occurs and toward which anions move.
  - The cathode is the electrode where reduction occurs and toward which cations move.
- A salt bridge is a tube filled with electrolyte that is used to join two half-cells in such a way that the electrochemical circuit is completed but the contents of the half-cells do not mix.
  - The standard hydrogen electrode is based on the reduction of hydrogen ion, at 1.000 M concentration, to hydrogen gas at 1.000 atm pressure. It is assigned a half-cell potential of 0.000 V.
  - Cathodic protection is achieved by electrically joining a more active metal to a less active one that is to be protected. The more active metal will be oxidized, protecting the less active one from corrosion.

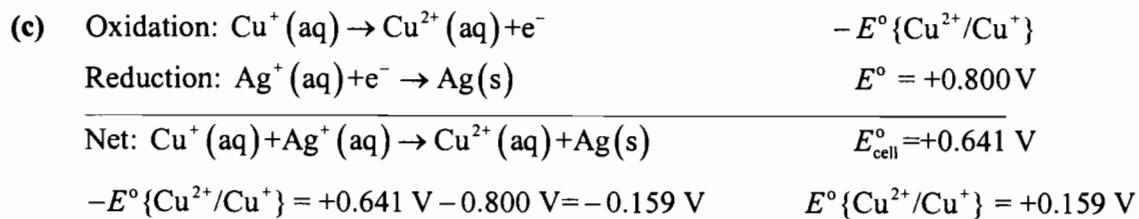
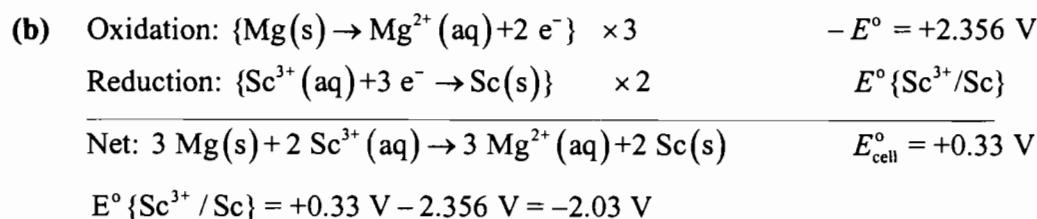
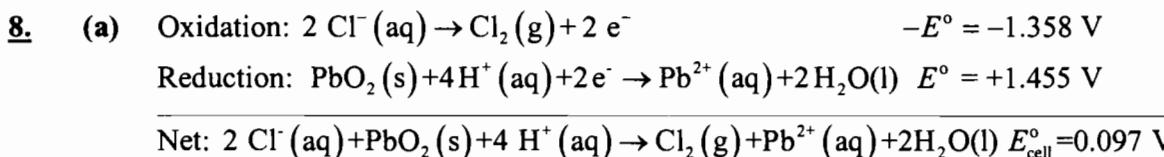
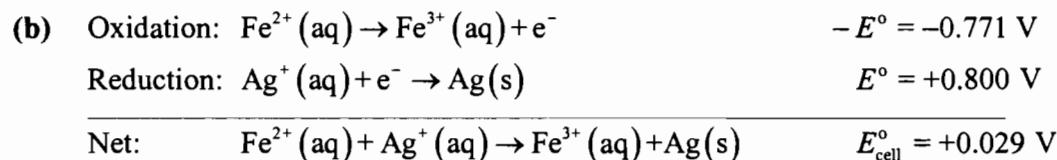
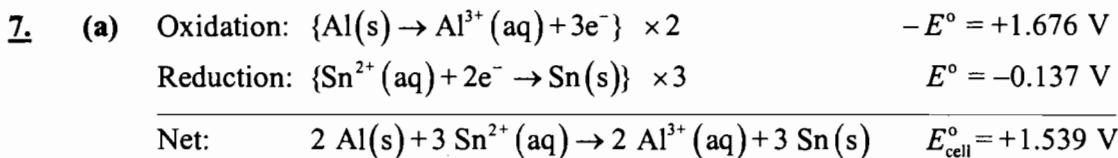
- (d) A fuel cell is a voltaic cell in which a reaction that normally occurs as a combustion reaction serves as the cell reaction. Reactants are continually supplied and products removed from such a cell.
3. (a) A half-reaction is either the oxidation reaction or the reduction reaction of a cell. On the other hand, the net reaction is an oxidation-reduction reaction, the combination of two half-reactions.
- (b) In a voltaic or galvanic cell, a chemical change produces electricity. This type of cell has  $E > 0$ . In an electrolytic cell, the passage of electric current produces a chemical change. This type of cell has  $E < 0$ .
- (c) A primary battery is nonreversible, like a dry cell. A secondary battery can be recharged and reused.
- (d)  $E_{\text{cell}}^{\circ}$  is the cell potential when all reactants and all products are in their standard states.  $E_{\text{cell}}$  is the cell potential when reactants and products are not necessarily in their standard states.
4. The correct statement is (d). Electrons are produced at the anode and move toward the cathode, regardless of the electrode material. The electrons do not move through the salt bridge; ions do. Electrons do not leave the cell; they provide current within the circuitry. Reduction occurs at the cathode in both galvanic and electrolytic cells—in all types of electrochemical cells, in fact.
5. (a) Oxidation:  $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$   
 Reduction:  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$   
 Net:  $\text{Fe}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
- (b) Oxidation:  $2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{e}^-$   
 Reduction:  $\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$   
 Net:  $2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$
- (c) Oxidation:  $\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$   
 Reduction:  $\{\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})\} \times 3$   
 Net:  $\text{Al}(\text{s}) + 3\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{Fe}^{2+}(\text{aq})$
- (d) Oxidation:  $\{\text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^-\} \times 5$   
 Reduction:  $\{\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})\} \times 6$   
 Net:  $5\text{Cl}^-(\text{aq}) + 6\text{MnO}_4^-(\text{aq}) + 18\text{H}^+(\text{aq}) \rightarrow 5\text{ClO}_3^-(\text{aq}) + 6\text{Mn}^{2+}(\text{aq}) + 9\text{H}_2\text{O}(\text{l})$

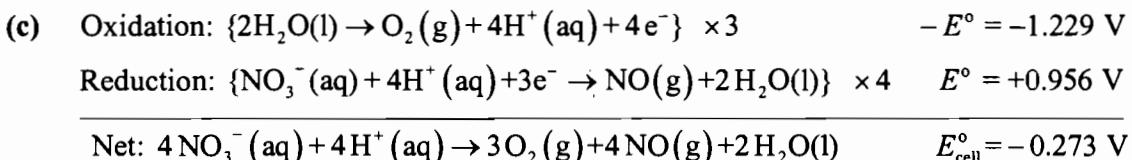
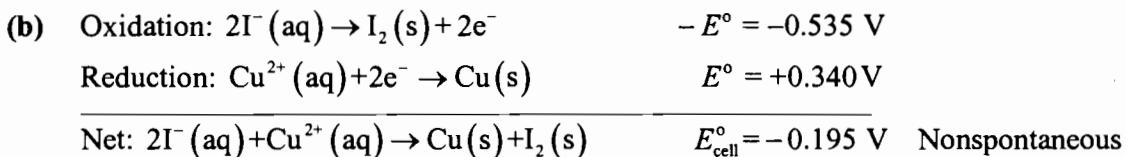
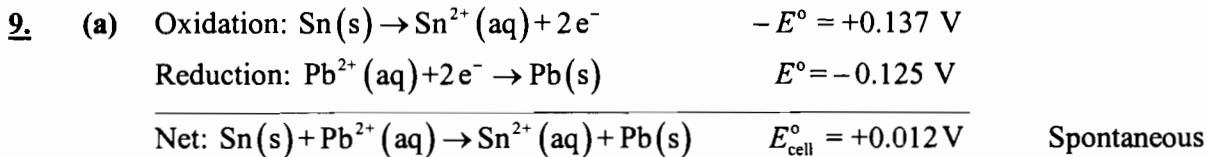


6. Since  $Zn^{2+}(aq)$  undergoes reduction, and the other metal (M) undergoes oxidation,

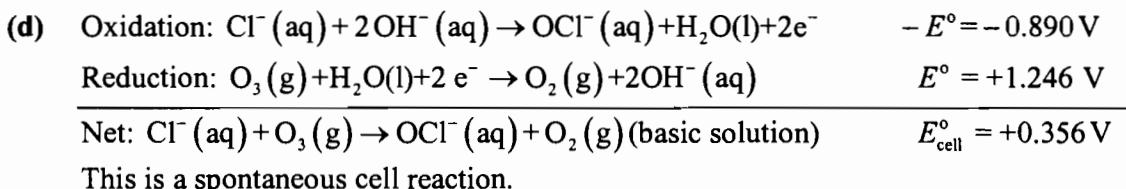
$$E_{cell}^o = E_{Zn}^o - E_M^o \quad \text{or} \quad E_M^o = E_{Zn}^o - E_{cell}^o$$

- (a)  $E_{Mn}^o = E_{Zn}^o - E_{cell}^o = -0.763 \text{ V} - 0.417 \text{ V} = -1.180 \text{ V}$   
 (b)  $E_{Po}^o = E_{Zn}^o - E_{cell}^o = -0.763 \text{ V} + 1.13 \text{ V} = +0.37 \text{ V}$   
 (c)  $E_{Ti}^o = E_{Zn}^o - E_{cell}^o = -0.763 \text{ V} - 0.87 \text{ V} = -1.63 \text{ V}$   
 (d)  $E_V^o = E_{Zn}^o - E_{cell}^o = -0.763 \text{ V} - 0.37 \text{ V} = -1.13 \text{ V}$



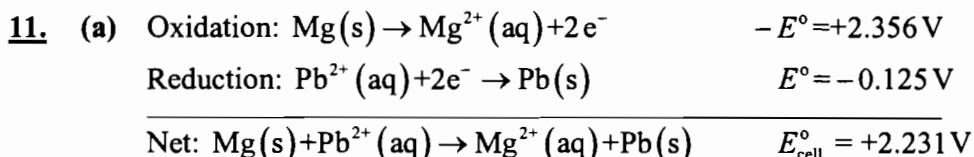


This is a nonspontaneous cell reaction.

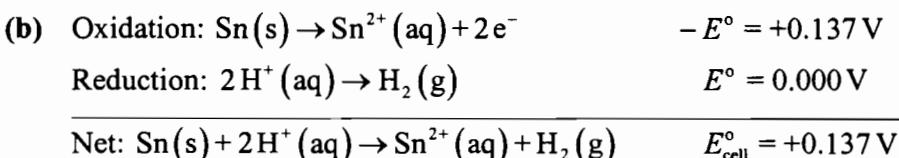


This is a spontaneous cell reaction.

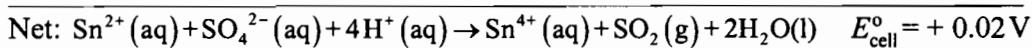
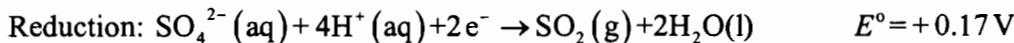
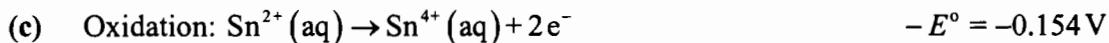
10. It is more difficult to oxidize  $\text{Hg}(\text{l})$  to  $\text{Hg}_2^{2+}(-0.797 \text{ V})$  than it is to reduce  $\text{H}^+$  to  $\text{H}_2$  ( $0.000 \text{ V}$ );  $\text{Hg}(\text{l})$  will not dissolve in 1 M HCl. The reduction of nitrate ion to  $\text{NO}(\text{g})$  in acidic solution is relatively spontaneous in acidic media ( $+0.956 \text{ V}$ ). This can help overcome the reluctance of  $\text{Hg}$  to be oxidized.  $\text{Hg}(\text{l})$  will react with and dissolve in the  $\text{HNO}_3(\text{aq})$ .



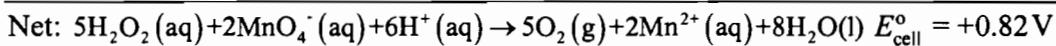
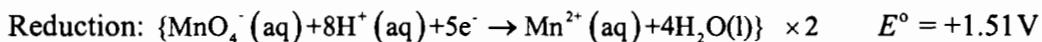
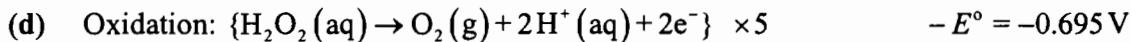
This reaction occurs to a significant extent.



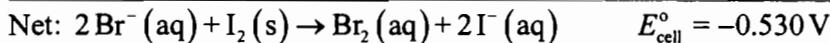
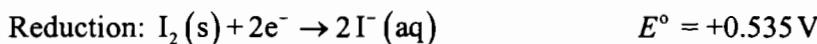
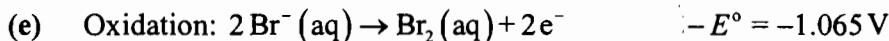
This reaction will occur to a significant extent.



This reaction will occur, but not to a large extent.



This reaction will occur to a significant extent.



This reaction will not occur to a significant extent.

12. The relatively small value of  $E_{\text{cell}}^\circ$  for a reaction indicates that the reaction will proceed in the forward reaction, but will stop short of completion. A much larger value of  $E_{\text{cell}}^\circ$  would be necessary before we would conclude that the reaction goes to completion. For example, we can compute the value of the equilibrium constant for this reaction. A value of 1000 or more is needed before we can describe the reaction as one that goes to completion.

$$E_{\text{cell}}^\circ = \frac{0.0257}{n} \ln K_{\text{eq}} \quad \ln K_{\text{eq}} = \frac{n \times E_{\text{cell}}^\circ}{0.0257} = \frac{2 \times 0.02}{0.0257} = 2 \quad K_{\text{eq}} = e^2 = 7$$

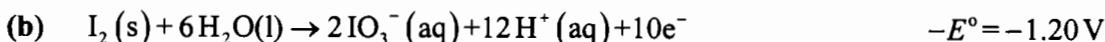
13. If  $E_{\text{cell}}^\circ$  is positive, the reaction will occur. For the reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}(\text{aq})$ :



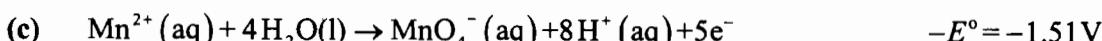
If the oxidation has  $-E^\circ$  smaller (more negative) than  $-1.33\text{ V}$ , the oxidation will not occur.



Hence,  $\text{Sn}^{2+}(\text{aq})$  can be oxidized to  $\text{Sn}^{4+}(\text{aq})$  by  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ .

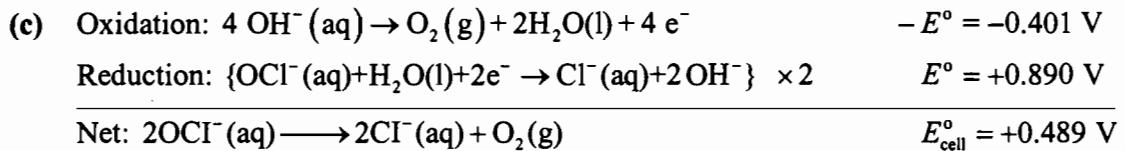


$\text{I}_2(\text{s})$  can be oxidized to  $\text{IO}_3^-(\text{aq})$  by  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ .

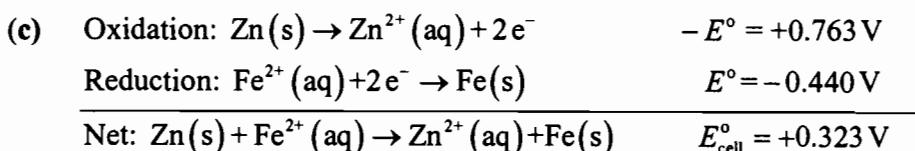
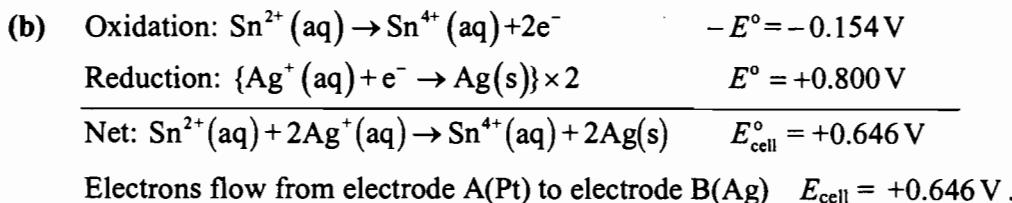
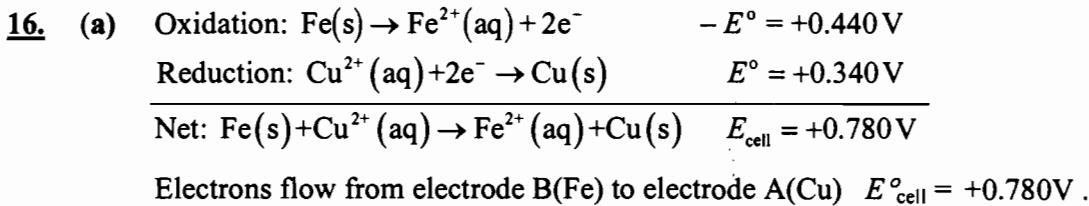


$\text{Mn}^{2+}(\text{aq})$  cannot be oxidized to  $\text{MnO}_4^-(\text{aq})$  by  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ .

- 14. (a)** Oxidation:  $\{Al(s) \rightarrow Al^{3+}(aq) + 3e^- \} \times 2$   $-E^\circ = +1.676 V$   
 Reduction:  $\{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)\} \times 3$   $E^\circ = +0.337 V$   
 Net:  $2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$   $E_{cell}^\circ = +2.013 V$   
 $\Delta G^\circ = -nFE_{cell}^\circ = -(6 \text{ mol } e^-)(96,485 \text{ C/mol } e^-)(2.013 \text{ V})$   
 $\Delta G^\circ = -1.165 \times 10^6 \text{ J} = -1.165 \times 10^3 \text{ kJ}$
- (b)** Oxidation:  $\{2I^-(aq) \rightarrow I_2(s) + 2e^- \} \times 2$   $-E^\circ = -0.535 V$   
 Reduction:  $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$   $E^\circ = +1.229 V$   
 Net:  $4I^-(aq) + O_2(g) + 4H^+(aq) \rightarrow 2I_2(s) + 2H_2O(l)$   $E_{cell}^\circ = +0.694 V$   
 $\Delta G^\circ = -nFE_{cell}^\circ = -(4 \text{ mol } e^-)(96,485 \text{ C/mol } e^-)(0.694 \text{ V}) = -2.68 \times 10^5 \text{ J} = -268 \text{ kJ}$
- (c)** Oxidation:  $\{Ag(s) \rightarrow Ag^+(aq) + e^- \} \times 6$   $-E^\circ = -0.800 V$   
 Reduction:  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$   $E^\circ = +1.33 V$   
 Net:  $6Ag(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Ag^+(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$   
 $E_{cell}^\circ = -0.800 V + 1.33 V = +0.53 V$   
 $\Delta G^\circ = -nFE_{cell}^\circ = -(6 \text{ mol } e^-)(96,485 \text{ C/mol } e^-)(0.53 \text{ V}) = -3.1 \times 10^5 \text{ J} = -3.1 \times 10^2 \text{ kJ}$
- 15.**  $\Delta G^\circ = -nFE_{cell}^\circ = -RT \ln K$ ;  $\ln K = \frac{nFE_{cell}^\circ}{RT}$ ; This becomes  $\ln K = \frac{n}{0.0257} E_{cell}^\circ$
- (a)** Oxidation:  $\{Ag(s) \rightarrow Ag^+(aq) + e^- \} \times 2$   $-E^\circ = -0.800 V$   
 Reduction:  $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$   $E^\circ = +0.154 V$   
 Net:  $2Ag(s) + Sn^{4+}(aq) \rightarrow 2Ag^+(aq) + Sn^{2+}(aq)$   $E_{cell}^\circ = -0.646 V$   
 $\ln K_{eq} = \frac{n}{0.0257} E_{cell}^\circ = \frac{2 \text{ mol } e^- \times (-0.646 \text{ V})}{0.0257} = -50.3$   
 $K_{eq} = e^{-50.3} = 1 \times 10^{-22} = \frac{[Sn^{2+}][Ag^+]}{[Sn^{4+}]}$
- (b)** Oxidation:  $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$   $-E^\circ = -1.358 V$   
 Reduction:  $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$   $E^\circ = +1.23 V$   
 Net:  $2Cl^-(aq) + MnO_2(s) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$   $E_{cell}^\circ = -0.13 V$   
 $\ln K_{eq} = \frac{2 \text{ mol } e^- \times (-0.13 \text{ V})}{0.0257} = -10.1$ ;  $K_{eq} = e^{-10.1} = 4 \times 10^{-5} = \frac{[Mn^{2+}][Cl_2(g)]}{[Cl^-]^2[H^+]^4}$

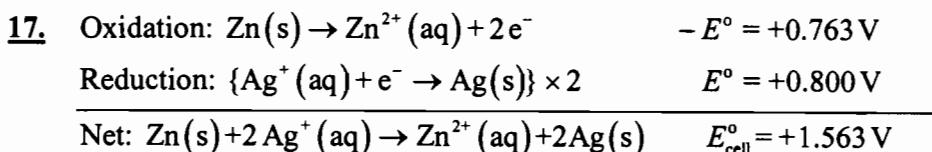


$$\ln K_{\text{eq}} = \frac{4 \text{ mol e}^- (0.489 \text{ V})}{0.0257} = 76.1 \quad K_{\text{eq}} = e^{76.1} = 1 \times 10^{33} = \frac{[\text{Cl}^-]^2 P\{\text{O}_2(\text{g})\}}{[\text{OCl}^-]^2}$$



$$E = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} = +0.323 \text{ V} - \frac{0.0592}{2} \log \frac{0.10 \text{ M}}{1.0 \times 10^{-3} \text{ M}} \\ = +0.323 \text{ V} - 0.0592 \text{ V} = +0.264 \text{ V}$$

Electrons flow from electrode A(Zn) to electrode B(Fe)  $E_{\text{cell}}^\circ = +0.264 \text{ V}$ .



$$E = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = +1.563 \text{ V} - \frac{0.0592}{2} \log \frac{1.00 \text{ M}}{x^2} = +1.250 \text{ V}$$

$$\log \frac{1.00 \text{ M}}{x^2} = \frac{-2 \times (1.250 - 1.563)}{0.0592} = 10.6; \quad x = \sqrt{2.5 \times 10^{-11}} = 5 \times 10^{-6} \text{ M}$$

- 18.** In each case, we employ the equation  $E_{\text{cell}} = 0.0592 \text{ pH}$ .

(a)  $E_{\text{cell}} = 0.0592 \text{ pH} = 0.0592 \times 5.25 = 0.311 \text{ V}$

(b)  $\text{pH} = -\log(0.0103) = 1.987 \quad E_{\text{cell}} = 0.0592 \text{ pH} = 0.0592 \times 1.987 = 0.118 \text{ V}$

(c)  $K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x^2}{0.158 - x} \approx \frac{x^2}{0.158}$

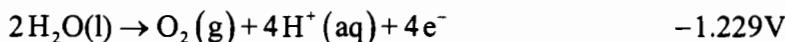
$$x = \sqrt{0.158 \times 1.8 \times 10^{-5}} = 1.7 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(1.7 \times 10^{-3}) = 2.77$$

$$E_{\text{cell}} = 0.0592 \text{ pH} = 0.0592 \times 2.77 = 0.164 \text{ V}$$

- 19.** We predict the possible products at the anode and at the cathode. Then we choose the oxidation and the reduction which, when combined, yield the least negative cell potential.

- (a) Possible products (of oxidation) at the anode are the following.

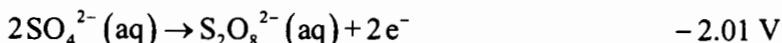
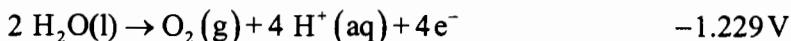


Possible products (of reduction) at the cathode are the following.



Because of the high overpotential for the production of  $\text{O}_2(\text{g})$  (see pg. 852 of text), the products of electrolysis of  $\text{CuCl}_2(\text{aq})$  will be  $\text{Cl}_2(\text{g})$  at the anode and  $\text{Cu}(\text{s})$  at the cathode.

- (b) Possible products (of oxidation) at the anode are the following.



Possible products (of reduction) at the cathode are the following.

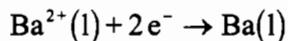


The products of electrolysis of  $\text{Na}_2\text{SO}_4(\text{aq})$  will be  $\text{O}_2(\text{g})$  at the anode, and  $\text{H}_2(\text{g})$  and  $\text{OH}^-(\text{aq})$  at the cathode.

- (c) The only possible product (of oxidation) at the anode is the following.

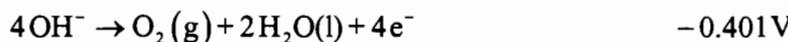


The only possible product (of reduction) at the cathode is the following.



The products of electrolysis of  $\text{BaCl}_2(\text{l})$  will be  $\text{Cl}_2(\text{g})$  at the anode and  $\text{Ba}(\text{l})$  at the cathode.

- (d) The only possible product (of oxidation) at the anode is the following.



Possible products (of reduction) at the cathode are the following.



The products of electrolysis of  $\text{KOH}(\text{aq})$  will be  $\text{O}_2(\text{g})$  at the anode,  $\text{H}_2(\text{g})$  and  $\text{OH}^-(\text{aq})$  at the cathode.

20. When  $\text{MgCl}_2(\text{l})$  is electrolyzed,  $\text{Mg}(\text{l})$  is produced at the cathode, with a half-cell voltage of  $-2.356\text{V}$ . On the other hand, when  $\text{MgCl}_2(\text{aq})$  is electrolyzed,  $\text{H}_2(\text{g})$  and  $\text{OH}^-(\text{aq})$  are produced at the cathode, with a standard half-cell voltage of  $0.000\text{ V}$ . If we wish to produce elemental magnesium, we must electrolyze molten  $\text{MgCl}_2$ , not its aqueous solution.

21. We calculate the total amount of charge passed and the number of moles of electrons.

$$\text{mol e}^- = 75 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.15 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} = 0.10 \text{ mol e}^-$$

$$(a) \text{ mass Zn} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Zn}^{2+}}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Zn}}{1 \text{ mol Zn}^{2+}} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 3.3 \text{ g Zn}$$

$$(b) \text{ mass Al} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Al}^{3+}}{3 \text{ mol e}^-} \times \frac{1 \text{ mol Al}}{1 \text{ mol Al}^{3+}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 0.90 \text{ g Al}$$

$$(c) \text{ mass Ag} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Ag}^+}{1 \text{ mol e}^-} \times \frac{1 \text{ mol Ag}}{1 \text{ mol Ag}^+} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 11 \text{ g Ag}$$

$$(d) \text{ mass Ni} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Ni}^{2+}}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Ni}}{1 \text{ mol Ni}^{2+}} \times \frac{58.69 \text{ g Ni}}{1 \text{ mol Ni}} = 2.9 \text{ g Ni}$$

- 22.** The two half reactions follow:  $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$  and  $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$ . Thus, two moles of electrons are needed to produce each mole of  $\text{Cu}(\text{s})$  and two moles of electrons are needed to produce each mole of  $\text{H}_2(\text{g})$ . With this information, we compute the moles of  $\text{H}_2(\text{g})$  that will be produced.

$$\text{mol H}_2(\text{g}) = 3.28 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{1 \text{ mol H}_2(\text{g})}{2 \text{ mol e}^-} = 0.0516 \text{ mol H}_2(\text{g})$$

Then we use the ideal gas equation to find the volume of  $\text{H}_2(\text{g})$ .

$$\text{Volume of H}_2(\text{g}) = \frac{0.0516 \text{ mol H}_2 \times \frac{0.08206 \text{ Latm}}{\text{mol K}} \times (273.2 + 28.2) \text{ K}}{763 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 1.27 \text{ L}$$

This answer assumes the  $\text{H}_2(\text{g})$  is not collected over water, and that the  $\text{H}_2(\text{g})$  formed is the only gas present in the container (i.e. no water vapor present)

## EXERCISES

### Standard Electrode Potential

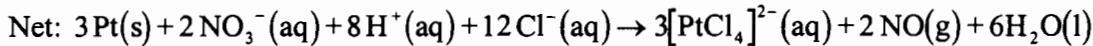
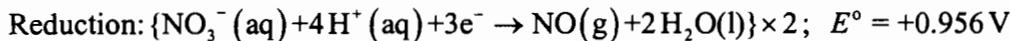
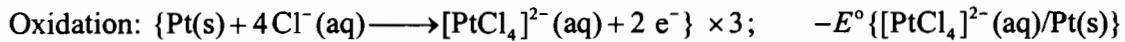
- 23. (a)** If the metal dissolves in  $\text{HNO}_3$ , it has a reduction potential that is smaller than  $E^\circ \{ \text{NO}_3^-(\text{aq})/\text{NO}(\text{g}) \} = 0.956 \text{ V}$ . If it also does not dissolve in  $\text{HCl}$ , it has a reduction potential that is larger than  $E^\circ \{ \text{H}^+(\text{aq})/\text{H}_2(\text{g}) \} = 0.000 \text{ V}$ . If it displaces  $\text{Ag}^+(\text{aq})$  from solution, then it has a reduction potential that is smaller than  $E^\circ \{ \text{Ag}^+(\text{aq})/\text{Ag}(\text{s}) \} = 0.800 \text{ V}$ . But if it does not displace  $\text{Cu}^{2+}(\text{aq})$  from solution, then its reduction potential is larger than

$$E^\circ \{ \text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s}) \} = 0.340 \text{ V} \quad 0.340 \text{ V} < E^\circ < 0.800 \text{ V}$$

- (b)** If the metal dissolves in  $\text{HCl}$ , it has a reduction potential that is smaller than  $E^\circ \{ \text{H}^+(\text{aq})/\text{H}_2(\text{g}) \} = 0.000 \text{ V}$ . If it does not displace  $\text{Zn}^{2+}(\text{aq})$  from solution, its reduction potential is larger than  $E^\circ \{ \text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s}) \} = -0.763 \text{ V}$ . If it also does not displace  $\text{Fe}^{2+}(\text{aq})$  from solution, its reduction potential is larger than

$$E^\circ \{ \text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s}) \} = -0.440 \text{ V} \quad -0.440 \text{ V} < E^\circ < 0.000 \text{ V}$$

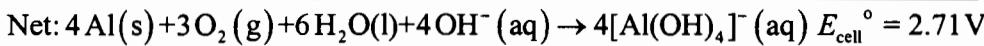
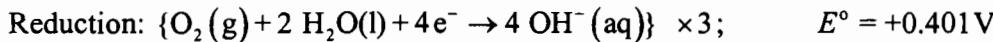
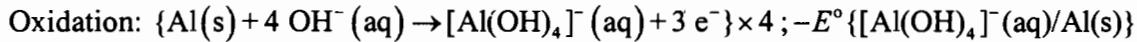
25. We separate the given equation into its two half-equations. One of them is the reduction of nitrate ion in acidic solution, whose standard half-cell potential we retrieve from Table 21-1 and use to solve the problem.



$$E_{\text{cell}}^\circ = 0.201 \text{ V} = +0.956 \text{ V} - E^\circ \{ [\text{PtCl}_4]^{2-} (\text{aq}) / \text{Pt(s)} \}$$

$$E^\circ \{ [\text{PtCl}_4]^{2-} (\text{aq}) / \text{Pt(s)} \} = 0.956 \text{ V} - 0.201 \text{ V} = +0.755 \text{ V}$$

27. We divide the net cell equation into two half-equations.

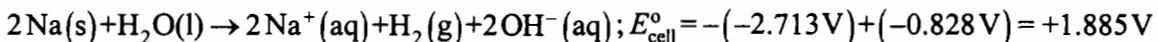


$$E_{\text{cell}}^\circ = 2.71 \text{ V} = +0.401 \text{ V} - E^\circ \{ [\text{Al(OH)}_4]^- (\text{aq}) / \text{Al(s)} \}$$

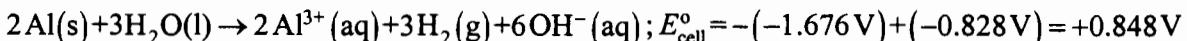
$$E^\circ \{ [\text{Al(OH)}_4]^- (\text{aq}) / \text{Al(s)} \} = 0.401 \text{ V} - 2.71 \text{ V} = -2.31 \text{ V}$$

## Predicting Oxidation-Reduction Reactions

29. Na(s) does not displace  $\text{Zn}^{2+} (\text{aq})$  in an aqueous solution; Na(s) reacts with water instead.

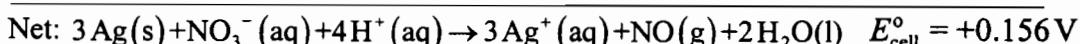
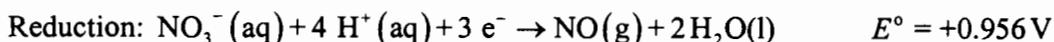


In contrast, aluminum metal reacts with  $\text{Zn}^{2+} (\text{aq})$  to displace Zn(s) from solution.

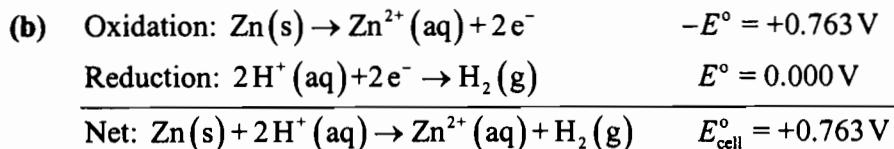


The standard cell potentials do not tell the whole story, for we might think that the reaction with the more positive value of  $E_{\text{cell}}^\circ$  would occur. In truth, Al(s) is coated with a thin layer of tightly adhering  $\text{Al}_2\text{O}_3 (\text{s})$ , which protects the metal from attack by water. Na(s) has no such protective coating.

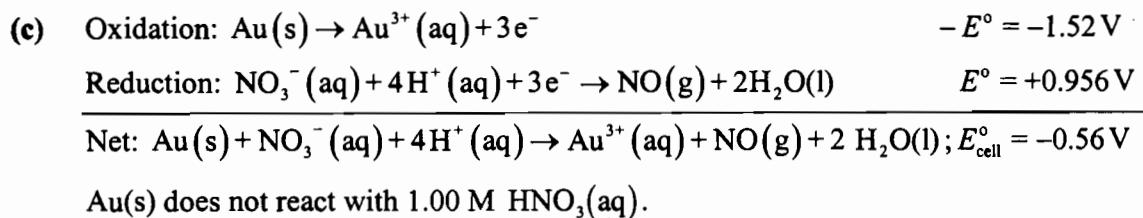
31. (a) Oxidation:  $\{ \text{Ag(s)} \rightarrow \text{Ag}^+ (\text{aq}) + \text{e}^- \} \times 3 \quad -E^\circ = -0.800 \text{ V}$



Ag(s) reacts with  $\text{HNO}_3 (\text{aq})$  to form a solution of  $\text{AgNO}_3 (\text{aq})$ .

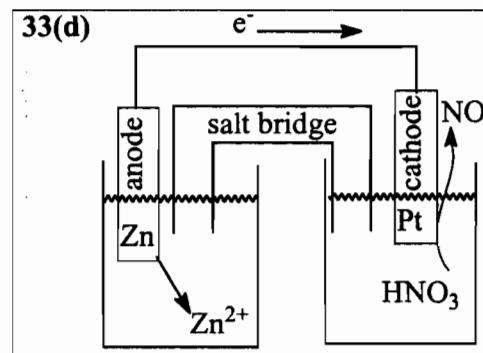
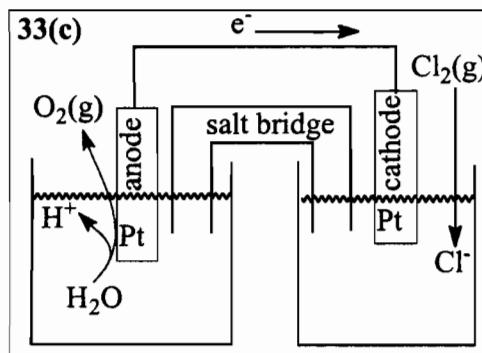
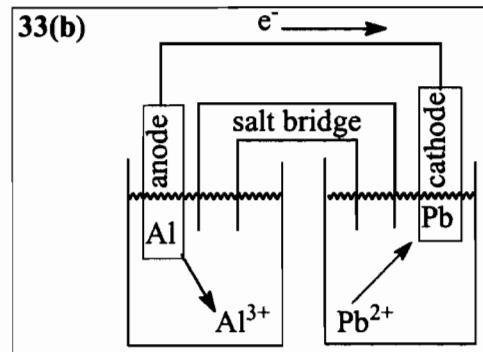
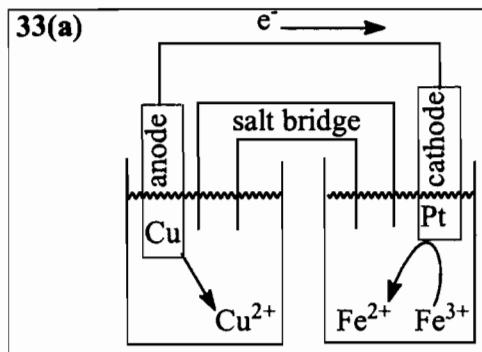


$\text{Zn(s)}$  reacts with  $\text{HI(aq)}$  to form a solution of  $\text{ZnI}_2(\text{aq})$ .



## Voltaic Cells

33. (a) Anode, Oxidation:  $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$   $-E^\circ = -0.340\text{ V}$   
 Cathode, Reduction:  $\{\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})\} \times 2$ ;  $E^\circ = +0.771\text{ V}$   
 Net:  $\text{Cu(s)} + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$   $E_{\text{cell}}^\circ = +0.431\text{ V}$
- (b) Anode, Oxidation:  $\{\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-\} \times 2$   $-E^\circ = +1.676\text{ V}$   
 Cathode, Reduction:  $\{\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb(s)}\} \times 3$ ;  $E^\circ = -0.125\text{ V}$   
 Net:  $2\text{Al(s)} + 3\text{Pb}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Pb(s)}$   $E_{\text{cell}}^\circ = +1.551\text{ V}$
- (c) Anode, Oxidation:  $2\text{H}_2\text{O(l)} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$   $-E^\circ = -1.229\text{ V}$   
 Cathode, Reduction:  $\{\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})\} \times 2$   $E^\circ = +1.358\text{ V}$   
 Net:  $2\text{H}_2\text{O(l)} + 2\text{Cl}_2(\text{g}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{Cl}^-(\text{aq})$   $E_{\text{cell}}^\circ = +0.129\text{ V}$
- (d) Anode, Oxidation:  $\{\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-\} \times 3$   $-E^\circ = +0.763\text{ V}$   
 Cathode, Reduction:  $\{\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO(g)} + 2\text{H}_2\text{O(l)}\} \times 2$ ;  $E^\circ = +0.956\text{ V}$   
 Net:  $3\text{Zn(s)} + 2\text{NO}_3^-(\text{aq}) + 8\text{H}^+(\text{aq}) \rightarrow 3\text{Zn}^{2+}(\text{aq}) + 2\text{NO(g)} + 4\text{H}_2\text{O(l)}$   $E_{\text{cell}}^\circ = +1.719\text{ V}$
- Cell diagram:  $\text{Zn(s)} \parallel \text{Zn}^{2+}(\text{aq}) \parallel \text{H}^+(\text{aq}), \text{NO}_3^-(\text{aq}) \parallel \text{NO(g)} \parallel \text{Pt(s)}$   
 The cells for parts (a) - (d) follow. The anode is on the left in each case.



### $\Delta G^\circ$ , $E_{\text{cell}}^\circ$ , and $K$

35. (a) Oxidation:  $\{\text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^-\} \times 2$ ;  $-E^\circ = -1.51\text{ V}$   
 Reduction:  $\{\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})\} \times 5$   $E^\circ = +1.763\text{ V}$

$$\text{Net: } 2\text{Mn}^{2+}(\text{aq}) + 5\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 2\text{H}_2\text{O}(\text{l}); \quad E_{\text{cell}}^\circ = +0.25\text{ V}$$

(b)  $\Delta G^\circ = -nFE_{\text{cell}}^\circ = -(10\text{ mol e}^-)(96,485\text{ C/mol e}^-)(0.25\text{ V}) = -2.4 \times 10^5\text{ J} = -2.4 \times 10^2\text{ kJ}$

(c)  $\ln K_{\text{eq}} = -\frac{\Delta G^\circ}{RT} = -\frac{-2.4 \times 10^5\text{ J}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1} \times 298\text{ K}} = 97; \quad K_{\text{eq}} = e^{97} = 1 \times 10^{42}$

- (d) Based on the extremely large value of  $K_{\text{eq}}$ , we conclude that this reaction should go to completion.

37. (a) A negative value of  $E_{\text{cell}}^\circ$  ( $-0.0050\text{ V}$ ) indicates that  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$  is positive which in turn indicates that  $K_{\text{eq}}$  is less than one ( $K_{\text{eq}} < 1.00$ );  $\Delta G^\circ = -RT\ln K_{\text{eq}}$ .

$$K_{\text{eq}} = \frac{[\text{Cu}^{2+}]^2[\text{Sn}^{2+}]}{[\text{Cu}^+]^2[\text{Sn}^{4+}]}$$

Thus, when all concentrations are the same, the ion product,  $Q$ , equals 1.00. From the negative standard cell potential, it is clear that  $K_{eq}$  must be (slightly) less than one. Therefore, all the concentrations cannot be 0.500 M at the same time.

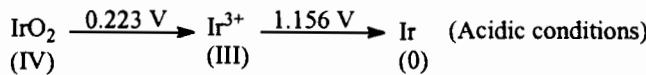
- (b) In order to establish equilibrium, that is, to have the ion product become less than 1.00, and equal the equilibrium constant, the concentrations of the products must decrease and those of the reactants must increase. A net reaction to the left will occur.

**39.** Cell reaction:  $\text{Zn(s)} + \text{Ag}_2\text{O(s)} \rightarrow \text{ZnO(s)} + 2\text{Ag(s)}$ . We assume that the cell operates at 298 K.

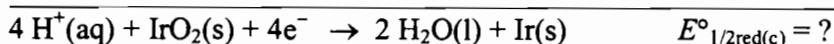
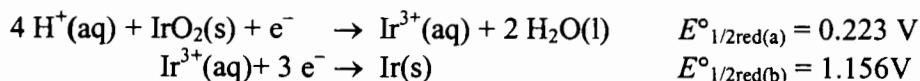
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ [\text{ZnO(s)}] + 2\Delta G_f^\circ [\text{Ag(s)}] - \Delta G_f^\circ [\text{Zn(s)}] - \Delta G_f^\circ [\text{Ag}_2\text{O(s)}] \\ &= -318.3 \text{ kJ/mol} + 2(0.00 \text{ kJ/mol}) - 0.00 \text{ kJ/mol} - (-11.20 \text{ kJ/mol}) \\ &= -307.1 \text{ kJ/mol} = -nFE_{\text{cell}}^\circ\end{aligned}$$

$$E_{\text{cell}}^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{-307.1 \times 10^3 \text{ J/mol}}{2 \text{ mol e}^-/\text{mol rxn} \times 96,485 \text{ C/mol e}^-} = 1.591 \text{ V}$$

**41.** From the data provided we can construct the following Latimer diagram.



Latimer diagrams are used to calculate the standard potentials of non-adjacent half-cell couples. Our objective in this question is to calculate the voltage differential between  $\text{IrO}_2$  and iridium metal (Ir), which are separated in the diagram by  $\text{Ir}^{3+}$ . The process basically involves adding two half-reactions to obtain a third half-reaction. The potentials for the two half-reactions cannot, however, simply be added to get the target half-cell voltage because the electrons are not cancelled in the process of adding the two half-reactions. Instead, to find  $E_{1/2 \text{ cell}}^\circ$  for the target half-reaction, we must use free energy changes, which are additive. To begin, we will balance the relevant half-reactions in acidic solution:



$$E_{1/2 \text{ red(c)}}^\circ \neq E_{1/2 \text{ red(a)}}^\circ + E_{1/2 \text{ red(b)}}^\circ \text{ but } \Delta G_{(a)}^\circ + \Delta G_{(b)}^\circ = \Delta G_{(c)}^\circ \text{ and } \Delta G^\circ = -nFE^\circ$$

$$-4F(E_{1/2 \text{ red(c)}}^\circ) = -1F(E_{1/2 \text{ red(a)}}^\circ) + -3F(E_{1/2 \text{ red(b)}}^\circ)$$

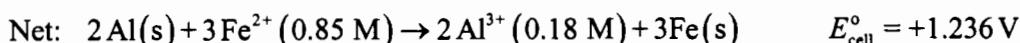
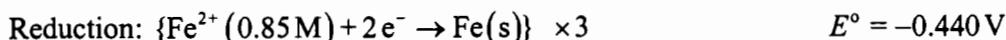
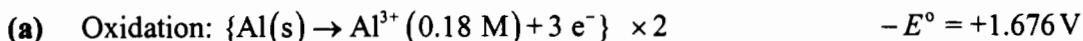
$$-4F(E_{1/2 \text{ red(c)}}^\circ) = -1F(0.223) + -3F(1.156)$$

$$E_{1/2 \text{ red(c)}}^\circ = \frac{-1F(0.223) + -3F(1.156)}{-4F} = \frac{-1(0.223) + -3(1.156)}{-4} = 0.923 \text{ V}$$

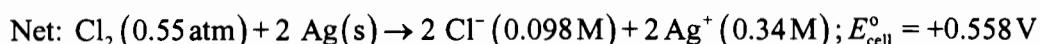
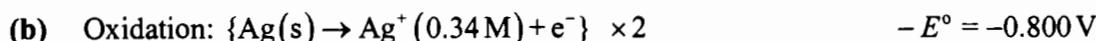
In other words,  $E_{(c)}^\circ$  is the weighted average of  $E_{(a)}^\circ$  and  $E_{(b)}^\circ$

## Concentration Dependence of $E_{\text{cell}}$ —the Nernst Equation

**43.** We first calculate  $E_{\text{cell}}^{\circ}$  for each reaction and then use the Nernst equation to calculate  $E_{\text{cell}}$ .



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Fe}^{2+}]^3} = 1.236 \text{ V} - \frac{0.0592}{6} \log \frac{(0.18 \text{ M})^2}{(0.85 \text{ M})^3} = 1.249 \text{ V}$$



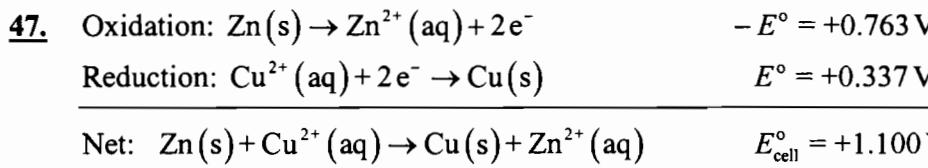
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log \frac{[\text{Cl}^-]^2 [\text{Ag}^+]^2}{P\{\text{Cl}_2(\text{g})\}} = +0.558 - \frac{0.0592}{2} \log \frac{(0.34)^2 (0.098)^2}{0.55} = +0.638 \text{ V}$$

**45.** All these observations can be understood in terms of the procedure we use to balance half-equations: the ion-electron method.

(a) The reactions for which  $E$  depends on pH are those that contain either  $\text{H}^+(\text{aq})$  or  $\text{OH}^-(\text{aq})$  in the balanced half equation. These reactions are those that involve oxoacids and oxoanions in which the central atom changes oxidation state.

(b)  $\text{H}^+(\text{aq})$  will inevitably be on the left side of the reduction of an oxoanion because reduction is accompanied by not only a decrease in oxidation state, but also by the loss of oxygen atoms, as in  $\text{ClO}_3^- \rightarrow \text{ClO}_2^-$ ,  $\text{SO}_4^{2-} \rightarrow \text{SO}_2$ , and  $\text{NO}_3^- \rightarrow \text{NO}$ . These oxygen atoms appear on the right-hand side as  $\text{H}_2\text{O}$  molecules. The hydrogens that are added to the right-hand side with the water molecules are then balanced with  $\text{H}^+(\text{aq})$  on the left-hand side.

(c) If a half-reaction with  $\text{H}^+(\text{aq})$  ions present is transferred to basic solution, it may be re-balanced by adding to each side  $\text{OH}^-(\text{aq})$  ions equal in number to the  $\text{H}^+(\text{aq})$  originally present. This results in  $\text{H}_2\text{O}(\text{l})$  on the side that had  $\text{H}^+(\text{aq})$  ions (the left side in this case) and  $\text{OH}^-(\text{aq})$  ions on the other side (the right side.)



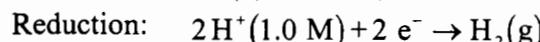
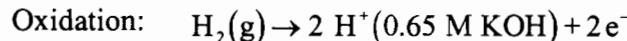
(a) We set  $E = 0.000\text{ V}$ ,  $[\text{Zn}^{2+}] = 1.00\text{ M}$ , and solve for  $[\text{Cu}^{2+}]$  in the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}; \quad 0.000 = 1.100 - 0.0296 \log \frac{1.0\text{ M}}{[\text{Cu}^{2+}]}$$

$$\log \frac{1.0\text{ M}}{[\text{Cu}^{2+}]} = \frac{0.000 - 1.100}{-0.0296} = 37.2; \quad [\text{Cu}^{2+}] = 10^{-37.2} = 6 \times 10^{-38}\text{ M}$$

(b) If we work the problem the other way, by assuming initial concentrations of  $[\text{Cu}^{2+}]_{\text{initial}} = 1.0\text{ M}$  and  $[\text{Zn}^{2+}]_{\text{initial}} = 0.0\text{ M}$ , we obtain  $[\text{Cu}^{2+}]_{\text{final}} = 6 \times 10^{-38}\text{ M}$  and  $[\text{Zn}^{2+}]_{\text{final}} = 1.0\text{ M}$ . We would say that this reaction goes to completion.

49. (a) The two half-equations and the cell equation are given below.  $E_{\text{cell}}^\circ = 0.000\text{ V}$



$$[\text{H}^+]_{\text{base}} = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.65} = 1.5 \times 10^{-14}\text{ M}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{2} \log \frac{[\text{H}^+]_{\text{base}}^2}{[\text{H}^+]_{\text{acid}}^2} = 0.000 - \frac{0.0592}{2} \log \frac{(1.5 \times 10^{-14})^2}{(1.0)^2} = +0.818\text{ V}$$

(b) For the reduction of  $\text{H}_2\text{O(l)}$  to  $\text{H}_2(\text{g})$  in basic solution,

$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow 2\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ ,  $E^\circ = -0.828\text{ V}$ . This reduction is the reverse of the reaction that occurs in the anode of the cell described, with one small difference: in the standard half-cell,  $[\text{OH}^-] = 1.00\text{ M}$ , while in the anode half-cell in the case at hand,  $[\text{OH}^-] = 0.65\text{ M}$ . Or, viewed in another way, in 1.00 M KOH,  $[\text{H}^+]$  is smaller still than in 0.65 M KOH. The forward reaction (dilution of  $\text{H}^+$ ) should be even more spontaneous with 1.00 M KOH than with 0.65 M KOH. We expect that  $E_{\text{cell}}^\circ$  (0.828 V) should be a little larger than  $E_{\text{cell}}$  (0.818 V), which, is in fact, the case.

**51.** First we need  $[\text{Ag}^+]$  in a saturated solution of  $\text{Ag}_2\text{CrO}_4$ .

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2s)^2 (s) = 4s^3 = 1.1 \times 10^{-12} \quad s = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 6.5 \times 10^{-5} \text{ M}$$

The cell diagrammed is a concentration cell, for which  $E_{\text{cell}}^{\circ} = 0.000 \text{ V}$ ,  $n = 1$ ,

$$[\text{Ag}^+]_{\text{anode}} = 2s = 1.3 \times 10^{-4} \text{ M}$$

Cell reaction:  $\text{Ag(s)} + \text{Ag}^+(0.125 \text{ M}) \rightarrow \text{Ag(s)} + \text{Ag}^+(1.3 \times 10^{-4} \text{ M})$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{1.3 \times 10^{-4} \text{ M}}{0.125 \text{ M}} = 0.000 + 0.177 \text{ V} = 0.177 \text{ V}$$

**53. (a)** Oxidation:  $\text{Sn(s)} \rightarrow \text{Sn}^{2+}(0.075 \text{ M}) + 2 \text{ e}^- \quad -E^{\circ} = +0.137 \text{ V}$

Reduction:  $\text{Pb}^{2+}(0.600 \text{ M}) + 2 \text{ e}^- \rightarrow \text{Pb(s)} \quad E^{\circ} = -0.125 \text{ V}$

Net:  $\text{Sn(s)} + \text{Pb}^{2+}(0.600 \text{ M}) \rightarrow \text{Pb(s)} + \text{Sn}^{2+}(0.075 \text{ M})$ ;  $E_{\text{cell}}^{\circ} = +0.012 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = 0.012 - 0.0296 \log \frac{0.075}{0.600} = 0.012 + 0.027 \\ = 0.039 \text{ V}$$

**(b)**  $E_{\text{cell}}$  decreases with time because the reaction forms  $[\text{Sn}^{2+}]$  and uses up  $[\text{Pb}^{2+}]$ .

**(c)** When  $[\text{Pb}^{2+}] = 0.500 \text{ M} = 0.600 \text{ M} - 0.100 \text{ M}$ ,  $[\text{Sn}^{2+}] = 0.075 \text{ M} + 0.100 \text{ M}$ , because the stoichiometry of the reaction is 1:1 for  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$ .

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = 0.012 - 0.0296 \log \frac{0.175}{0.500} = 0.012 + 0.013 = 0.025 \text{ V}$$

**(d)** Reaction:  $\text{Sn(s)} + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{Pb(s)} + \text{Sn}^{2+}(\text{aq})$

Initial:  $0.600 \text{ M} \quad 0.075 \text{ M}$

Changes:  $-x \text{ M} \quad +x \text{ M}$

Final:  $(0.600 - x) \text{ M} \quad (0.075 + x) \text{ M}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = 0.020 = 0.012 - 0.0296 \log \frac{0.075 + x}{0.600 - x}$$

$$\log \frac{0.075 + x}{0.600 - x} = \frac{E_{\text{cell}} - 0.012}{-0.0296} = \frac{0.020 - 0.012}{-0.0296} = -0.27; \quad \frac{0.075 + x}{0.600 - x} = 10^{-0.27} = 0.54$$

$$0.075 + x = 0.54(0.600 - x) = 0.324 - 0.54x; x = \frac{0.324 - 0.075}{1.54} = 0.162 \text{ M}$$

$$[\text{Sn}^{2+}] = 0.075 + 0.162 = 0.237 \text{ M}$$

- (e) Use the expression developed in part (d).

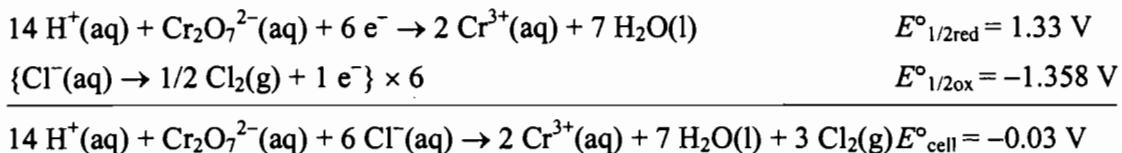
$$\log \frac{0.075 + x}{0.600 - x} = \frac{E_{\text{cell}} - 0.012}{-0.0296} = \frac{0.000 - 0.012}{-0.0296} = +0.41$$

$$\frac{0.075 + x}{0.600 - x} = 10^{+0.41} = 2.6; \quad 0.075 + x = 2.6(0.600 - x) = 1.6 - 2.6x$$

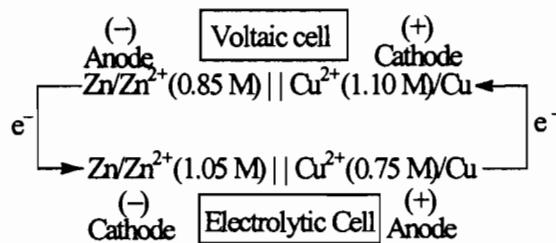
$$x = \frac{1.6 - 0.075}{3.6} = 0.42 \text{ M}$$

$$[\text{Sn}^{2+}] = 0.075 + 0.42 = 0.50 \text{ M}; \quad [\text{Pb}^{2+}] = 0.600 - 0.42 = 0.18 \text{ M}$$

55. First we will need to come up with a balanced equation for the overall redox reaction. Clearly, the reaction must involve the oxidation of  $\text{Cl}^-$ (aq) and the reduction of  $\text{Cr}_2\text{O}_7^{2-}$ (aq):

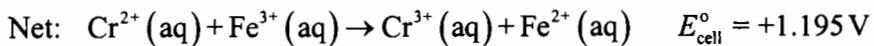
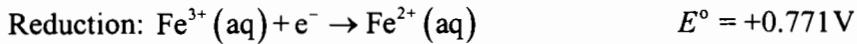
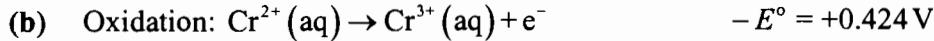
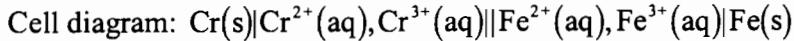


Since the cell voltage is negative, the oxidation of  $\text{Cl}^-$ (aq) to  $\text{Cl}_2$ (g) by  $\text{Cr}_2\text{O}_7^{2-}$ (aq) at standard conditions will not occur spontaneously. We could obtain some  $\text{Cl}_2$ (g) from this reaction by driving it to the product side with an external voltage. In other words, the reverse reaction is the spontaneous reaction at standard conditions and if we want to obtain some  $\text{Cl}_2$ (g) from the system, we must push the non-spontaneous reaction in its forward direction with an external voltage, (i.e., a DC power source). Since  $E^{\circ}_{\text{cell}}$  is only slightly negative, we could also drive the reaction by removing products as they are formed and replenishing reactants as they are consumed.



## Batteries and Fuel Cells

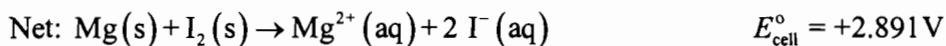
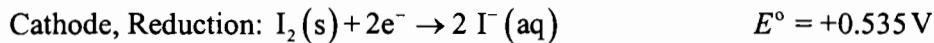
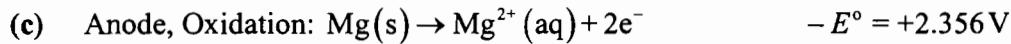
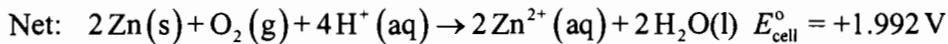
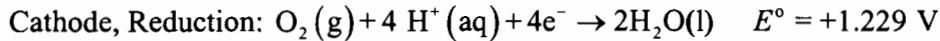
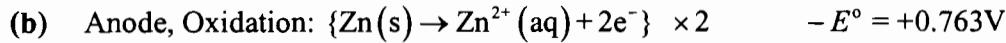
57. (a) The cell diagram begins with the anode and ends with the cathode.



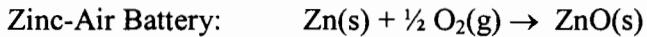
59. (a) Cell reaction:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

$$\Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ [\text{H}_2\text{O}(\text{l})] = 2(-237.1 \text{ kJ/mol}) = -474.2 \text{ kJ/mol}$$

$$E_{\text{cell}}^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{-474.2 \times 10^3 \text{ J/mol}}{4 \text{ mol e}^- \times 96485 \text{ C/mol e}^-} = 1.229 \text{ V}$$



61. Aluminum-Air Battery:  $2\text{Al(s)} + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s})$



Calculate the quantity of charge transferred when 1.00 g of metal is consumed in each cell.

Aluminum-Air Cell:

$$1.00 \text{ g Al(s)} \times \frac{1 \text{ mol Al(s)}}{26.98 \text{ g Al(s)}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al(s)}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} = 1.07 \times 10^4 \text{ C}$$

Zinc-Air Cell:

$$1.00 \text{ g Zn(s)} \times \frac{1 \text{ mol Zn(s)}}{65.39 \text{ g Zn(s)}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Zn(s)}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} = 2.95 \times 10^3 \text{ C}$$

## Iron-Air Cell:

$$1.00 \text{ g Fe(s)} \times \frac{1 \text{ mol Fe(s)}}{55.847 \text{ g Fe(s)}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Fe(s)}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} = 3.46 \times 10^3 \text{ C}$$

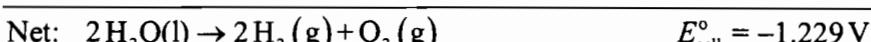
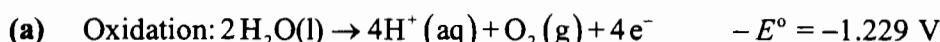
As expected, aluminum has the greatest quantity of charge transferred per unit mass (1.00 g) of metal oxidized. This is because aluminum has the smallest molar mass and forms the most highly charged cation (3+ vs 2+ for Zn and Fe).

## Electrochemical Mechanism of Corrosion

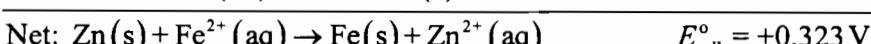
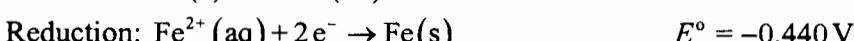
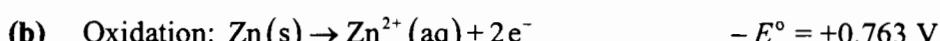
- 63.** (a) Because copper is a less active metal than is iron, this situation would be similar to that of an iron or steel can plated with tin in which the coating has been scratched. Oxidation of iron metal to  $\text{Fe}^{2+}(\text{aq})$  should be enhanced in the body of the nail (blue precipitate), and hydroxide ion should be produced in the vicinity of the copper wire (pink color), which serves as the cathode.
- (b) Because a scratch stresses the iron and exposes “fresh” metal, it is more susceptible to corrosion. We expect enhanced blue precipitate in the vicinity of the scratch.
- (c) Zinc should protect the iron nail from corrosion. There should be almost no blue precipitate; the zinc corrodes instead. The pink color of  $\text{OH}^-$  continues to form.
- 65.** During the process of corrosion, the metal that corrodes loses electrons. Thus, the metal in these instances behaves as an anode and, hence, carries a negative charge. One way in which we could retard oxidation of the metal would be to convert it into a cathode. Once transformed into a cathode, the metal would develop a positive charge and no longer release electrons (or oxidize). This change in polarity can be accomplished by hooking up the metal to an inert electrode in the ground and then applying a voltage across the two metals in such a way that the inert electrode becomes the anode and the metal that needs protecting becomes the cathode. This way, any oxidation that occurs will take place at the negatively charged inert electrode rather than the positively charged metal electrode.

## Electrolysis Reactions

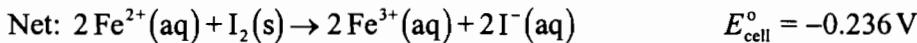
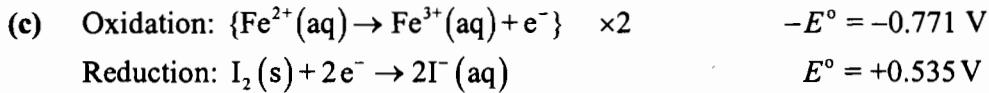
- 67.** We determine the standard cell voltage of each chemical reaction. Those voltages that are negative are those of chemical reactions that require electrolysis.



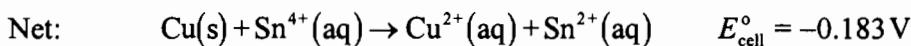
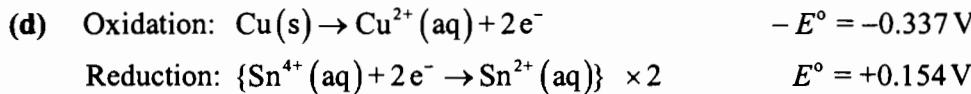
This reaction requires electrolysis, with an applied voltage greater than +1.229 V.



This is a spontaneous reaction.

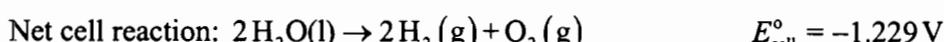
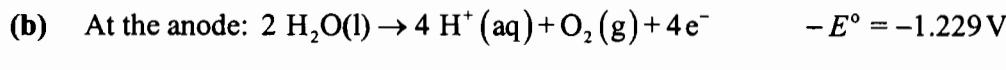


This reaction requires electrolysis, with an applied voltage greater than  $+0.236 \text{ V}$ .



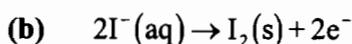
This reaction requires electrolysis, with an applied voltage greater than  $+0.183 \text{ V}$ .

69. (a) The two gases that are produced are  $H_2(g)$  and  $O_2(g)$ .



71. (a)  $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

$$\text{mass of Zn} = 42.5 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1.87 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol } e^-}{96485 \text{ C}} \times \frac{1 \text{ mol Zn}}{2 \text{ mol } e^-} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 1.62 \text{ g Zn}$$

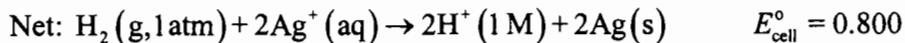
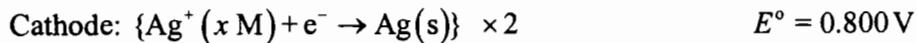


$$\text{time needed} = 2.79 \text{ g } I_2 \times \frac{1 \text{ mol } I_2}{253.8 \text{ g } I_2} \times \frac{2 \text{ mol } e^-}{1 \text{ mol } I_2} \times \frac{96485 \text{ C}}{1 \text{ mol } e^-} \times \frac{1 \text{ s}}{1.75 \text{ C}} \times \frac{1 \text{ min}}{60 \text{ s}} = 20.2 \text{ min}$$

73. (a) charge =  $1.206 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.87 \text{ g Ag}} \times \frac{1 \text{ mol } e^-}{1 \text{ mol Ag}} \times \frac{96,485 \text{ C}}{1 \text{ mol } e^-} = 1079 \text{ C}$

(b) current =  $\frac{1079 \text{ C}}{1412 \text{ s}} = 0.7642 \text{ A}$

## FEATURE PROBLEMS



- (b) Since the voltage in the anode half-cell remains constant, we use the Nernst equation to calculate the half-cell voltage in the cathode half-cell, with two moles of electrons. This is then added to  $-E$  for the anode half-cell. Because  $-E^\circ = 0.000$  for the anode half cell,  $E_{\text{cell}} = E_{\text{cathode}}$

$$E = E^\circ - \frac{0.0592}{2} \log \frac{1}{[\text{Ag}^+]^2} = 0.800 + 0.0592 \log [\text{Ag}^+] = 0.800 + 0.0592 \log x$$

- (c) (i) Initially  $[\text{Ag}^+] = 0.0100$ ;  $E = 0.800 + 0.0592 \log 0.0100 = 0.682 \text{ V} = E_{\text{cell}}$

Note that 50.0 mL of titrant is required for the titration, since both  $\text{AgNO}_3$  and  $\text{KI}$  have the same concentrations and they react in equimolar ratios.

- (ii) After 20.0 mL of titrant is added, the total volume of solution is 70.0 mL and the unreacted  $\text{Ag}^+$  is that in the untitrated 30.0 mL of 0.0100 M  $\text{AgNO}_3(\text{aq})$ .

$$[\text{Ag}^+] = \frac{30.0 \text{ mL} \times 0.0100 \text{ M Ag}^+}{70.0 \text{ mL}} = 0.00429 \text{ M}$$

$$E = 0.800 + 0.0592 \log (0.00429) = 0.660 \text{ V} = E_{\text{cell}}$$

- (iii) After 49.0 mL of titrant is added, the total volume of solution is 99.0 mL and the unreacted  $\text{Ag}^+$  is that in the untitrated 1.0 mL of 0.0100 M  $\text{AgNO}_3(\text{aq})$ .

$$[\text{Ag}^+] = \frac{1.0 \text{ mL} \times 0.0100 \text{ M Ag}^+}{99.0 \text{ mL}} = 0.00010 \text{ M}$$

$$E = 0.800 + 0.0592 \log (0.00010) = 0.563 \text{ V} = E_{\text{cell}}$$

- (iv) At the equivalence point, we have a saturated solution of  $\text{AgI}$ , for which

$$[\text{Ag}^+] = \sqrt{K_{\text{sp}}(\text{AgI})} = \sqrt{8.5 \times 10^{-17}} = 9.2 \times 10^{-9}$$

$$E = 0.800 + 0.0592 \log (9.2 \times 10^{-9}) = 0.324 \text{ V} = E_{\text{cell}}$$

After the equivalence point, the  $[\text{Ag}^+]$  is determined by the  $[\text{I}^-]$  resulting from the excess  $\text{KI}(\text{aq})$ .

- (v) When 51.0 mL of titrant is added, the total volume of solution is 101.0 mL and the excess  $I^-$  is that in 1.0 mL of 0.0100 M KI(aq).

$$[I^-] = \frac{1.0 \text{ mL} \times 0.0100 \text{ M } I^-}{101.0 \text{ mL}} = 0.000099 \text{ M}$$

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.5 \times 10^{-17}}{0.000099} = 8.6 \times 10^{-13} \text{ M}$$

$$E = 0.800 + 0.0592 \log (8.6 \times 10^{-13}) = 0.086 \text{ V} = E_{cell}$$

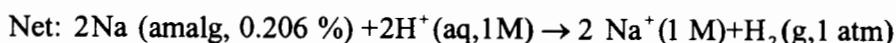
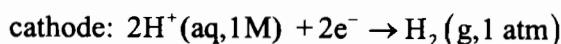
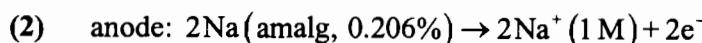
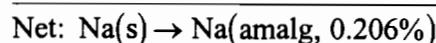
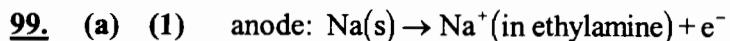
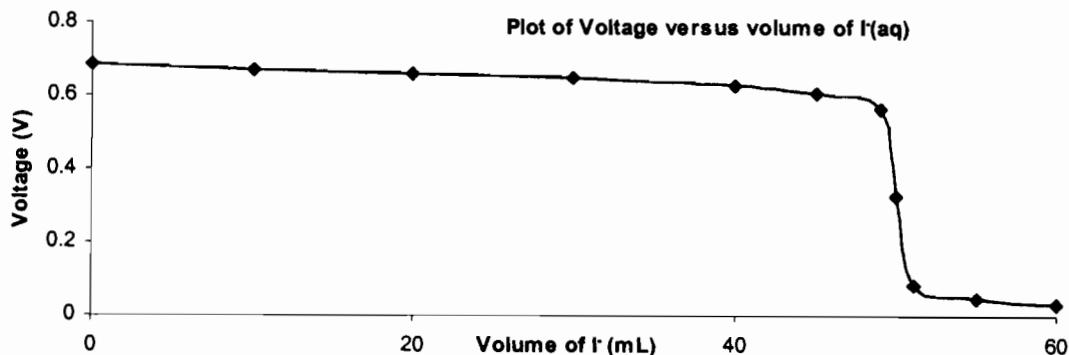
- (vi) When 60.0 mL of titrant is added, the total volume of solution is 110.0 mL and the excess  $I^-$  is that in 10.0 mL of 0.0100 M KI(aq).

$$[I^-] = \frac{10.0 \text{ mL} \times 0.0100 \text{ M } I^-}{110.0 \text{ mL}} = 0.00091 \text{ M}$$

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.5 \times 10^{-17}}{0.00091} = 9.3 \times 10^{-14} \text{ M}$$

$$E = 0.800 + 0.0592 \log (9.3 \times 10^{-14}) = 0.029 \text{ V} = E_{cell}$$

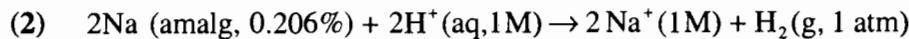
- (d) The titration curve is presented below.



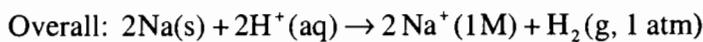
(b) (1)  $\Delta G = -1 \text{ mol e}^- \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times 0.8453 \text{ V} = -8.156 \times 10^4 \text{ J}$  or  $-81.56 \text{ kJ}$

(2)  $\Delta G = -2 \text{ mol e}^- \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times 1.8673 \text{ V} = -36.033 \times 10^4 \text{ J}$  or  $-360.33 \text{ kJ}$

(c) (1)  $2\text{Na(s)} \rightarrow 2\text{Na(amalg, 0.206\%)}$   $\Delta G_1 = -2 \times 8.156 \times 10^4 \text{ J}$



$$\Delta G_2 = -36.033 \times 10^4 \text{ J}$$



$$\Delta G = \Delta G_1 + \Delta G_2 = -16.312 \times 10^4 \text{ J} - 36.033 \times 10^4 \text{ J} = -52.345 \times 10^4 \text{ J}$$
 or  $-523.45 \text{ kJ}$

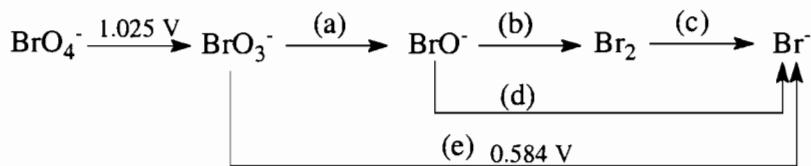
Since standard conditions are implied in the overall reaction,  $\Delta G = \Delta G^\circ$ .

(d)  $E_{cell}^\circ = -\frac{-52.345 \times 10^4 \text{ J}}{2 \text{ mol e}^- \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ J}}{1 \text{ V} \cdot \text{C}}} = +2.713 \text{ V}$

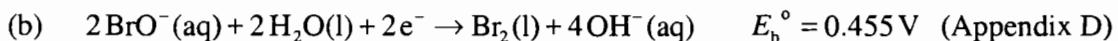
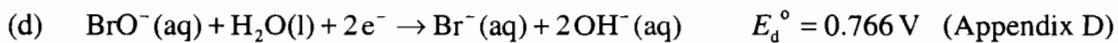
$$\begin{aligned} +2.713 \text{ V} &= E^\circ \{ \text{H}^+(\text{1 M})/\text{H}_2(\text{1 atm}) \} - E^\circ \{ \text{Na}^+(\text{1 M})/\text{Na(s)} \} \\ &= 0.000 \text{ V} - E^\circ \{ \text{Na}^+(\text{1 M})/\text{Na(s)} \} \end{aligned}$$

$E^\circ \{ \text{Na}^+(\text{1 M})/\text{Na(s)} \} = -2.713 \text{ V}$ . This is precisely the value in Appendix D.

100. The question marks in the original Latimer diagram have been replaced with letters in the diagram below to make the solution easier to follow:



By using Appendix D and the methods of page 834 we obtain:



(a)	$\{ \text{BrO}_3^- (\text{aq}) + 2 \text{H}_2\text{O(l)} + 4 \text{e}^- \rightarrow \text{BrO}^- (\text{aq}) + 4 \text{OH}^- (\text{aq}) \} \times 2$	$E_a^\circ = ?$
(b)	$2 \text{BrO}^- (\text{aq}) + 2 \text{H}_2\text{O(l)} + 2 \text{e}^- \rightarrow \text{Br}_2 (\text{l}) + 4 \text{OH}^- (\text{aq})$	$E_b^\circ = 0.455 \text{ V}$
(c)	$\text{Br}_2 (\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Br}^- (\text{aq})$	$E_c^\circ = 1.065 \text{ V}$
(e)	$2 \text{BrO}_3^- (\text{aq}) + 6 \text{H}_2\text{O(l)} + 12 \text{e}^- \rightarrow 12 \text{OH}^- (\text{aq}) + 2 \text{Br}^- (\text{aq})$	$E_e^\circ = 0.584 \text{ V}$

$$\Delta G_{\text{Total}}^\circ = \Delta G_{(a)}^\circ + \Delta G_{(b)}^\circ + \Delta G_{(c)}^\circ$$

$$-12F(E_e^\circ) = -8F(E_a^\circ) + -2F(E_b^\circ) + -2F(E_c^\circ)$$

$$-12F(0.584 \text{ V}) = -8F(E_a^\circ) + -2F(0.455 \text{ V}) + -2F(1.065 \text{ V})$$

$$E_a^\circ = \frac{-12F(0.584 \text{ V}) + 2F(0.455 \text{ V}) + 2F(1.065 \text{ V})}{-8F}$$

$$E_a^\circ = 0.496 \text{ V}$$

101. (a) The capacitance of the cell membrane is given by the following equation,

$$C = \frac{\epsilon_0 \epsilon A}{l} \quad \text{where } \epsilon_0 \epsilon = 3 \times 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2},$$

$A = 1 \times 10^{-6} \text{ cm}^2$ ; and  $l = 1 \times 10^{-6} \text{ cm}$ .

Together with the factors necessary to convert from cm to m and from  $\text{cm}^2$  to  $\text{m}^2$ , these data yield

$$C = \frac{(3) \left( 8.854 \times 10^{-12} \frac{\text{C}^2}{\text{N}^1 \text{ m}^2} \right) (1 \times 10^{-6} \text{ cm}^2) \left( \frac{1 \text{ m}}{100 \text{ cm}} \right)^2}{(1 \times 10^{-6} \text{ cm}) \left( \frac{1 \text{ m}}{100 \text{ cm}} \right)}$$

$$C = 2.66 \times 10^{-13} \frac{\text{C}^2}{\text{N m}}$$

$$C = \left( 2.66 \times 10^{-13} \frac{\text{C}^2}{\text{N m}} \right) \left( \frac{1 \text{ F}}{1 \frac{\text{C}^2}{\text{N m}}} \right) = 2.66 \times 10^{-13} \text{ F}$$

- (b) Since the capacitance  $C$  is the charge in coulombs per volt, the charge on the membrane,  $Q$ , is given by the product of the capacitance and the potential across the cell membrane.

$$Q = 2.66 \times 10^{-13} \frac{C}{V} \times 0.085 \text{ V} = 2.26 \times 10^{-14} \text{ C}$$

- (c) The number of  $\text{K}^+$  ions required to produce this charge is

$$\frac{Q}{e} = \frac{2.26 \times 10^{-14} \text{ C}}{1.602 \times 10^{-19} \text{ C/ion}} = 1.41 \times 10^5 \text{ K}^+ \text{ ions}$$

- (d) The number of  $\text{K}^+$  ions in a typical cell is

$$\left( 6.022 \times 10^{23} \frac{\text{ions}}{\text{mol}} \right) \left( 155 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) \left( \frac{1 \text{ L}}{1000 \text{ cm}^3} \right) (1 \times 10^{-8} \text{ cm}^3) = 9.3 \times 10^{11} \text{ ions}$$

- (e) The fraction of the ions involved in establishing the charge on the cell membrane is

$$\frac{1.4 \times 10^5 \text{ ions}}{9.3 \times 10^{11} \text{ ions}} = 1.5 \times 10^{-7} (\sim 0.000015 \%)$$

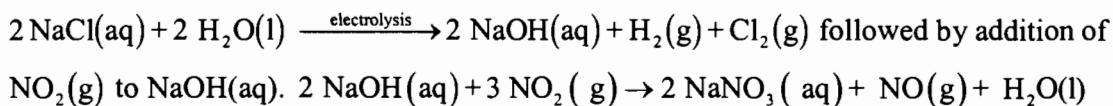
Thus, the concentration of  $\text{K}^+$  ions in the cell remains constant at 155 mM.

# CHAPTER 22

## MAIN GROUP ELEMENTS I: METALS

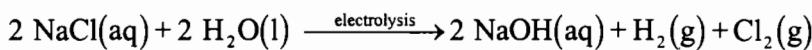
### PRACTICE EXAMPLES

- 1A** From Figure 22-2, the route from sodium chloride to sodium nitrate begins with electrolysis of  $\text{NaCl}(\text{aq})$  to form  $\text{NaOH}(\text{aq})$



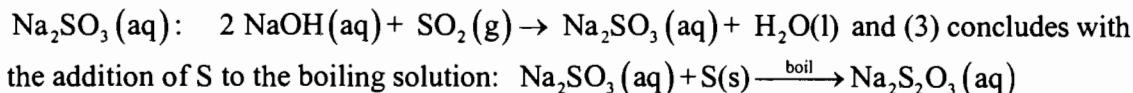
- 1B** From Figure 22-2, we see that the route from sodium chloride to sodium thiosulfate

(1) begins with the electrolysis of  $\text{NaCl}(\text{aq})$  to produce  $\text{NaOH}(\text{aq})$ ,



(2) continues through the reaction of  $\text{SO}_2(\text{g})$  with the  $\text{NaOH}(\text{aq})$  in an acid-base reaction

$[\text{SO}_2(\text{g})$  is an acid anhydride] to produce



- 2A** Moles of  $\text{NaOH} = C \times V = 0.0133 \text{ M} \times 0.00759 \text{ L} = 1.01 \times 10^{-4} \text{ mol NaOH}$

$$[\text{H}_3\text{O}^+] = \frac{1.01 \times 10^{-4} \text{ mol}}{0.0250 \text{ L}} = 4.04 \times 10^{-3} \text{ M} \quad \text{pH} = -\log(4.04 \times 10^{-3}); \quad \text{pH} = 2.394$$

- 2B**  $185 \text{ ppm Ca}^{2+} \longrightarrow \frac{185 \text{ mg Ca}^{2+}}{1 \text{ L}} \times \frac{1 \text{ mmol Ca}^{2+}}{40.078 \text{ mg Ca}^{2+}} \times \frac{1 \text{ mol Ca}^{2+}}{1000 \text{ mmol Ca}^{2+}} \times \frac{2 \text{ mol Na}^+}{1 \text{ mol Ca}^{2+}}$   
 $= 9.23 \times 10^{-3} \text{ M Na}^+$

### REVIEW QUESTIONS

1. **(a)** A dimer is a molecule that is formed by the joining together of two identical simpler molecules (called monomers). For instance,  $\text{N}_2\text{O}_4$  is a dimer of  $\text{NO}_2$ .
- (b)** An adduct is formed when two simple molecules come together and a covalent bond, often a coordinate covalent bond, forms between them.  $\text{NH}_3 \cdot \text{BF}_3$  is an adduct of  $\text{NH}_3$  and  $\text{BF}_3$ .
- (c)** Calcination is the process of heating calcium carbonate strongly to drive off  $\text{CO}_2(\text{g})$  and form calcium oxide.
- (d)** An amphoteric oxide is one that reacts with either a strong acid or with a strong base.

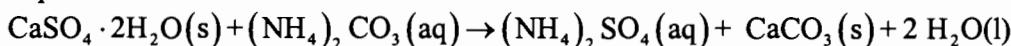
2. (a) A diagonal relationship refers to the similarity between two elements that are diagonally related to each other in the periodic table, such as Li and Mg, or Be and Al. Even though these elements are in different periodic families, they have some similarities in physical and chemical properties.
- (b) Deionized water is prepared by ion exchange by passing it through material in which the ions  $H^+$  or  $OH^-$  are present. These ions substitute or exchange for the ions in the water, in a two-step process: first the cations in the water are replaced by  $H^+$ , then the anions by  $OH^-$ . The result is water virtually free of ionic contaminants.
- (c) The thermite reaction refers to the reduction of a metal oxide with another, more active, metal in a highly exothermic reaction, for instance:  
 $Fe_2O_3(s) + 2 Al(s) \rightarrow 2 Fe(\text{liquid}) + Al_2O_3(s)$
- (d) The “inert pair” effect refers to the tendency of heavier representative metals to have oxidation states in which they have lost their  $np$  electrons, but not their  $ns^2$  electrons. Thus, they have an oxidation state two units less than their periodic table family number. Examples include  $Pb^{2+}$ ,  $Sn^{2+}$ ,  $Bi^{3+}$ ,  $Sb^{3+}$ ,  $Tl^+$ .
3. (a) The peroxide ion is  $O_2^{2-}$ ; the superoxide ion is  $O_2^-$ .
- (b) Quicklime is the common name for  $CaO(s)$ ; slaked lime is the common name for  $Ca(OH)_2(s)$ .
- (c) Temporary hard water contains divalent cations, such as  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Fe^{2+}$  and the bicarbonate anion,  $HCO_3^-$ . Heating produces,  $H_2O(l)$ ,  $CO_2(g)$ , and a carbonate precipitate. Permanent hard water does not form a precipitate upon heating; the ions it contains, such as  $SO_4^{2-}$  are thermally stable.
- (d) A soap is a potassium or sodium salt of a deprotonated carboxylic acid ( $-\text{COO}^-$ ) that has a long hydrocarbon chain. A detergent is a synthetic sodium or potassium salt of a long hydrocarbon chain sulfonic acid ( $-\text{OSO}_3\text{H}$ ).
4. (a)  $PbO$ ; lead(II) oxide
- (b)  $SnF_2$ ; tin(II) fluoride
- (c)  $CaSO_4 \bullet \frac{1}{2} H_2O$ ; calcium sulfate hemihydrate
- (d)  $Li_3N$ ; lithium nitride
- (e)  $Ca(OH)_2$ ; calcium hydroxide
- (f)  $KO_2$ ; potassium superoxide
- (g)  $Mg(HCO_3)_2$ ; magnesium hydrogen carbonate

5. (a)  $\text{Li}_2\text{CO}_3(\text{s}) \xrightarrow{\Delta} \text{Li}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$   
 (b)  $\text{CaCO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$   
 (c)  $2\text{Al}(\text{s}) + 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}^+(\text{aq}) + 2[\text{Al}(\text{OH})_4]^- (\text{aq}) + 3\text{H}_2(\text{g})$   
 (d)  $\text{BaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ba}(\text{OH})_2(\text{s, in limited water})$   
 (e)  $2\text{Na}_2\text{O}_2(\text{s}) + 2\text{CO}_2(\text{g}) \rightarrow 2\text{Na}_2\text{CO}_3(\text{s}) + \text{O}_2(\text{g})$

6. (a)  $\text{MgCO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$   
 (b)  $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$   
 $2\text{Al}(\text{s}) + 2\text{NaOH}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}[\text{Al}(\text{OH})_4](\text{aq}) + 3\text{H}_2(\text{g})$   
 (c)  $2\text{NaCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{conc., aq}) \rightarrow 2\text{HCl}(\text{g}) + \text{Na}_2\text{SO}_4(\text{s})$

7. (a)  $\text{K}_2\text{CO}_3(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow \text{BaCO}_3(\text{s}) + 2\text{KOH}(\text{aq})$   
 (b)  $\text{Mg}(\text{HCO}_3)_2(\text{aq}) \xrightarrow{\Delta} \text{MgCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$   
 (c)  $\text{SnO}(\text{s}) + \text{C}(\text{s}) \xrightarrow{\Delta} \text{Sn}(\text{l}) + \text{CO}(\text{g})$   
 (d)  $\text{CaF}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{conc., aq}) \rightarrow 2\text{HF}(\text{g}) + \text{CaSO}_4(\text{s})$   
 (e)  $\text{NaHCO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$   
 (f)  $\text{PbO}_2(\text{s}) + 4\text{HBr}(\text{aq}) \rightarrow \text{PbBr}_2(\text{s}) + \text{Br}_2(\text{l}) + 2\text{H}_2\text{O}(\text{l})$

8. Replace the names with chemical formulas and balance the result.



9. Temporary hard water is softened by the addition of an alkaline (basic) material. All the substances listed form alkaline solutions except  $\text{NH}_4\text{Cl}$ .  $\text{NH}_4^+$  hydrolyzes to form an acidic solution, and thus, cannot be used to soften temporary hard water.

10. (a)  $\text{SrCO}_3(\text{s}) \xrightarrow{\Delta} \text{SrO}(\text{s}) + \text{CO}_2(\text{g})$   
 (b)  $\text{Al}_2\text{O}_3(\text{s}) \xrightarrow{\Delta} \text{no reaction}$   
 (c)  $\text{Li}_2\text{CO}_3(\text{s}) \xrightarrow{\Delta} \text{Li}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$

11. (a)  $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{NaHCO}_3(\text{aq}) \rightarrow \text{PbCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) + 2\text{NaNO}_3(\text{aq})$   
 (b)  $\text{Li}_2\text{O}(\text{s}) + (\text{NH}_4)_2\text{CO}_3(\text{aq}) \rightarrow \text{Li}_2\text{CO}_3(\text{s}) + 2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$   
 $\text{NH}_4^+(\text{aq})$  is present in very limited amount because the solution is strongly basic;  
 $\text{Li}_2\text{O}$  is the anhydride of a strong base.

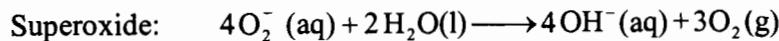
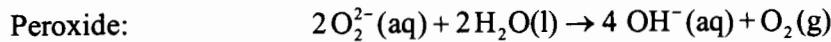
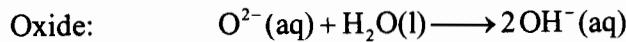
- (c)  $\text{H}_2\text{SO}_4(\text{aq}) + \text{BaO}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{BaSO}_4(\text{s})$   
 (d)  $2\text{PbO}(\text{s}) + \text{Ca}(\text{OCl})_2(\text{aq}) \longrightarrow 2\text{PbO}_2(\text{s}) + \text{CaCl}_2(\text{aq})$

12. To answer this one, you really do not need to formally study chemistry. You just have to observe the world around you. Neither aluminum foil nor aluminum cookware reacts with water. But to explain this observation, you have to know that of these four active metals, only aluminum forms an oxide that adheres tightly to its surface, thereby preventing further reaction.
13. The correct answer is (a). Balanced equations for the three pairs follow.
- $$\text{Ca}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{OH})_2(\text{s}) + \text{H}_2(\text{g}) \quad \text{CaH}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{OH})_2(\text{s}) + 2\text{H}_2(\text{g})$$
- $$2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g}) \quad 2\text{Na}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{NaOH}(\text{aq}) + \text{O}_2(\text{g})$$
- $$2\text{K}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{KOH}(\text{aq}) + \text{H}_2(\text{g}) \quad 4\text{KO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{KOH}(\text{aq}) + 3\text{O}_2(\text{g})$$
14. (a) Stalactites are primarily  $\text{CaCO}_3(\text{s})$   
 (b) Gypsum is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
 (c) “bathtub ring” is a salt of  $\text{Ca}^{2+}$  and a long-carbon chain carboxylate anion. An example would be calcium palmitate:  $\text{Ca}[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2(\text{s})$   
 (d) barium “milkshake” is an aqueous temporary suspension of  $\text{BaSO}_4(\text{s})$   
 (e) blue sapphires are  $\text{Al}_2\text{O}_3$  with  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  ions replacing some  $\text{Al}^{3+}$  ions.

## EXERCISES

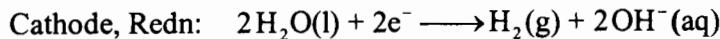
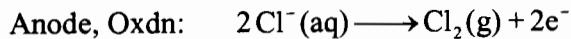
### Group I (Alkali) Metals

15. (a)  $2\text{Cs}(\text{s}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{CsCl}(\text{s})$   
 (b)  $2\text{Na}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{Na}_2\text{O}_2(\text{s})$   
 (c)  $\text{Li}_2\text{CO}_3(\text{s}) \xrightarrow{\Delta} \text{Li}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$   
 (d)  $\text{Na}_2\text{SO}_4(\text{s}) + 4\text{C}(\text{s}) \rightarrow \text{Na}_2\text{S}(\text{s}) + 4\text{CO}(\text{g})$   
 (e)  $\text{K}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{KO}_2(\text{s})$
17. Both  $\text{LiCl}$  and  $\text{KCl}$  are soluble in water, but  $\text{Li}_3\text{PO}_4$  is not very soluble. Hence the addition of  $\text{K}_3\text{PO}_4(\text{aq})$  to a solution of the white solid will produce a precipitate if the white solid is  $\text{LiCl}$ , but no precipitate if the white solid is  $\text{KCl}$ . The best method is a flame test; lithium gives a red color to a flame, while the potassium flame test is violet.
19. In addition to  $\text{OH}^-(\text{aq})$ ,  $\text{O}_2(\text{g})$  is formed in the case of peroxide and superoxide. The resulting equations are balanced by inspection if one pays attention to charge balance.



21. (a)  $H_2(g)$  and  $Cl_2(g)$  are produced during the electrolysis of  $NaCl(aq)$ .

The electrode reactions are:



We can compute the amount of  $OH^-$  produced at the cathode.

$$mol\ OH^- = 2.50\ min \times \frac{60\ s}{1\ min} \times \frac{0.810\ C}{1\ s} \times \frac{1\ mole\ e^-}{96500\ C} \times \frac{2\ mol\ OH^-}{2\ mole^-} = 1.26 \times 10^{-3}\ mol\ OH^-$$

Then we compute the  $[OH^-]$  and, from that, the pH of the solution.

$$[OH^-] = \frac{1.26 \times 10^{-3}\ mol\ OH^-}{0.872\ L\ soln} = 1.45 \times 10^{-3}\ M \quad pOH = -\log(1.45 \times 10^{-3}) = 2.839$$

$$pH = 14.000 - 2.839 = 11.161$$

- (b) As long as  $NaCl$  is in excess and the volume of the solution is nearly constant, the solution pH only depend on the number of electrons transferred (limiting reagent).

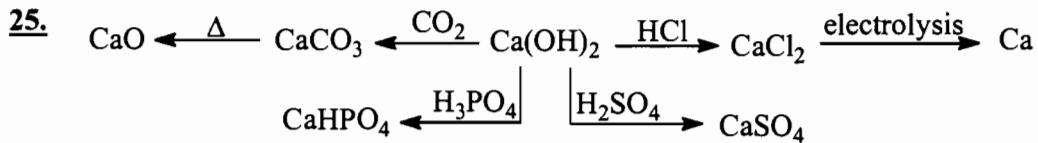
23. (a) We first compute the mass of  $NaHCO_3$  that should be produced from 1.00 ton  $NaCl$ , assuming that all of the Na in the  $NaCl$  ends up in the  $NaHCO_3$ . We use the unit, ton-mole, to simplify the calculations.

$$\begin{aligned} \text{mass } NaHCO_3 &= 1.00 \text{ ton } NaCl \times \frac{1 \text{ ton-mol } NaCl}{58.4 \text{ ton } NaCl} \times \frac{1 \text{ ton-mol Na}}{1 \text{ ton-mol } NaCl} \\ &\quad \times \frac{1 \text{ ton-mol } NaHCO_3}{1 \text{ ton-mol Na}} \times \frac{84.0 \text{ ton } NaHCO_3}{1 \text{ ton mol } NaHCO_3} = 1.44 \text{ ton } NaHCO_3 \end{aligned}$$

$$\% \text{ yield} = \frac{1.03 \text{ ton } NaHCO_3 \text{ produced}}{1.44 \text{ ton } NaHCO_3 \text{ expected}} \times 100\% = 71.5\% \text{ yield}$$

- (b)  $NH_3$  is used in the principal step of the Solvay process to produce a solution in which  $NaHCO_3$  is formed and from which it will precipitate. The filtrate contains  $NH_4Cl$ , from which  $NH_3$  is recovered by treatment with  $Ca(OH)_2$ . Thus,  $NH_3$  is simply used during the Solvay process to produce the proper conditions for the desired reactions. Any net consumption of  $NH_3$  is the result of unavoidable losses during production.

## Group 2 (Alkaline earth) metals



The reactions are as follows.

$$\text{Ca}(\text{OH})_2(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$$

$$\text{CaCl}_2(\text{l}) \xrightarrow{\Delta, \text{electrolysis}} \text{Ca}(\text{l}) + \text{Cl}_2(\text{g})$$

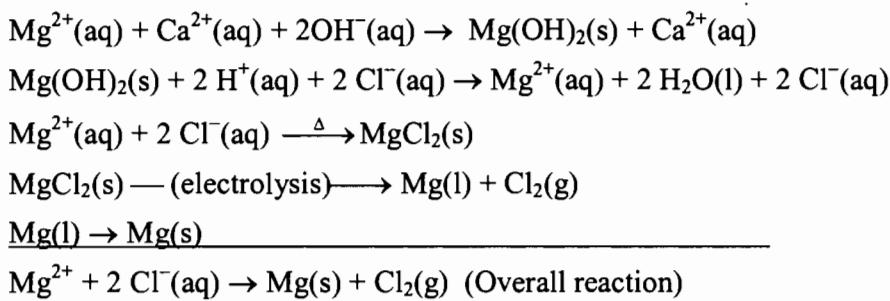
$$\text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

$$\text{Ca}(\text{OH})_2(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CaSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$$

$$\text{Ca}(\text{OH})_2(\text{s}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow \text{CaHPO}_4(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$$

Actually  $\text{CaO}(\text{s})$  is the industrial starting material from which  $\text{Ca}(\text{OH})_2$  is made.  $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$

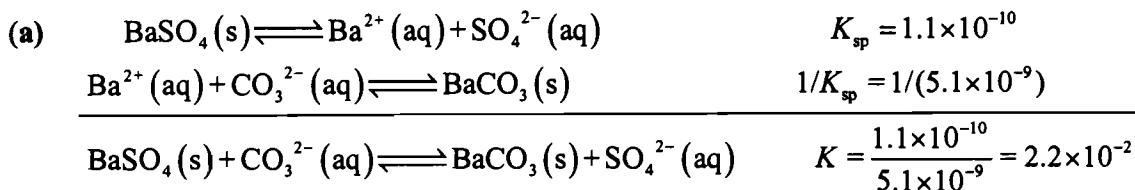
27. The reactions involved:



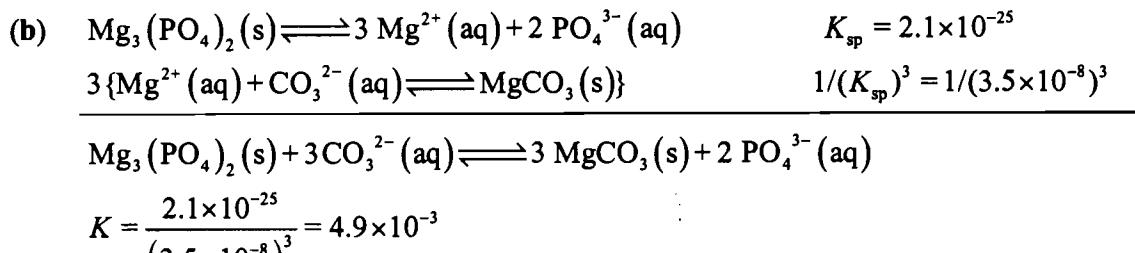
As can be seen, the process does not violate the principle of conservation of charge.

29. (a)  $\text{BeF}_2(\text{s}) + \text{Mg}(\text{s}) \xrightarrow{\Delta} \text{Be}(\text{s}) + \text{MgF}_2(\text{s})$
- (b)  $\text{Ba}(\text{s}) + \text{Br}_2(\text{l}) \rightarrow \text{BaBr}_2(\text{s})$
- (c)  $\text{UO}_2(\text{s}) + 2 \text{Ca}(\text{s}) \rightarrow \text{U}(\text{s}) + 2 \text{CaO}(\text{s})$
- (d)  $\text{MgCO}_3 \cdot \text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{MgO}(\text{s}) + \text{CaO}(\text{s}) + 2 \text{CO}_2(\text{g})$
- (e)  $2 \text{H}_3\text{PO}_4(\text{aq}) + 3 \text{CaO}(\text{s}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 3 \text{H}_2\text{O}(\text{l})$

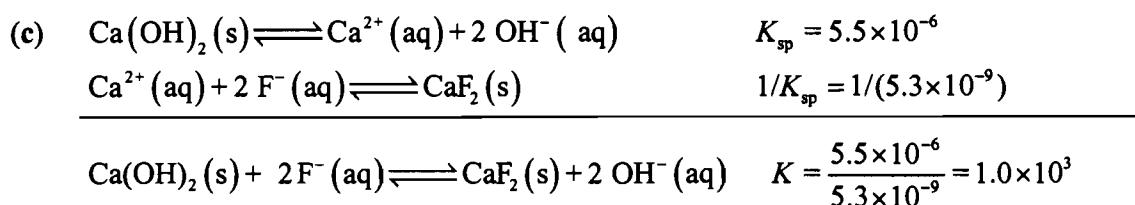
31. Let us compute the value of the equilibrium constant for each reaction by combining the two solubility product constants. Large values of equilibrium constants indicate that the reaction is displaced far to the right. Values of  $K$  that are much smaller than 1 indicate that the reaction is displaced far to the left.



Equilibrium lies slightly to the left.



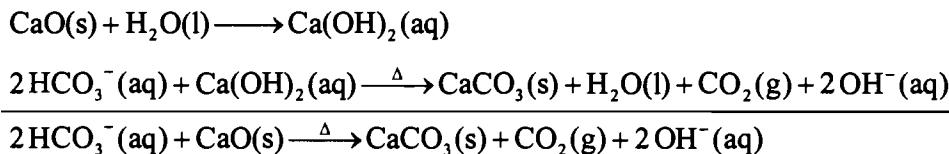
Equilibrium lies to the left



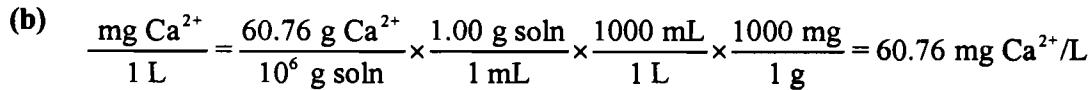
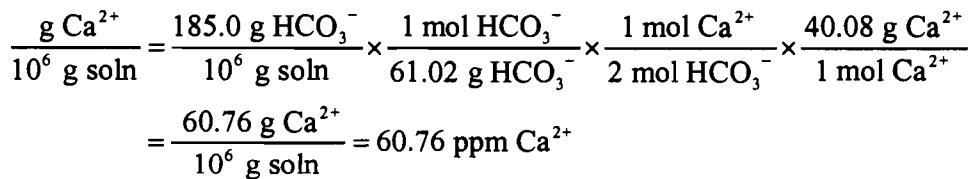
Equilibrium lies to the right

## Hard Water

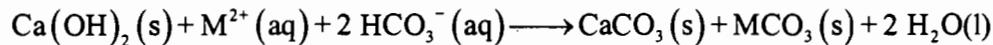
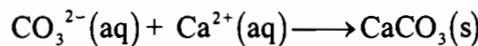
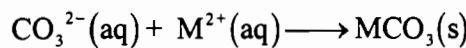
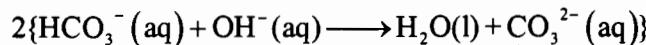
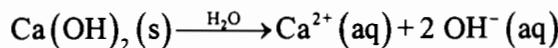
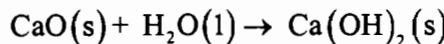
33. Temporary hard water contains  $\text{HCO}_3^-$ . Quicklime is  $\text{CaO}$ :



35. (a) There will be two  $\text{HCO}_3^-$  ions for each  $\text{Ca}^{2+}$  ion.



- (c) First we combine equations representing the neutralization of bicarbonate ion with hydroxide ion and the formation of a generalized carbonate precipitate  $[\text{MCO}_3(\text{s})]$  to determine the overall stoichiometry of the reaction. We also add to the combination the slaking of lime,  $\text{CaO}(\text{s})$ . Remember that two  $\text{HCO}_3^-$  ions are associated with each  $\text{M}^{2+}(\text{aq})$  ion.



Then we determine the mass of  $\text{Ca}(\text{OH})_2$  needed.

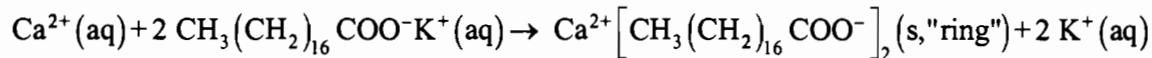
$$\begin{aligned} \text{mass Ca}(\text{OH})_2 &= 1.00 \times 10^6 \text{ g water} \times \frac{185.0 \text{ g HCO}_3^-}{10^6 \text{ g water}} \times \frac{1 \text{ mol HCO}_3^-}{61.02 \text{ g HCO}_3^-} \\ &\quad \times \frac{1 \text{ mol Ca}(\text{OH})_2}{2 \text{ mol HCO}_3^-} \times \frac{74.09 \text{ g Ca}(\text{OH})_2}{1 \text{ mol Ca}(\text{OH})_2} = 112.3 \text{ g Ca}(\text{OH})_2 \end{aligned}$$

37.  $\text{pH} = 2.37 = -\log[\text{H}^+]$ . The  $[\text{H}^+] = 10^{-2.37} = 4.27 \times 10^{-3} \text{ M}$ . For every 2 moles of  $\text{H}^+$ , one mole of  $\text{Ca}^{2+}$  is absorbed. Hence, the concentration of  $\text{Ca}^{2+}$  is  $2.13 \times 10^{-3} \text{ M}$ . Convert this to parts per million (mg  $\text{Ca}^{2+}$  per 1000 g solution).

$$\text{ppm Ca}^{2+} = \frac{2.13 \times 10^{-3} \text{ mol Ca}^{2+}}{1 \text{ L solution}} \times \frac{1 \text{ L solution}}{1000 \text{ g solution}} \times \frac{40.08 \text{ g Ca}^{2+}}{1 \text{ mol Ca}^{2+}} \times \frac{1000 \text{ mg Ca}^{2+}}{1 \text{ g Ca}^{2+}} = \frac{85 \text{ mg Ca}^{2+}}{1000 \text{ g solution}}$$

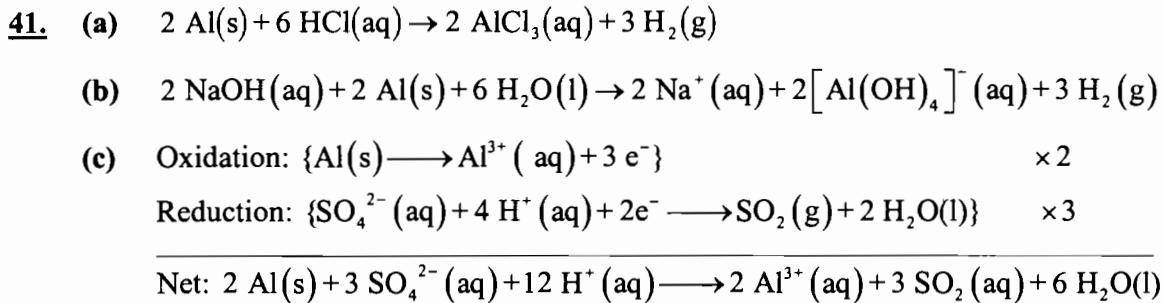
The concentration of  $\text{Ca}^{2+}$  is 85 ppm.

39. We first write the balanced equation for the formation of bathtub ring.

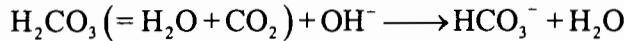


$$\begin{aligned} \text{"ring" mass} &= 32.1 \text{ L} \times \frac{82.6 \text{ g Ca}^{2+}}{1000 \text{ L water}} \times \frac{1 \text{ mol Ca}^{2+}}{40.08 \text{ g Ca}^{2+}} \times \frac{1 \text{ mol "ring" }}{1 \text{ mol Ca}^{2+}} \times \frac{607.0 \text{ g "ring" }}{1 \text{ mol "ring" }} \\ &= 40.2 \text{ g of bathtub ring} \end{aligned}$$

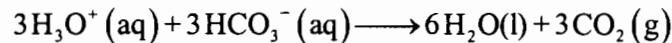
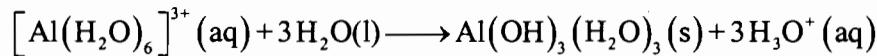
## A Group 13 Metal: Aluminum



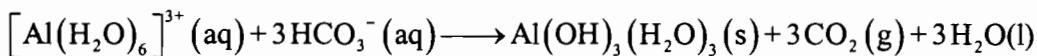
- 43.** One method of analyzing this reaction is to envision the  $\text{HCO}_3^-$  ion as a combination of  $\text{CO}_2$  and  $\text{OH}^-$ . Then the  $\text{OH}^-$  reacts with  $\text{Al}^{3+}$  and forms  $\text{Al}(\text{OH})_3$ . [This method of envisioning  $\text{HCO}_3^-$  is somewhat of a trick, but it does have its basis in reality. After all,



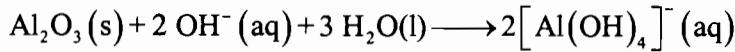
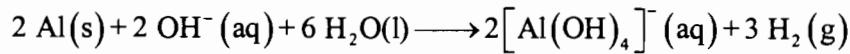
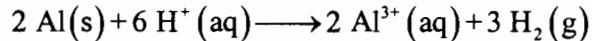
Another method is to consider the reaction as, first, the hydrolysis of hydrated aluminum ion to produce  $\text{Al}(\text{OH})_3\text{(s)}$  and an acidic solution, followed by the reaction of the acid with bicarbonate ion.



This gives the same net reaction:

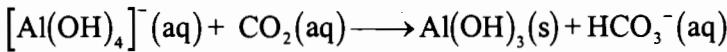


- 45.** Aluminum and its oxide are soluble in both acid and in base.



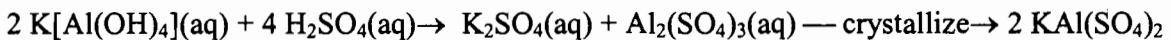
$\text{Al(s)}$  is resistant to corrosion only over the pH range 4.5 to 8.5. Thus, Al is non-reactive only when the medium to which it is exposed is neither highly acidic nor highly basic.

47.  $\text{CO}_2(\text{g})$  is, of course, the anhydride of an acid. The reaction here is an acid-base reaction.



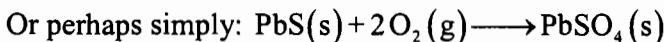
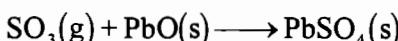
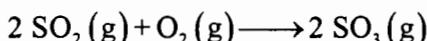
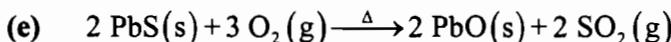
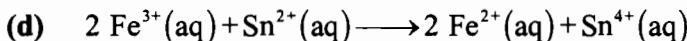
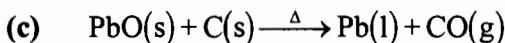
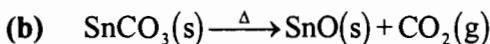
$\text{HCl}(\text{aq})$ , being a strong acid, can't be used because it will dissolve the  $\text{Al}(\text{OH})_3(\text{s})$ .

49.  $2 \text{KOH}(\text{aq}) + 2 \text{Al}(\text{s}) + 6 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{K}[\text{Al}(\text{OH})_4](\text{aq}) + 3 \text{H}_2(\text{g})$

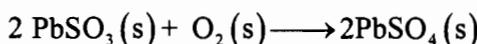
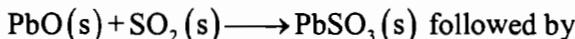


### Some Group 14 Metals: Tin and Lead

51. (a)  $\text{PbO}(\text{s}) + 2 \text{HNO}_3(\text{aq}) \longrightarrow \text{Pb}(\text{NO}_3)_2(\text{s}) + \text{H}_2\text{O}(\text{l})$



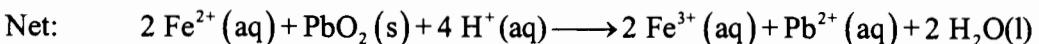
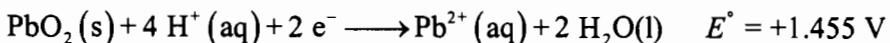
Yet a third possibility:



53. We use the Nernst equation to determine whether the cell voltage still is positive when the reaction has gone to completion.

(a) Oxidation:  $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^- \} \times 2 \quad -E^\circ = -0.771 \text{ V}$

Reduction:



$$E_{\text{cell}}^\circ = -0.771 \text{ V} + 1.455 \text{ V} = +0.684 \text{ V}$$

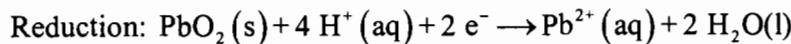
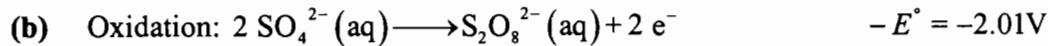
In this case, when the reaction has gone to completion,

$$[\text{Fe}^{2+}] = 0.001 \text{ M}, [\text{Fe}^{3+}] = 0.999 \text{ M}, \text{ and } [\text{Pb}^{2+}] = 0.500 \text{ M}.$$

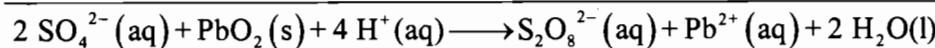
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Fe}^{3+}]^2 [\text{Pb}^{2+}]}{[\text{Fe}^{2+}]^2}$$

$$= 0.684 \text{ V} - \frac{0.0592}{2} \log \frac{[0.999]^2 [0.500]}{[0.001]^2} = 0.684 \text{ V} - 0.169 \text{ V} = 0.515 \text{ V.}$$

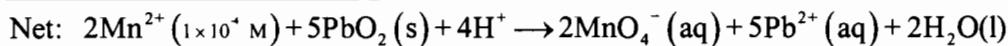
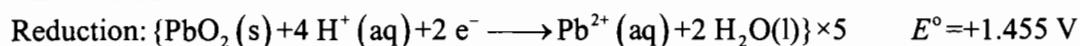
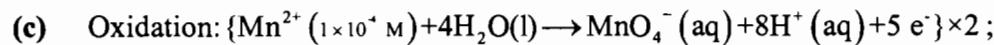
Yes, this reaction will go to completion.



$$E^{\circ} = +1.455 \text{ V}$$

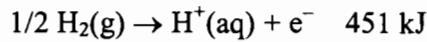
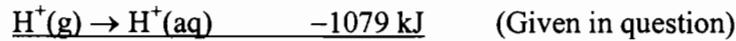
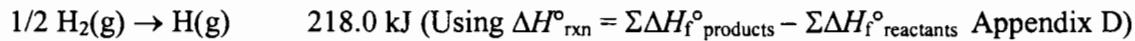
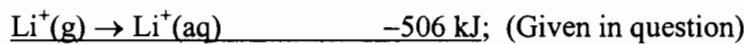


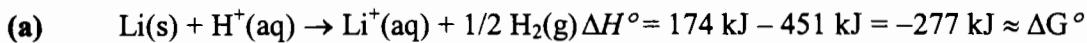
$$E_{\text{cell}}^{\circ} = -2.01 + 1.455 = -0.56 \text{ V} \quad \text{This reaction is not even spontaneous initially.}$$



$E_{\text{cell}}^{\circ} = -1.51 + 1.455 = -0.06 \text{ V.}$  The standard cell potential indicates that this reaction is not spontaneous when all concentrations are 1 M. Since the concentration of a reactant ( $\text{Mn}^{2+}$ ) is lower than 1.00 M, this reaction is even less spontaneous than the standard cell potential indicates.

## Feature Problems





$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-277 \times 10^3 \text{ J}}{-1 \text{ mol e}^- \left( 96,485 \frac{\text{C}}{\text{mol e}^-} \right)} = 2.87 \frac{\text{J}}{\text{C}} = 2.87 \text{ V} \text{ (3.040 V in Appendix D)}$$

(b)  $\Delta S = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$   
 $= [1 \text{ mol} \left( 13.4 \frac{\text{J}}{\text{Kmol}} \right) + 0.5 \text{ mol} \left( 130.7 \frac{\text{J}}{\text{Kmol}} \right)] -$   
 $[1 \text{ mol} \left( 29.12 \frac{\text{J}}{\text{Kmol}} \right) + 1 \text{ mol} \left( 0 \frac{\text{J}}{\text{Kmol}} \right)]$   
 $= 49.6 \frac{\text{J}}{\text{K}}$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -277 \text{ kJ} - 298.15 \text{ K} \left( 49.6 \frac{\text{J}}{\text{K}} \right) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -292 \times 10^3 \text{ J}$$

$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-292 \times 10^3 \text{ J}}{-1 \text{ mol e}^- \left( 96,485 \frac{\text{C}}{\text{mol e}^-} \right)} = 3.03 \frac{\text{J}}{\text{C}} = 3.03 \text{ V} \text{ (3.040 V in Appendix D)}$$

72. (a)

$$\frac{0.438 \text{ mol NaCl}}{\text{L}} \times \frac{58.443 \text{ g NaCl}}{1 \text{ mol NaCl}} = 26.6 \text{ g NaCl}$$

$$\frac{0.0512 \text{ mol MgCl}_2}{\text{L}} \times \frac{95.211 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2} = 4.87 \text{ g MgCl}_2$$

 31.5 g of salt  
per liter of  
seawater

$$18 \text{ tbs NaHCO}_3 \times \frac{10 \text{ g NaHCO}_3}{1 \text{ tbs NaHCO}_3} = 180 \text{ g NaHCO}_3$$

$$10 \text{ tbs NaCl} \times \frac{10 \text{ g NaCl}}{1 \text{ tbs NaCl}} = 100 \text{ g NaCl}$$

 307 g of salt per  
gal. of lake water  
(3.7854 L/gal)

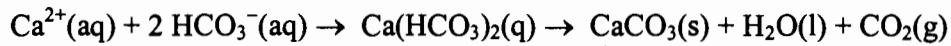
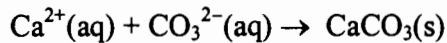
$$8 \text{ tsp MgSO}_4 \bullet 7 \text{ H}_2\text{O} \times \frac{1 \text{ tbs}}{3 \text{ tsp}} \times \frac{10 \text{ g MgSO}_4 \bullet 7 \text{ H}_2\text{O}}{1 \text{ tbs MgSO}_4 \bullet 7 \text{ H}_2\text{O}} = 27 \text{ g MgSO}_4 \bullet 7 \text{ H}_2\text{O}$$

(b) The pH of the lake will be determined by the amphiprotic bicarbonate ion,  $(\text{HCO}_3^-)$ , which hydrolyzes in water ( $K_{a_1} = 4.4 \times 10^{-7}$  or  $\text{p}K_{a_1} = 6.36$  and  $K_{a_2} = 4.7 \times 10^{-11}$  or  $\text{p}K_{a_2} = 10.33$ ). We saw earlier (chapter 18 question 100) that the pH of a solution of alanine, a diprotic species is independent of concentration (as long as it is

relatively concentrated). The  $\text{pH} = \frac{(\text{p}K_{\text{a}_1} + \text{p}K_{\text{a}_2})}{2} = \frac{(6.36 + 10.33)}{2} = 8.35$

This is not as basic as the actual pH of the lake. Addition of Borax (sodium salt of boric acid) would aid in increasing the pH of the solution (since borax is the salt of a weak acid, it is a base). The lake may be more basic due to the presence of other basic anions, namely carbonate ion ( $\text{CO}_3^{2-}$ ).

- (c) Tufa are mostly calcium carbonate ( $\text{CaCO}_3(\text{s})$ ). Since they form near underwater springs, one must assume that the springs have a high concentration of calcium ion ( $\text{Ca}^{2+}(\text{aq})$ ). We then couple this with the fact that the lake has a high salinity (high carbonate and bicarbonate ion content). We can assume that two major reactions are responsible for the formation of a tufa (see below):

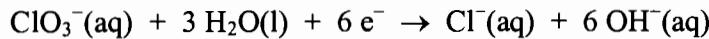


# CHAPTER 23

## MAIN-GROUP ELEMENTS II: NONMETALS

### PRACTICE EXAMPLES

**1A** This question involves calculating  $E^\circ$  for the reduction half-reaction:



Here we will consider just one of the several approaches available to solve this problem. The four half-reactions (and their associated  $E^\circ$  values) that are used in this method to come up with the “missing  $E^\circ$  value” are given below. (Note: the  $E^\circ$  for the first reaction was determined in example 23-1)

- 1)  $\text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{ClO}_2^-(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad E^\circ = 0.295 \text{ V} \quad \Delta G^\circ_1 = -2FE^\circ$
- 2)  $\text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{OCl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad E^\circ = 0.681 \text{ V} \quad \Delta G^\circ_2 = -2FE^\circ$
- 3)  $\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 1 \text{e}^- \rightarrow 1/2 \text{Cl}_2(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad E^\circ = 0.421 \text{ V} \quad \Delta G^\circ_3 = -1FE^\circ$
- 4)  $1/2 \text{Cl}_2(\text{aq}) + 1 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) \quad E^\circ = 1.358 \text{ V} \quad \Delta G^\circ_4 = -1FE^\circ$

Although the reactions themselves may be added to obtain the desired equation, the  $E^\circ$  for this equation is not the sum of the  $E^\circ$  values for the above four reactions. The  $E^\circ$  values for the desired equation is actually the weighted average of the  $E^\circ$  values for reactions 1) to 4). It can be calculated by summing up the free energy changes for the four reactions (the standard voltages for half-reactions of the same type are not additive. The  $\Delta G^\circ$  values for these reactions can, however, be summed together).

When 1), 2), 3) and 4) are added together we obtain

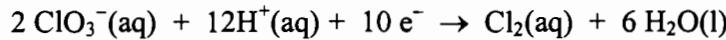
- 1)  $\text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{ClO}_2^-(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad E^\circ_1 = 0.295 \text{ V}$
  - + 2)  $\text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{OCl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad E^\circ_2 = 0.681 \text{ V}$
  - + 3)  $\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 1 \text{e}^- \rightarrow 1/2 \text{Cl}_2(\text{aq}) + 2 \text{OH}^-(\text{aq}) \quad E^\circ_3 = 0.421 \text{ V}$
  - + 4)  $1/2 \text{Cl}_2(\text{aq}) + 1 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) \quad E^\circ_4 = 1.358 \text{ V}$
- 
- $$\text{ClO}_3^-(\text{aq}) + 3 \text{H}_2\text{O}(\text{l}) + 6 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 6 \text{OH}^-(\text{aq}) \quad E^\circ_5 = ?$$

$$\text{and} \quad \Delta G^\circ_5 = \Delta G^\circ_1 + \Delta G^\circ_2 + \Delta G^\circ_3 + \Delta G^\circ_4$$

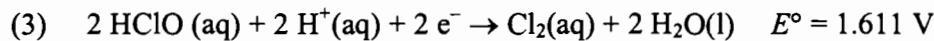
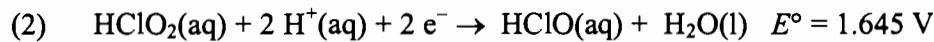
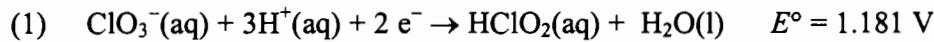
$$\text{so,} \quad -6FE^\circ_5 = -2F(0.295 \text{ V}) + -2F(0.681 \text{ V}) + -1F(0.421 \text{ V}) + -1F(1.358 \text{ V})$$

$$\text{Hence, } E^\circ_5 = \frac{-2F(0.295 \text{ V}) + -2F(0.681 \text{ V}) + -1F(0.421 \text{ V}) + -1F(1.358 \text{ V})}{-6F} = 0.622 \text{ V}$$

**1B.** This question involves calculating  $E^\circ$  for the reduction half-reaction:

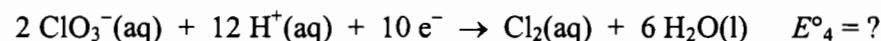
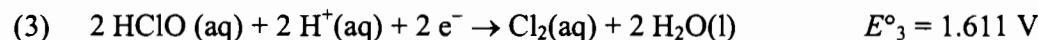
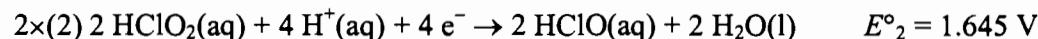
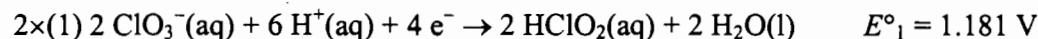


The three half-reactions (and their associated  $E^\circ$  values) are given below:



(remember that  $\Delta G^\circ = -nFE^\circ$ )

Although the reactions themselves can be added to obtain the desired equation, the  $E^\circ$  for this equation is not the sum of the  $E^\circ$  values for the above three reactions. The  $E^\circ$  for the desired equation is actually the weighted average of the  $E^\circ$  values for reactions (1) to (3). It can be obtained by summing up the free energy changes for the three reactions. (For reactions of the same type, standard voltages are not additive;  $\Delta G^\circ$  values are additive, however). When (1) and (2) (each multiplied by two) are added to (3) we obtain:



and  $\Delta G^\circ_4 = \Delta G^\circ_1 + \Delta G^\circ_2 + \Delta G^\circ_3$

so,  $-10FE^\circ_4 = -4F(1.181 \text{ V}) + -4F(1.645 \text{ V}) + -2F(1.611 \text{ V})$

$$\text{Hence, } E^\circ_4 = \frac{-4F(1.181 \text{ V}) + -4F(1.645 \text{ V}) + -2F(1.611 \text{ V})}{-10 \text{ F}} = 1.453 \text{ V}$$

**2A** The dissociation reaction is the reverse of the formation reaction and thus  $\Delta G^\circ$  for the dissociation reaction is the negative of  $\Delta G_f^\circ$



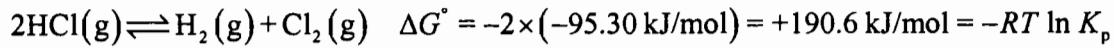
We know that

$$\Delta G^\circ = -RT \ln K_p \quad +273.2 \times 10^3 \text{ J/mol} = -8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln K_p$$

$$\ln K_p = \frac{273.2 \times 10^3 \text{ J mol}^{-1}}{-8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = -110 K_p = e^{-110} = 1.7 \times 10^{-48} \approx 2 \times 10^{-48}$$

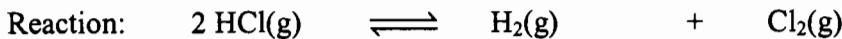
Virtually no dissociation of HF(g) into its elements occurs.

- 2B** The dissociation reaction with all integer coefficients is twice the reverse of the formation reaction.



$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-190.6 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = -76.9 \quad K_p = e^{-76.9} = 4 \times 10^{-34}$$

We assume an initial  $\text{HCl}(g)$  pressure of  $P$  atm, and calculate the final pressure of  $\text{Cl}_2(g)$  and  $\text{H}_2(g)$ ,  $x$  atm.

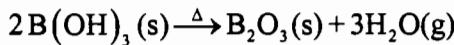
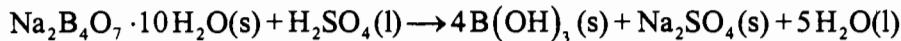


$$K_p = \frac{P\{\text{H}_2(g)\}P\{\text{Cl}_2(g)\}}{P\{\text{HCl}(g)\}^2} = \frac{x \cdot x}{(P - 2x)^2} = \left(\frac{x}{P - 2x}\right)^2 \quad \frac{x}{P - 2x} = \sqrt{4 \times 10^{-34}} = 2 \times 10^{-17}$$

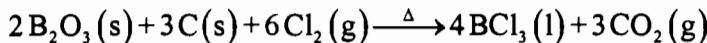
$$x = 2 \times 10^{-17} (P - 2x) \approx 2 \times 10^{-17} P$$

$$\% \text{ decomposition} = \frac{2x}{P} \times 100\% = 2 \times 2 \times 10^{-17} \times 100\% = 4 \times 10^{-15}\% \text{ decomposed}$$

- 3A** The first two reactions, are those from Example 23-3, used to produce  $\text{B}_2\text{O}_3$ .



The next reaction is conversion to  $\text{BCl}_3$  with heat, carbon, and chlorine.



$\text{LiAlH}_4$  is used as a reducing agent to produce diborane.



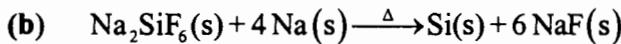
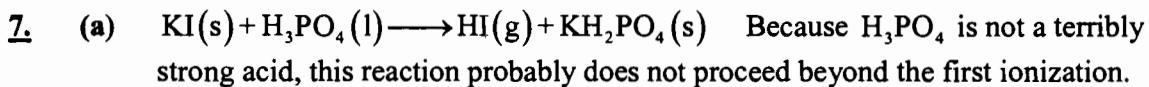
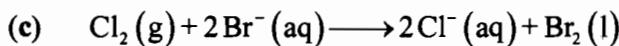
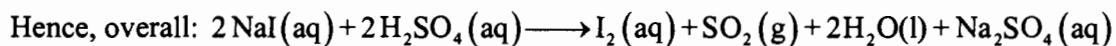
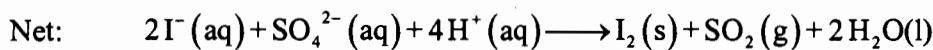
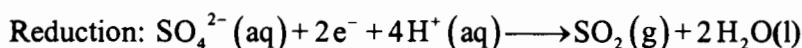
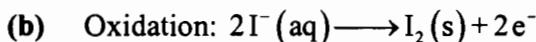
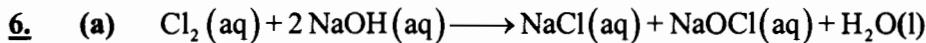
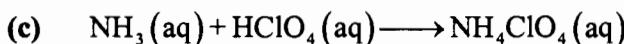
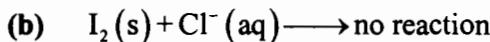
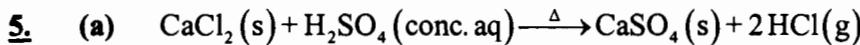
- 3B** We first roast  $\text{ZnS}(s)$  to produce  $\text{SO}_2(g)$ :  $2\text{ZnS}(s) + 3\text{O}_2(g) \rightarrow 2\text{ZnO}(s) + 2\text{SO}_2(g)$



## REVIEW QUESTIONS

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1. (a) A polyhalide ion is an anion consisting of two or more halogen atoms, such as  $I_3^-$ .  
(b) A polyphosphate is polymeric anion with a chain-like structure composed of  $PO_{2.5}$  and  $PO_3^-$  units linked to each other and terminal  $PO_{3.5}^{2-}$  units by bridging oxygen atoms.  
(c) Allotropy refers to an element existing in several forms in the same state (usually the solid state) of matter. Examples include diamond and graphite, red and white phosphorus, and the metallic and nonmetallic forms of arsenic and antimony.  
(d) Disproportionation refers to a substance being both oxidized and reduced in the same reaction.
2. (a) The Frasch process is used to mine underground deposits of sulfur. Superheated water and compressed air are pumped down into the mine, melting the sulfur and forcing it to the surface, where it cools and dries to form solid sulfur.  
(b) The contact process refers to oxidizing  $SO_2(g)$  with  $O_2(g)$  to  $SO_3(g)$  using a  $V_2O_5(s)$  catalyst. It is an essential step in the modern industrial production of sulfuric acid.  
(c) Eutrophication is the result of an excess of nutrients in bodies of water, such as ponds, which causes rapid and excessive plant growth in the water. This depletes the oxygen content of the water and marine life dies off. The decaying plant and animal life fill the pond from the bottom, eventually turning it into a marsh.  
(d) A three-center bond is a pair of electrons spanning three atoms, such as occurs in boron hydrides.
3. (a) An acid salt's anion is a partly ionized polyprotic acid:  $HSO_4^-$  or  $HPO_4^{2-}$ . An acid anhydride is a compound that forms an acid on the addition of water: typically nonmetal oxides:  $SO_3$  and  $CO_2$ .  
(b) The azide ion is  $N_3^-$ , its salts typically are unstable, often explosively so. The nitride ion is  $N^{3-}$ ; it often forms when active metals, such as magnesium, react with  $N_2(g)$ .  
(c) A silane is a compound of silicon and hydrogen. A silicone has a  $—Si—O—Si—$  backbone terminated by  $—OH$  groups, with hydrocarbon groups attached to each of the silicon atoms.  
(d) A colloidal dispersion of a solid in a liquid that flows readily is known as a sol. One that has had sufficient liquid removed that it does not flow readily is called a gel.
4. (a)  $KBrO_3$ , potassium bromate    (b)  $I_3^-$ , triiodide ion  
(c)  $NaClO$ , sodium hypochlorite    (d)  $NaH_2PO_4$ , sodium dihydrogen phosphate  
(e)  $Pb(N_3)_2$ , lead (II) azide    (f)  $BaS_2O_3$ , barium thiosulfate

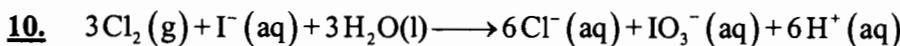


9. First compute the theoretical yield of P from 8.00 tons of phosphate rock, then the percent yield in this case.

$$\begin{aligned} \text{no. ton P} &= 8.00 \text{ ton rock} \times \frac{31 \text{ ton P}_4\text{O}_{10}}{100.00 \text{ ton rock}} \times \frac{1 \text{ ton-mol P}_4\text{O}_{10}}{283.8 \text{ ton P}_4\text{O}_{10}} \times \frac{4 \text{ ton-mol P}}{1 \text{ ton-mol P}_4\text{O}_{10}} \\ &\times \frac{31.0 \text{ ton P}}{1 \text{ ton-mol P}_2\text{O}_5} = 1.1 \text{ ton P} \end{aligned}$$

The mass of a ton-mole in tons is numerically equal to the mass of a (gram-)mole in grams.

$$\% \text{yield} = \frac{1.00 \text{ ton P produced}}{1.1 \text{ ton P calculated}} \times 100\% = 91\% \text{ yield}$$



11. Number of cubic kilometers of seawater that would have to be processed to yield 45 million tons of  $\text{H}_2\text{SO}_4$

$$\begin{aligned}
 &= 45 \times 10^6 \text{ tons H}_2\text{SO}_4 \times \frac{2000 \text{ lb}}{1 \text{ ton}} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.08 \text{ g H}_2\text{SO}_4} \times \frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol H}_2\text{SO}_4} \times \\
 &\quad \frac{96.06 \text{ g SO}_4^{2-}}{1 \text{ mol SO}_4^{2-}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \times \frac{1 \text{ L seawater}}{2650 \text{ mg SO}_4^{2-}} \times \frac{1 \text{ m}^3}{1000 \text{ L}} \times \left( \frac{1 \text{ km}}{1000 \text{ m}} \right)^3 \\
 &= 15 \text{ km}^3 \text{ of seawater.}
 \end{aligned}$$

12. (a) Reduction:  $\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq}) \quad E^\circ = +1.358 \text{ V}$   
 Oxidation:  $2\text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{s}) + 2\text{e}^- \quad -E^\circ = -0.535 \text{ V}$   
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \quad -E^\circ = -1.229 \text{ V}$

The production of  $\text{I}_2(\text{s})$  is more likely; it results in the larger standard cell potential.

- (b)  $\text{NH}_4^+$  has nitrogen in its lowest common oxidation state.  $\text{NH}_4^+$  cannot be reduced further. Thus,  $\text{NH}_4^+$  is oxidized and  $\text{H}_2\text{O}_2$  must be reduced to  $\text{H}_2\text{O}$ .

13. (a)  $\text{KI}(\text{s}) + \text{H}_3\text{PO}_4(\text{conc, aq}) \xrightarrow{\Delta} \text{KH}_2\text{PO}_4(\text{aq}) + \text{HI}(\text{g})$   
 (b)  $\text{K}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{KOH}(\text{aq})$   
 (c)  $\text{I}_2(\text{s}) + \text{KI}(\text{aq}) \rightarrow \text{KI}_3(\text{aq})$   
 (d)  $5\text{HSO}_3^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + \text{H}^+ \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{SO}_4^{2-}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

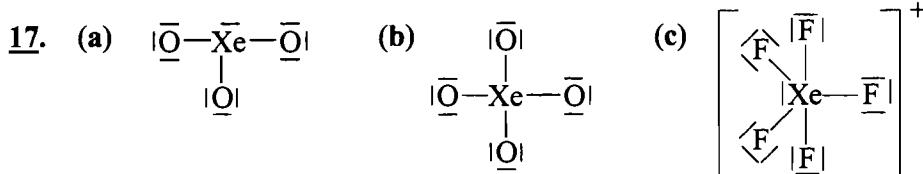
14. (a) sodium perxenate (b) barium peroxide  
 (c) mercury(II) thiocyanate (d) barium nitride  
 (e) silver (I) thiosulfate

15. (a)  $\text{PCl}_2\text{F}_3$  (b)  $\text{KNCO}$   
 (c)  $\text{FePO}_4$  (d)  $\text{Ba}(\text{N}_3)_2$   
 (e)  $\text{Mg}_2(\text{P}_2\text{O}_7)$

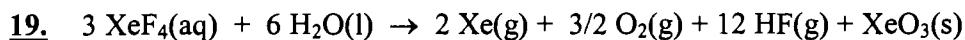
16. (a)  $\text{AgAt}$ , silver astatide (b)  $\text{Na}_4\text{XeO}_6$ , sodium perxenate  
 (c)  $\text{MgPo}$ , magnesium polonide (d)  $\text{H}_2\text{TeO}_3$ , tellurous acid  
 (e)  $\text{K}_2\text{SeSO}_3$ , potassium thioselenate (f)  $\text{KAtO}_4$ , potassium perastatate

## EXERCISES

### Noble Gas Compounds

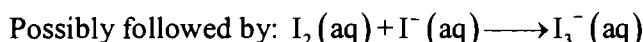
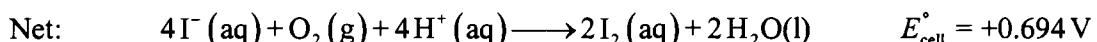
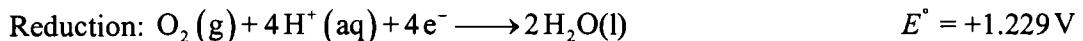
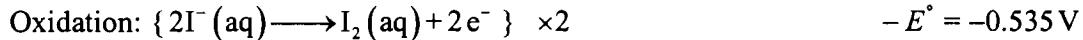


- (a) The Lewis structure has three ligands and one lone pair on Xe.  $\text{XeO}_3$  has a trigonal pyramidal shape.
- (b) The Lewis structure has four ligands on Xe.  $\text{XeO}_4$  has a tetrahedral shape.
- (c) There are five ligands and one lone pair on Xe in  $\text{XeF}_5^+$ . Its shape is square pyramidal.

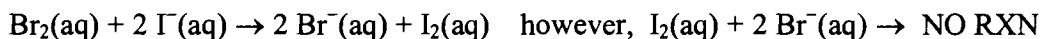


### The Halogens

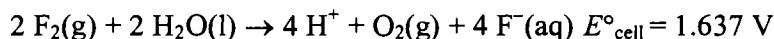
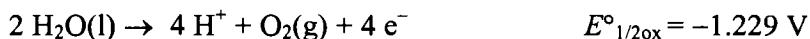
21. Iodide ion is slowly oxidized to iodine, which is yellow-brown in aqueous solution, by oxygen in the air.



23. Displacement reactions involve one element displacing another element from solution. The element that dissolves in the solution is more “active” than the element supplanted from solution. Within the halogen group the activity decreases from top to bottom. Thus, each halogen is able to displace the members of the group below it, but not those above it. For instance, molecular bromine can oxidize aqueous iodide ion but molecular iodine is incapable of oxidizing bromide ion:



The only halogen with sufficient oxidizing power to displace  $\text{O}_2(\text{g})$  from water is  $\text{F}_2(\text{g})$ :



The large positive standard reduction potential for this reaction indicates that the reaction will occur spontaneously, with products being strongly preferred under standard state conditions.

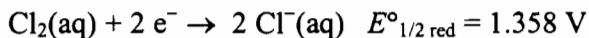
None of the halogens react with water to form  $H_2(g)$ . In order to displace molecular hydrogen from water, one must add a strong reducing agent, such as sodium metal.

25. (a) mass  $F_2 = 1 \text{ km}^3 \times \left( \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{100 \text{ cm}}{1 \text{ m}} \right)^3 \times \frac{1.03 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ lb}}{454 \text{ g}} \times \frac{1 \text{ ton}}{2000 \text{ lb}} \times \frac{1 \text{ g } F^-}{1 \text{ ton}} \times \frac{37.996 \text{ g } F_2}{37.996 \text{ g } F^-}$   
 $= 1 \times 10^9 \text{ g } F_2 = 1 \times 10^6 \text{ kg } F_2$

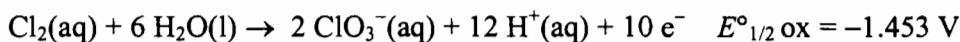
(b) Bromine is extracted by displacing it from solution with  $Cl_2(g)$ . Since there is no chemical oxidizing agent that is stronger than  $F_2(g)$ , this method of displacement would not work for  $F_2(g)$ . Even if there were a chemical oxidizing agent stronger than  $F_2(g)$  it would displace  $O_2$  before it displaced  $F_2(g)$ . Obtaining  $F_2(g)$  would require electrolysis of its molten salts, obtained by evaporating the seawater.

27. In order for the disproportionation reaction to occur under standard conditions, the  $E^\circ$  for the overall reaction must be greater than zero. To answer this question, we must refer to the Latimer diagrams provided in Figure 23-2 and the answer to practice example 23-1B.

(i) Reduction half reaction (acidic solution)



(ii) Oxidation half reaction (acidic solution)



Combining (i)  $\times 5$  with (ii)  $\times 1$ , we obtain the desired disproportionation reaction:



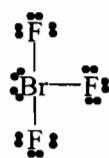
Since the final cell voltage is negative, the disproportionation reaction will not occur spontaneously under standard conditions. Alternatively, we can calculate  $K_{\text{eq}}$  by using  $\ln K_{\text{eq}} = -\Delta G^\circ/RT$  and  $\Delta G^\circ = -nFE^\circ$ . This method gives a  $K_{\text{eq}} = 8.6 \times 10^{-17}$ . Clearly, the reaction will not go to completion.

29. First we must draw the Lewis structure for all of the species listed. Following this, we will deduce their electron-group geometries and molecular shapes following the VSEPR approach.

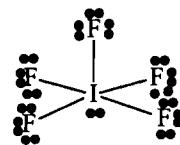
(a)  $BrF_3$ : 28 valence electrons

VSEPR class:  $AX_3E_2$

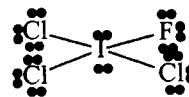
Thus  $BrF_3$  is T-shaped



- (b)  $\text{IF}_5$  42 valence electrons  
 VSEPR class:  $\text{AX}_5\text{E}$   
 Thus  $\text{IF}_5$  is square pyramidal



- (c)  $\text{Cl}_3\text{IF}^-$  36 valence electrons  
 VSEPR class:  $\text{AX}_4\text{E}_2$   
 Thus  $\text{Cl}_3\text{IF}^-$  is square planar



## Oxygen

31. Since the  $pK_a$  for  $\text{H}_2\text{O}_2$  had been provided to us, we can find the solution  $p\text{H}$  simply by solving an I.C.E. table for the hydrolysis of a 3.0 %  $\text{H}_2\text{O}_2$  solution (by mass). Of course, in order to use this method, the mass percent must first be converted to molarity. We must assume that the density of the solution is  $1.0 \text{ g mL}^{-1}$ .

$$[\text{H}_2\text{O}_2] = \frac{3.0 \text{ g H}_2\text{O}_2}{100 \text{ g solution}} \times \frac{1 \text{ g solution}}{1 \text{ mL solution}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.015 \text{ g H}_2\text{O}_2} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.88 \text{ M}$$

The  $pK_a$  for  $\text{H}_2\text{O}_2$  is 11.75. The  $K_a$  for  $\text{H}_2\text{O}_2$  is therefore  $10^{-11.75}$  or  $1.8 \times 10^{-12}$ . By comparison with pure water, which has a  $K_a$  of  $1.8 \times 10^{-16}$  at  $25^\circ\text{C}$ , one can see that  $\text{H}_2\text{O}_2$  is indeed a stronger acid than water but differences in acidity between the two is not that great. Consequently, we cannot ignore the contribution of protons of pure water when we workout the  $p\text{H}$  of the solution at equilibrium.

Reaction:	$\text{H}_2\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{K_a = 1.8 \times 10^{-12}} \text{H}_3\text{O}^+(\text{aq}) + \text{HO}_2^-(\text{aq})$		
Initial	0.88 M	—	$1.0 \times 10^{-7} \text{ M}$
Change	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
Equilibrium	$0.88-x \text{ M} (\sim 0.88 \text{ M})$	$(1.0 \times 10^{-7} + x) \text{ M}$	$x \text{ M}$

$$\text{So, } 1.8 \times 10^{-12} = \frac{x(x + 1.0 \times 10^{-7})}{0.88}$$

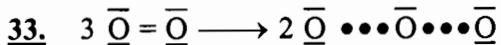
$$x^2 + 1.0 \times 10^{-7}x - 1.58 \times 10^{-12} = 0$$

$$x = \frac{-1.0 \times 10^{-7} \pm \sqrt{1.0 \times 10^{-14} + 4(1.58 \times 10^{-12})}}{2}$$

The root that makes sense in this context is  $x = 1.2 \times 10^{-6} \text{ M}$ .

$$\text{Thus, } [\text{H}_3\text{O}^+] = 1.2 \times 10^{-6} \text{ M} + 1.0 \times 10^{-7} \text{ M} = 1.3 \times 10^{-6} \text{ M}$$

Consequently, the  $p\text{H}$  for the 3.0 %  $\text{H}_2\text{O}_2$  solution (by mass) should be 5.89 (i.e., the solution is weakly acidic)



Bonds broken:  $3 \times (\text{O}=\text{O}) = 3 \times 498 \text{ kJ/mol} = 1494 \text{ kJ/mol}$

Bonds formed:  $4 \times (\text{O} \cdots \text{O})$

$$\Delta H^\circ = +285 \text{ kJ/mol} = \text{bonds broken} - \text{bonds formed} = 1494 \text{ kJ/mol} - 4 \times (\text{O} \cdots \text{O})$$

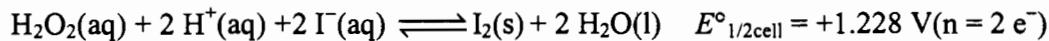
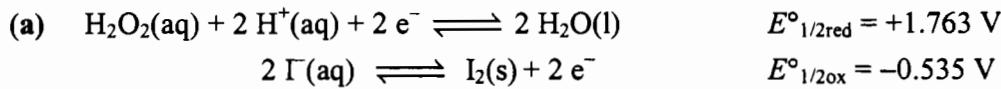
$$4 \times (\text{O} \cdots \text{O}) = 1494 \text{ kJ/mol} - 285 \text{ kJ/mol} = 1209 \text{ kJ/mol}$$

$$\text{O} \cdots \text{O} = 1209 \text{ kJ/mol} + 4 = 302 \text{ kJ/mol}$$

35. (a)  $\text{H}_2\text{S}$ , while polar, forms only weak hydrogen bonds.  $\text{H}_2\text{O}$  forms much stronger hydrogen bonds, leading to a higher boiling point.

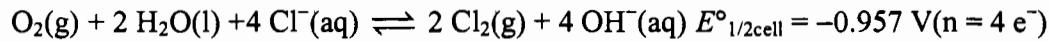
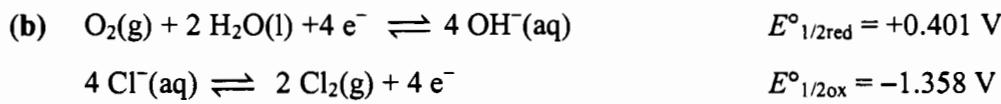
- (b) All electrons are paired in  $\text{O}_3$ , producing a diamagnetic molecule.  $|\underline{\text{O}}-\underline{\text{O}}=\underline{\text{O}}|$

37. Reactions that have  $K_{\text{eq}}$  values greater than 1000 are considered to be essentially quantitative (i.e. they go virtually to completion). So to answer this question we need only calculate the equilibrium constant for each reaction via. the equation  $E^\circ_{\text{cell}} = (0.0257/n)\ln K_{\text{eq}}$



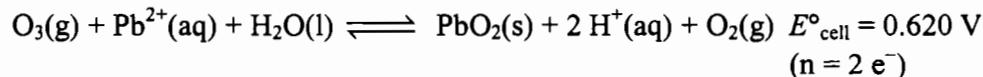
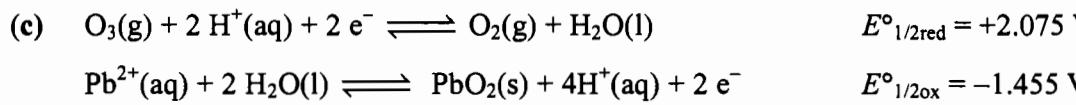
$$\ln K_{\text{eq}} = \frac{1.228 \text{ V} \times 2}{0.0257 \text{ V}} = 95.56 \quad K_{\text{eq}} = 3.2 \times 10^{41}$$

Therefore the reaction goes to completion (or very nearly so).



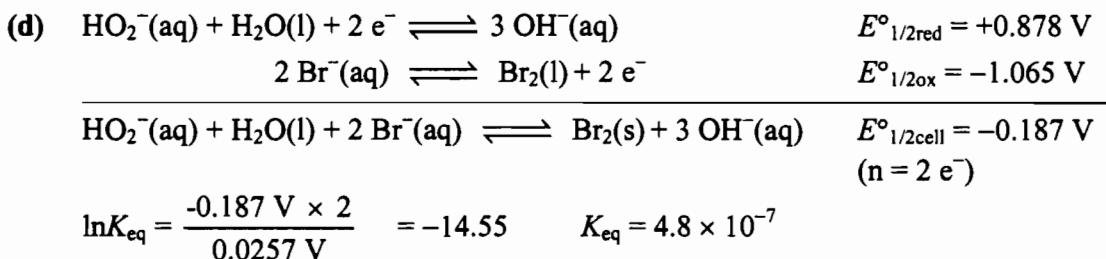
$$\ln K_{\text{eq}} = \frac{-0.957 \text{ V} \times 4}{0.0257 \text{ V}} = -148.95 \quad K_{\text{eq}} = 2.1 \times 10^{-65}$$

The extremely small value of  $K_{\text{eq}}$  indicates that reactants are strongly preferred and thus, the reaction does not even come close to going to completion.



$$\ln K_{\text{eq}} = \frac{+0.62 \text{ V} \times 2}{0.0257 \text{ V}} = 48.25 \quad K_{\text{eq}} = 9.0 \times 10^{20}$$

Therefore the reaction goes to completion (or very nearly so).



The extremely small value of  $K_{\text{eq}}$  indicates the reaction heavily favors reactants at equilibrium and thus, the reaction does not even come close to going to completion.

## Sulfur

39. (a) ZnS, zinc sulfide  
(b)  $\text{KHSO}_3$ , potassium hydrogen sulfite  
(c)  $\text{K}_2\text{S}_2\text{O}_3$ , potassium thiosulfate  
(d)  $\text{SF}_4$ , sulfur tetrafluoride

41. (a)  $\text{FeS}(\text{s}) + 2 \text{HCl}(\text{aq}) \longrightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2\text{S}(\text{aq})$   
 $\text{MnS}(\text{s}), \text{ZnS}(\text{s}), \text{etc. also are possible.}$

(b)  $\text{CaSO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \longrightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$

(c) Oxidation:  $\text{SO}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^-$   
Reduction:  $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

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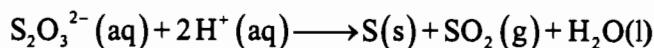
Net:  $\text{SO}_2(\text{aq}) + \text{MnO}_2(\text{s}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

(d) Oxidation:  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{SO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 4\text{e}^-$   
Reduction:  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 6\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{S}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$

---

Net:  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{S}(\text{s}) + \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

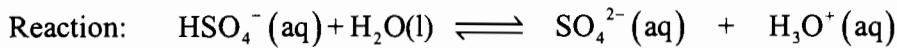
43. The decomposition of thiosulfate ion is promoted in an acidic solution. If the white solid is  $\text{Na}_2\text{SO}_4$ , there will be no reaction with strong acids such as  $\text{HCl}$ . By contrast, if the white solid is  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{SO}_2(\text{g})$  will be liberated and a pale yellow precipitate of  $\text{S(s, rhombic)}$  will form upon addition of  $\text{HCl(aq)}$ .



Consequently, the solid can be identified by adding a strong mineral acid such as HCl(aq).

45.  $\text{Na}^+$  (aq) will not hydrolyze, being the cation of a strong base. But  $\text{HSO}_4^-$  (aq) will ionize further,  $K_2 = 1.1 \times 10^{-2}$  for  $\text{HSO}_4^-$  (aq). We set up the situation, and solve the quadratic equation to obtain  $[\text{H}_3\text{O}^+]$ .

$$[\text{HSO}_4^-] = \frac{12.5 \text{ g NaHSO}_4}{250.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} \times \frac{1 \text{ mol NaHSO}_4}{120.1 \text{ g NaHSO}_4} \times \frac{1 \text{ mol HSO}_4^-}{1 \text{ mol NaHSO}_4} = 0.416 \text{ M}$$



$$\text{Initial: } \quad 0.416 \text{ M} \quad \quad \quad 0 \text{ M} \quad \quad \quad \approx 0 \text{ M}$$

$$\text{Changes: } \quad -x \text{ M} \quad \quad \quad +x \text{ M} \quad \quad \quad +x \text{ M}$$

$$\text{Equil: } \quad (0.416 - x) \text{ M} \quad \quad \quad x \text{ M} \quad \quad \quad x \text{ M}$$

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 0.011 = \frac{x^2}{0.416 - x}$$

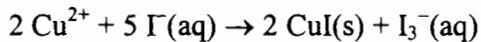
$$x^2 = 0.0046 - 0.011x$$

$$0 = x^2 + 0.011x - 0.0046$$

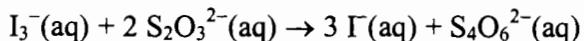
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.011 \pm \sqrt{1.2 \times 10^{-4} + 1.8 \times 10^{-2}}}{2} = 0.062 = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.062) = 1.21$$

47. The question is concerned with assaying for the mass percent of copper in an ore. The assay in this instance involves the quantitative determination of the amount of metal in an ore by chemical analysis. The titration for copper in the sample does not occur directly, but rather indirectly via the number of moles of  $\text{I}_3^-$  (aq) produced from the reaction of  $\text{Cu}^{2+}$  with  $\text{I}^-$ :



The number of moles of  $\text{I}_3^-$  (aq) produced is determined by titrating the iodide-treated sample with sodium thiosulfate. The balanced oxidation reaction that forms the basis for the titration is:



The stoichiometric ratio is one  $\text{I}_3^-$  (aq) reacting with two  $\text{S}_2\text{O}_3^{2-}$  (aq) in this titration.

The number of moles of  $\text{I}_3^-$  formed

$$= 0.01212 \text{ L S}_2\text{O}_3^{2-} \text{ (aq)} \times \frac{0.1000 \text{ moles S}_2\text{O}_3^{2-}}{1 \text{ L S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mol I}_3^-}{2 \text{ mol S}_2\text{O}_3^{2-}} = 6.060 \times 10^{-4} \text{ moles I}_3^-$$

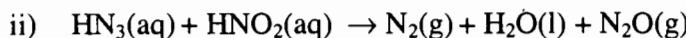
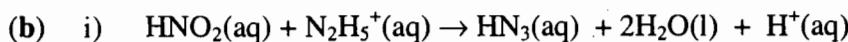
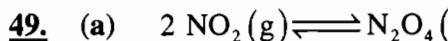
Therefore, the number of moles of  $\text{Cu}^{2+}$  released when the sample is dissolved is

$$= 6.060 \times 10^{-4} \text{ moles } I_3^- \times \frac{2 \text{ mol Cu}^{2+}}{1 \text{ mol } I_3^-} = 1.212 \times 10^{-3} \text{ moles of Cu}^{2+}$$

Consequently, the mass percent for copper in the ore is

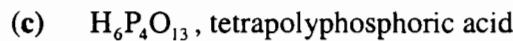
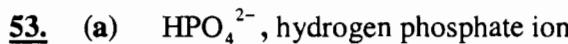
$$1.212 \times 10^{-3} \text{ moles of Cu}^{2+} \times \frac{63.546 \text{ g Cu}^{2+}}{1 \text{ mol Cu}^{2+}} \times \frac{1}{1.100 \text{ g of Cu ore}} \times 100\% = 7.002\%$$

## Nitrogen

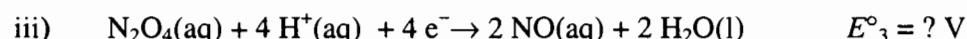
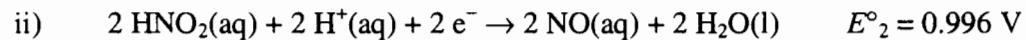
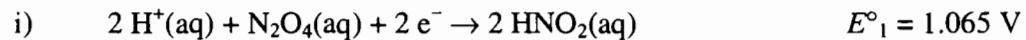


**51.**

(a)	$(\text{CH}_3)_2\text{NNH}_2$ : Each molecule has a total of 26 valence electrons.	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C} \text{---} \ddot{\text{N}} \text{---} \ddot{\text{N}} \text{---} \text{H} \\    \qquad \qquad   \\  \text{H} \qquad \text{H}-\text{C} \text{---} \text{H} \\    \\  \text{H}  \end{array}  $
(b)	$\text{ClNO}_2$ : Each molecule has a total of 24 valence electrons.	$  \begin{array}{c}  :\ddot{\text{O}}: \\     \\  :\ddot{\text{Cl}} \text{---} \text{N}^+ \text{---} \ddot{\text{O}}^{\ddagger}:  \end{array}  $
(c)	$\text{H}_3\text{PO}_3$ Each molecule has a total of 26 valence electrons.	$  \begin{array}{c}  :\ddot{\text{O}}: \\     \\  \text{H} \text{---} \ddot{\text{P}} \text{---} \ddot{\text{O}} \text{---} \text{H} \\    \\  \text{H}  \end{array}  $



**55.**

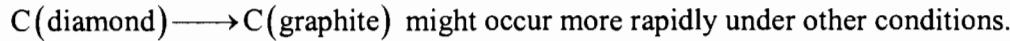


Recall that  $\Delta G^\circ = -nFE^\circ$  and that  $\Delta G^\circ$  values, not standard voltages are additive for reactions in which the number of electrons do not cancel out.

$$\text{So, } -4FE^\circ_3 = -2F(1.065 \text{ V}) + -2F(0.996 \text{ V})E^\circ_3 = 1.031 \text{ V (4 sig figs)}$$

## Carbon and Silicon

57. In the sense that diamonds react imperceptibly slowly at room temperature (either with oxygen to form carbon dioxide, or in its transformation to the more stable graphite), it is true that “diamonds last forever.” However, at elevated temperatures, diamond will burn to form  $\text{CO}_2(\text{g})$  and thus the statement is false. Also, the transformation



Eventually, of course, the conversion to graphite occurs.

59. (a)  $3 \text{SiO}_2(\text{s}) + 4 \text{Al}(\text{s}) \xrightarrow{\Delta} 2 \text{Al}_2\text{O}_3(\text{s}) + 3 \text{Si}(\text{s})$   
 (b)  $\text{K}_2\text{CO}_3(\text{s}) + \text{SiO}_2(\text{s}) \xrightarrow{\Delta} \text{CO}_2(\text{g}) + \text{K}_2\text{SiO}_3(\text{s})$   
 (c)  $\text{Al}_4\text{C}_3(\text{s}) + 12 \text{H}_2\text{O}(\text{l}) \longrightarrow 3 \text{CH}_4(\text{g}) + 4\text{Al}(\text{OH})_3(\text{s})$

61. A silane is a silicon-hydrogen compound, with the general formula  $\text{Si}_n\text{H}_{2n+2}$ . A silanol is a compound in which one or more of the hydrogens of silane is replaced by an  $-\text{OH}$  group. Then, the general formula becomes  $\text{Si}_n\text{H}_{2n+1}(\text{OH})$ . In both of these classes of compounds the number of silicon atoms,  $n$ , ranges from 1 to 6. Silicones are produced when silanols condense into chains, with the elimination of a water molecule between every two silanol molecules.

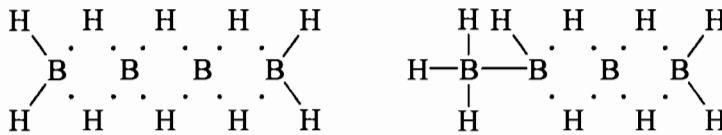


63. (1)  $2 \text{CH}_4(\text{g}) + \text{S}_8(\text{g}) \longrightarrow 2 \text{CS}_2(\text{g}) + 4 \text{H}_2\text{S}(\text{g})$   
 (2)  $\text{CS}_2(\text{g}) + 3 \text{Cl}_2(\text{g}) \longrightarrow \text{CCl}_4(\text{l}) + \text{S}_2\text{Cl}_2(\text{l})$   
 (3)  $4 \text{CS}_2(\text{g}) + 8 \text{S}_2\text{Cl}_2(\text{g}) \longrightarrow 4 \text{CCl}_4(\text{l}) + 3 \text{S}_8(\text{s})$

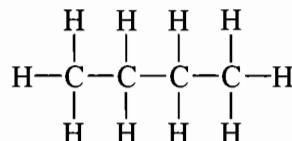
65. Muscovite or white mica has the formula  $\text{KAl}_2(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$ . Since they are not segregated into  $\text{O}_2$  units in the formula, all of the oxygen atoms in the mineral must be in the  $-2$  oxidation state. Potassium is obviously in the  $+1$  oxidation state as are the hydrogen atoms in the hydroxyl groups. Up to this point we have  $-24$  from the twelve oxygen atoms and  $+3$  from the potassium and hydrogen atoms for a net number of  $-21$  for the oxidation state. We still have three aluminum atoms and three silicon atoms to account for. In oxygen-rich salts such as mica, we would expect that the silicon and the aluminum atoms would be in their highest possible oxidation states, namely  $+4$  and  $+3$ , respectively. Since the salt is neutral, the oxidation numbers for the silicon and aluminum atoms must add up to  $+21$ . This is precisely that total that is obtained if the silicon and aluminum atoms are in their highest possible oxidation states:  $(3 \times +3) + 3 \times +4 = +21$ . Consequently, the empirical formula for white Muscovite is consistent with the expected oxidation state for each element present.

## Boron

- 67.** (a)  $\text{B}_4\text{H}_{10}$  contains a total of  $4 \times 3 + 10 \times 1 = 22$  valence electrons or 11 pairs. Ten of these pairs could be allocated to form 10 B—H bonds, leaving but one pair to bond the four B atoms together, clearly an electron deficient situation.
- (b) In our analysis in the first part, we noted that the four B atoms had but one electron pair to bond them together. To bond these four atoms into a chain requires three electron pairs. Since each electron pair in a bridging bond replaces two “normal” bonds, there must be at least two bridging bonds in the  $\text{B}_4\text{H}_{10}$  molecules. By analogy with  $\text{B}_2\text{H}_6$ , we might write the structure below left. But this structure uses only a total of 20 electrons. (The bridge bonds are shown as dots, normal bonds—electron pairs—as dashes.) In the structure at right below, we have retained some of the form of  $\text{B}_2\text{H}_6$ , and produced a compound with the formula  $\text{B}_4\text{H}_{10}$  and 11 electron pairs. (The experimentally determined structure of  $\text{B}_4\text{H}_{10}$  consists of a four-membered ring of alternating B and H atoms, held together by bridging bonds. Two of the B atoms have two H atoms bonds to each of them by normal covalent bonds. The other two B atoms have one H atom covalently bonded to each. One final B—B bond joins these last two B atoms, across the diameter of the ring.). See diagram below:



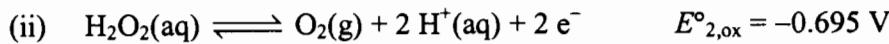
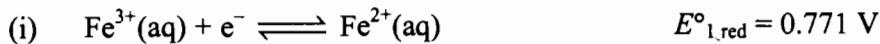
- (c)  $\text{C}_4\text{H}_{10}$  contains a total of  $4 \times 4 + 10 \times 1 = 26$  valence electrons or 13 pairs. A plausible Lewis structure follows.



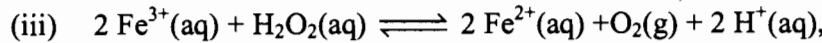
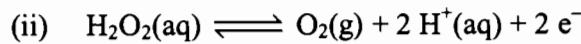
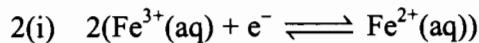
- 69.** (a)  $2\text{BBr}_3(\text{l}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{B}(\text{s}) + 6\text{HBr}(\text{g})$
- (b) i)  $\text{B}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) \xrightarrow{\Delta} 3\text{CO}(\text{g}) + 2\text{B}(\text{s})$   
 ii)  $2\text{B}(\text{s}) + 3\text{F}_2(\text{g}) \xrightarrow{\Delta} 2\text{BF}_3(\text{g})$
- (c)  $2\text{B}(\text{s}) + 3\text{N}_2\text{O}(\text{g}) \xrightarrow{\Delta} 3\text{N}_2(\text{g}) + \text{B}_2\text{O}_3(\text{s})$

## FEATURE PROBLEMS

89. We begin by calculating the standard voltages for the two steps in the decomposition mechanism. Step 1 involves the reduction of  $\text{Fe}^{3+}$  and the oxidation of  $\text{H}_2\text{O}_2$ . The two half-reactions that constitute this step are:

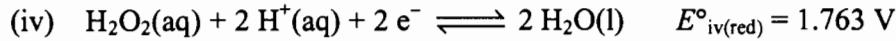


The balanced reaction is obtained by combining reaction (i), multiplied by two, with reaction (ii).

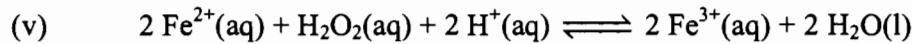
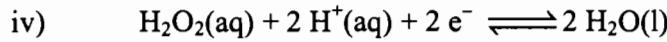


for which  $E^\circ_{\text{cell}} = E^\circ_{\text{i(red)}} + E^\circ_{\text{ii(ox)}} = 0.771 \text{ V} + (-0.695 \text{ V}) = 0.076 \text{ V}$

Since the overall cell potential is positive, this step is spontaneous. The next step involves oxidation of  $\text{Fe}^{2+}(\text{aq})$  back to  $\text{Fe}^{3+}(\text{aq})$ , (i.e. the reverse of reaction (i) and the reduction of  $\text{H}_2\text{O}_2(\text{aq})$  to  $\text{H}_2\text{O}(\text{l})$  in acidic solution, for which the half-reaction is



Combining (iv) with two times the reverse of (i) gives the overall reaction for the second step:

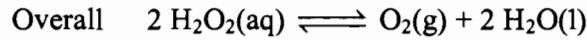
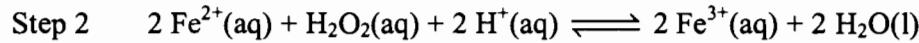
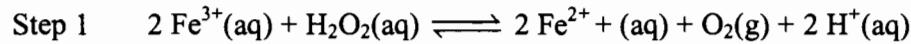


Thus the overall cell potential for the second step in the mechanism, via equation (v) is

$$E^\circ_{\text{cell}} = -E^\circ_{\text{i(red)}} + E^\circ_{\text{iv(red)}} = -0.771 \text{ V} + (1.763 \text{ V}) = 0.992 \text{ V}.$$

Since the overall standard cell potential is positive, like step 1, this reaction is spontaneous.

The overall reaction arising from the combination of these two steps is:



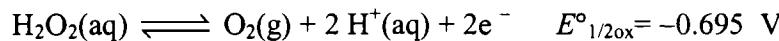
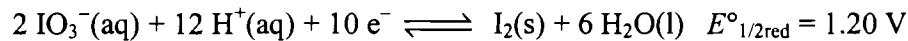
The overall potential,  $E^\circ_{\text{overall}} = E^\circ_{\text{step1}} + E^\circ_{\text{step2}} = 0.076 \text{ V} + 0.992 \text{ V} = 1.068 \text{ V}$   
 Therefore, the reaction is spontaneous at standard conditions.

To determine the minimum and maximum  $E^\circ$  values necessary for the catalyst, we need to consider each step separately.

In step 1, if  $E^\circ_{(1)}$  is less than 0.695 V, the overall voltage for the first step will be negative and hence non-spontaneous. In step 2, if the oxidation half-reaction has a potential that is more negative than  $-1.763 \text{ V}$ , the overall potential for this step will be negative, and hence non-spontaneous. Consequently,  $E^\circ_{(1)}$  must fall between 0.695 V and 1.763 V in order for both steps to be spontaneous. On this basis we find that

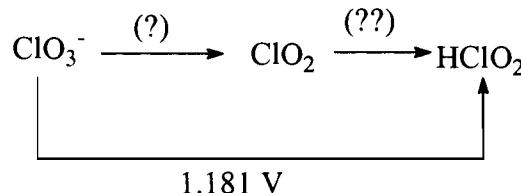
- (a)  $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Cu}(\text{s}) \quad E^\circ_{1/2\text{red}} = 0.337 \text{ V}$  cannot catalyze the reaction.
- (b)  $\text{Br}_2(\text{l}) + 2 \text{e}^- \rightleftharpoons 2 \text{Br}^-(\text{aq}) \quad E^\circ_{1/2\text{red}} = 1.065 \text{ V}$  may catalyze the reaction.
- (c)  $\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightleftharpoons \text{Al}(\text{s}) \quad E^\circ_{1/2\text{red}} = -1.676 \text{ V}$  cannot catalyze the reaction.
- (d)  $\text{Au}^{3+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Au}^+(\text{s}) \quad E^\circ_{1/2\text{red}} = 1.36 \text{ V}$  may catalyze the reaction.

In the reaction of hydrogen peroxide with iodic acid in acidic solution, the relevant half-reactions are:

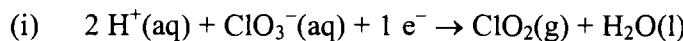


Thus, both steps in the decomposition of  $\text{H}_2\text{O}_2$ , as described above, are spontaneous if  $\text{IO}_3^-$  is used as the catalyst. As the iodate gets reduced to  $\text{I}_2$ , the  $\text{I}_2$  forms a highly colored complex with the starch, resulting in the appearance of a deep blue color solution. Some of the  $\text{H}_2\text{O}_2$  will be simultaneously oxidized to  $\text{O}_2(\text{g})$  by the iodic acid. When sufficient  $\text{I}_2(\text{s})$  accumulates, the reduction of  $\text{H}_2\text{O}_2$  by  $\text{I}_2$  begins to take place and the deep blue color fades as  $\text{I}_2$  is consumed in the reaction. Additional iodate is formed concurrently, and this goes on to oxidize the  $\text{H}_2\text{O}_2(\text{aq})$ , thereby causing the cycle to repeat itself. Each cycle results in some  $\text{H}_2\text{O}_2$  being depleted. Thus, the oscillations of color can continue until the  $\text{H}_2\text{O}_2$  has been largely consumed.

**90.**

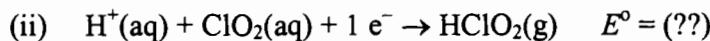


In order to add  $\text{ClO}_2$  to the Latimer diagram drawn above, we must calculate the voltages denoted by (?) and (??). The equation associated with the reduction potential (?) is

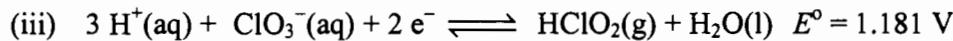


The standard voltage for this half-reaction is given in Appendix D:

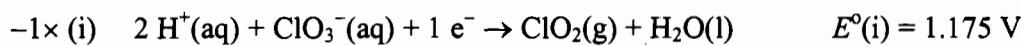
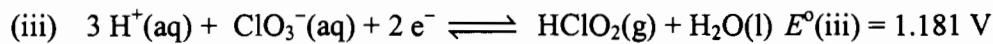
To finish up this problem, we just need to calculate the standard voltage (??) for the half-reaction (ii):



To obtain the voltage for reaction (ii), we need to subtract reaction (i) from reaction (iii) below, which has been taken from Figure 23-2:



Thus,



Since reactions (i) and (iii) are both reduction half reactions, we cannot simply subtract the potential for (i) from the potential for (iii). Instead, we are forced to obtain the voltage for (ii) via the free energy changes for the three half reactions. Thus,

$$\Delta G(\text{ii}) = \Delta G(\text{iii}) - \Delta G(\text{i}) = -1F E^\circ(\text{ii}) = -2F(1.181 \text{ V}) + 1F(1.175 \text{ V})$$

Dividing both sides by  $-F$  gives

$$E^\circ(\text{ii}) = 2(1.181 \text{ V}) - 1.175 \text{ V} \quad \text{So, } E^\circ(\text{ii}) = 1.187 \text{ V.}$$

- 91. (a)** As before, we can organize a solution around the balanced chemical equation.



$$\text{Initial: } 1.33 \times 10^{-3} \text{ M} \quad 0 \text{ M}$$

$$\text{Initial: } 0.0133 \text{ mmol}$$

$$\text{Changes: } -x \text{ mmol} \quad +x \text{ mmol}$$

$$\text{Equil: } (0.0133 - x) \text{ mmol} \quad x \text{ mmol}$$

$$K_c = 85.5 = \frac{[\text{I}_2(\text{CCl}_4)]}{[\text{I}_2(\text{aq})]} = \frac{\frac{x}{10.0 \text{ mL}}}{\frac{0.0133 - x}{10.0 \text{ mL}}}$$

$$x = 1.13, -85.5x \quad 86.5x = 1.13,$$

$$x = \frac{1.13}{86.5} = 0.01315 \text{ mmol I}_2 \text{ in CCl}_4$$

$$\text{I}_2(\text{aq}) = (0.0133 - 0.01315) \text{ mmol} = 0.00015 \text{ mmol}$$

$$\text{mass I}_2 = 0.00015 \text{ mmol} \times \frac{253.8 \text{ mg I}_2}{1 \text{ mmol I}_2} = 3.8 \times 10^{-2} \text{ mg I}_2 = 0.038 \text{ mg I}_2$$

- (b) We have the same set-up, except that the initial amount  $I_2(aq) = 0.00015\text{ mmol}$ .

$$K_c = 85.5 = \frac{[I_2(\text{CCl}_4)]}{[I_2(\text{aq})]} = \frac{x}{0.00015 - x}$$

$$x = 0.0128 - 85.5x$$

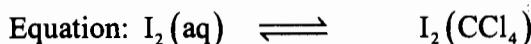
$$86.5x = 0.0128$$

$$x = \frac{0.0128}{86.5} = 0.0001480 \text{ mmol} = I_2(\text{CCl}_4),$$

$$I_2(\text{aq}) = 0.00015 - 0.0001480 = 2.0 \times 10^{-6} \text{ mmol } I_2$$

$$\text{mass } I_2 = 2.0 \times 10^{-6} \text{ mmol in H}_2\text{O} \times \frac{253.8 \text{ mg } I_2}{1 \text{ mol } I_2} = 5.1 \times 10^{-4} \text{ mg } I_2 = 0.00051 \text{ mg } I_2$$

- (c) If twice the volume of  $\text{CCl}_4$  were used for the initial extraction, the equilibrium concentrations would have been different from part 1.



$$\text{Initial: } 1.33 \times 10^{-3} \text{ M} \quad 0 \text{ M}$$

$$\text{Initial: } 0.0133 \text{ mmol}$$

$$\text{Changes: } -x \text{ mmol} \quad +x \text{ mmol}$$

$$\text{Equil: } (0.0133 - x) \text{ mmol} \quad x \text{ mmol}$$

$$K_c = 85.5 = \frac{[I_2(\text{CCl}_4)]}{[I_2(\text{aq})]} = \frac{\frac{x}{20.0 \text{ mL}}}{\frac{0.0133 - x}{10.0 \text{ mL}}}$$

$$x \div 2 = 1.13_7 - 85.5x$$

$$86.0x = 1.13_7$$

$$x = \frac{1.13_7}{86.0} = 1.32_2 \times 10^{-2} \text{ mmol} = \text{amount } I_2(\text{CCl}_4)$$

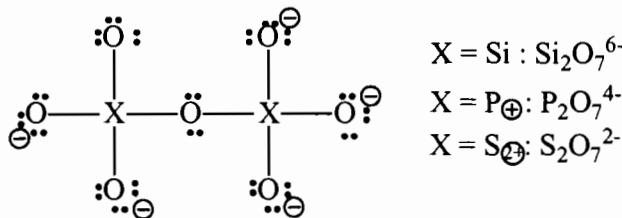
$$\text{total mass } I_2 = \frac{1.33 \times 10^{-3} \text{ mmol } I_2}{1 \text{ mL}} \times 10.0 \text{ mL soln} \times \frac{253.8 \text{ mg } I_2}{1 \text{ mol } I_2} = 3.376 \text{ mg } I_2$$

$$\text{mass } I_2 \text{ in } \text{CCl}_4 = 1.32_2 \times 10^{-2} \text{ mmol} \times \frac{253.8 \text{ mg } I_2}{1 \text{ mol } I_2} = 3.356 \text{ mg } I_2$$

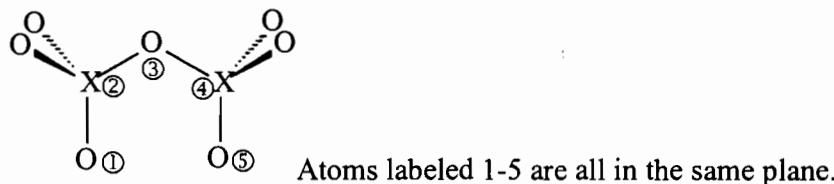
$$\text{mass } I_2 \text{ remaining in water} = 3.376 \text{ mg} - 3.356 \text{ mg} = 0.020 \text{ mg}$$

Thus, two smaller volume extractions are much more efficient than one large volume extraction.

92. (a) The pyroanions, a series of structurally analogous anions with the general formula  $X_2O_7^{n-}$ , are known for Si, P and S. The Lewis structures for these three anions are drawn below: (Note: Every member of the series has 56 valence  $e^-$ )



Based upon a VSEPR approach, we would predict tetrahedral geometry for each X atom (i.e. Si,  $P^+$ ,  $S^{2+}$ ) and a bent geometry for each bridging oxygen atom. Therefore, a maximum of five atoms in each pyroanion can lie in a plane:



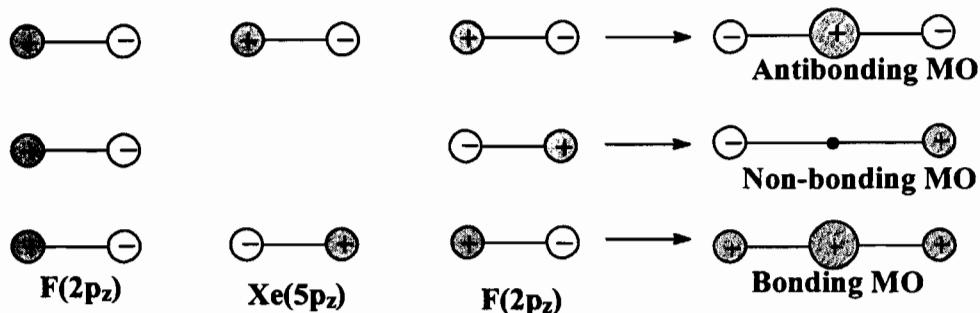
- (b) The related “mononuclear” acids, which contain just one third-row element are  $H_4SiO_4$ ,  $H_3PO_3$  and  $H_2SO_4$ . A series of pyroacids can be produced by strongly heating the “mononuclear” acids in the absence of air. In each case, the reaction proceeds via loss of water:



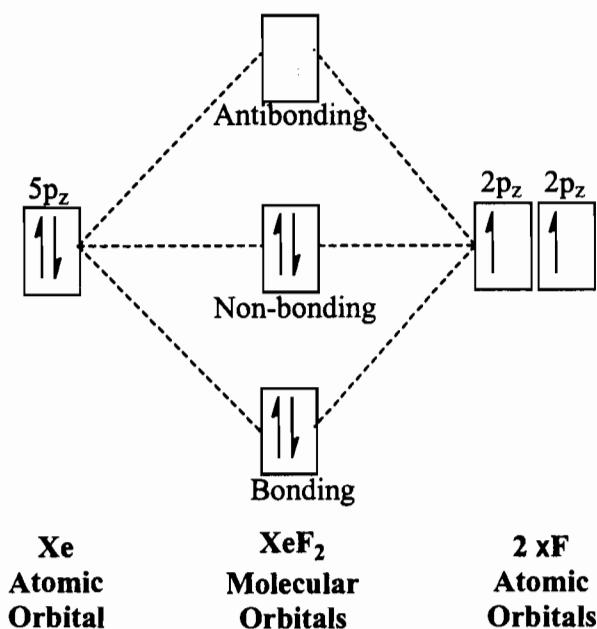
- (c) The highest oxidation state that Cl can achieve is VII (+7); consequently, the chlorine containing compound that is analogous to the mononuclear acids mentioned earlier is  $HClO_4$ . The strong heating of perchloric acid in the absence of air, should, in principle, afford  $Cl_2O_7$ , which is the neutral chlorine analogue of the pyroanions. Thus,  $Cl_2O_7$  is the anhydride of perchloric acid.



93. (a) The bonding in the  $XeF_2$  molecule can be explained quite simply in terms of a 3-center, 4 electron bond that spans all three atoms in the molecule. The bonding in this molecular orbital description involves the filled  $5p_z$  orbital of Xe and the half-filled  $2p_z$  orbitals of the two F-atoms. The linear combination of these three atomic orbitals affords one bonding, one non-bonding and one anti-bonding orbital, as depicted below:



- (b) If one assumes that the order of energies for molecular orbitals is:  
 bonding MO < non-bonding MO < antibonding MO,  
 the following molecular orbital representation of the bonding can be sketched.



Thus, a single bonding pair of electrons is responsible for holding all three atoms together. The non-bonding pair of electrons is localized primarily on the two F-atoms. This suggests that the bond possesses substantial ionic character. Bond order is defined as one-half the difference between the number of bonding electrons and the number of antibonding electrons. In the case of XeF<sub>2</sub>, the overall bond order is

$$\text{therefore: } \frac{2 e^- - 0 e^-}{2 e^-} = 1.0. \text{ (i.e., each Xe-F bond has a bond order of 0.5)}$$

- (c) By invoking a molecular orbital description based upon three-center bonding for the three F—Xe—F units in XeF<sub>6</sub>, one obtains an octahedral structure in which there are six identical Xe—F bonds. The extra nonbonding pair of electrons is delocalized

over the entire structure in this scheme. In spite of its manifest appeal, this explanation of the bonding in  $\text{XeF}_6$  is incorrect, or at best a stretch, because the actual structure for this molecule is a distorted octahedron. A more accurate description of the stereochemistry adopted by  $\text{XeF}_6$  is provided by VSEPR theory. In this approach, the shape of the molecule is determined by repulsions between bonding and non-bonding electrons in the valence shell of the central Xe atom.

Accordingly, in  $\text{XeF}_6$ , six bonding pairs and one lone pair of electrons surround the Xe. Having the repulsions of 7 pairs of electrons to cope with, the  $\text{XeF}_6$  molecule adopts a distorted structure that approaches either a monocapped octahedron or a pentagonal bipyramidal arrangement of electron pairs, depending on how one chooses to view the structure. In either case, these two shapes are much closer to the true shape for  $\text{XeF}_6$  than that predicted by the molecular orbital treatment involving three, three-center bonds. By contrast, the molecular orbital description involving three-center bonds gives far better results when applied to  $\text{XeF}_4$ . In this instance, with two three-center F—Xe—F bonds in the structure, molecular orbital theory predicts that  $\text{XeF}_4$  should adopt a square planar structure.

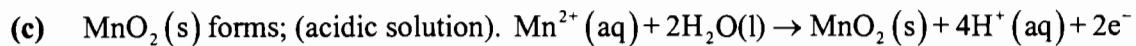
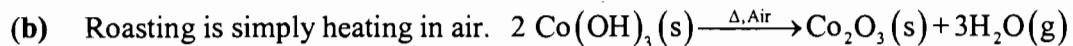
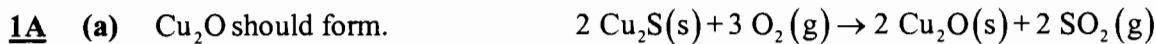
The result here is quite satisfactory because  $\text{XeF}_4$  does in fact exhibit square planar geometry. It is worth noting, however, that a square planar shape for  $\text{XeF}_4$  is also predicted by VSEPR theory. Despite the fact that the molecular orbital method has made some inroads as of late, VSEPR is still the best approach available for rationalizing the molecular geometries of noble gas compounds.

94. (a) In the phase diagram sketched in the problem, extend the liquid-vapor equilibrium curve (the vapor pressure curve) to lower temperatures (supercooled liquid region). Extend the  $\text{S}_\alpha$ -vapor equilibrium curve (sublimation curve) to the temperature at which it intersects the extended vapor pressure curve. This should come at 113 °C. Draw a line from this point of intersection to the “peak” of the  $\text{S}_\beta$  phase region. Erase the three lines that bound the  $\text{S}_\beta$  region in the original sketch. The remaining three lines would represent the equilibria,  $\text{S}_\alpha$ -V,  $\text{S}_\alpha$ -L, and L-V, producing the phase diagram if  $\text{S}_\alpha$  (rhombic) were the only solid form of sulfur.
- (b) If rhombic sulfur is heated rapidly, the transition to monoclinic sulfur at 95.3 °C might not occur. (Solid-state transitions are often very slow.) In this case, rhombic sulfur would melt at 113 °C, as described in the modified phase diagram in part (a). If the molten rhombic sulfur is further heated and then cooled, the liquid very likely will freeze at the equilibrium temperature of 119 °C, producing *monoclinic*, not rhombic, sulfur.

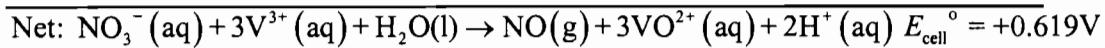
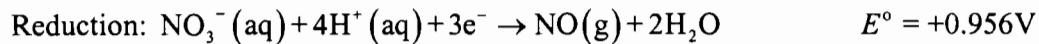
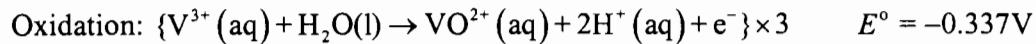
# CHAPTER 24

## THE TRANSITION ELEMENTS

### PRACTICE EXAMPLES



**2A** We write and combine the half-equations for oxidation and reduction. If  $E^\circ > 0$ , the reaction is spontaneous.

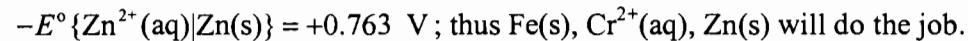


Nitric acid can be used to oxidize V<sup>3+</sup>(aq) to VO<sup>2+</sup>(aq).

**2B** The reducing couple that we seek must have a half-cell potential of such a size and sign that a positive sum results when this half-cell potential is combined with  $E^\circ \{\text{VO}^{2+}(\text{aq})|\text{V}^{3+}(\text{aq})\} = 0.041 \text{ V}$  (this is the weighted average of the VO<sup>2+</sup>|V<sup>3+</sup> and V<sup>3+</sup>|V<sup>2+</sup> reduction potentials) and a negative sum must be produced when this half-cell potential is combined with  $E^\circ \{\text{V}^{2+}(\text{aq})|\text{V}(\text{s})\} = -1.13 \text{ V}$ .

So,  $-E^\circ$  for the couple must be  $> -0.041 \text{ V}$  and  $< +1.13 \text{ V}$  (i.e. it cannot be more positive than 1.13 V, nor more negative than -0.041 V)

Some possible reducing couples from Table 21-1 are:



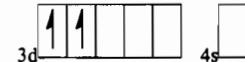
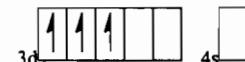
### REVIEW QUESTIONS

1. (a) A domain is a region within a metal in which the magnetic moments of the metal atoms align. In some ways, it behaves as a small magnet.

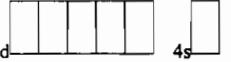
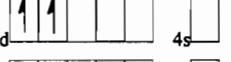
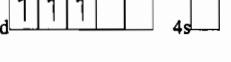
- (b) Flotation is a process of separating metal ore from the extra rock, called *gangue*. It involves agitating the crushed rock and ore with water and a detergent. The ore particles stick to the bubbles and are skimmed off.
- (c) Leaching refers to treating ore-bearing material with a chemical solution to dissolve the desired metallic elements. The solution generally is trickled through the material, and the resulting metal-bearing solution is collected at the bottom.
- (d) An amalgam is an alloy (or solution) of another metal in mercury.
2. (a) The lanthanide contraction refers to the steady decrease in the size of atoms and (particularly) +3 ions as one proceeds across the lanthanide series from La to Lu.
- (b) Zone refining uses a ring oven to melt a portion of a cylindrical metal bar. Impurities are more soluble in the molten metal and tend to remain in the molten portion. The molten region then is swept down the bar to the end, carrying the impurities with it. The process can be repeated several times, concentrating impurities at one end of the bar, which is cut off and returned to be refined.
- (c) The basic oxygen process is a relatively recently (1950s) developed technique of steel making in which molten pig iron is treated with oxygen gas (at about 10 atm pressure) and powdered limestone to reduce the carbon content and remove the undesirable impurities.
- (d) Slag formation occurs when a flux, such as limestone, is added to an ore being reduced or a metal being refined.  $\text{CaO(s)}$  forms from thermal decomposition and this unites with  $\text{SiO}_2$  to form  $\text{CaSiO}_3$ . In this molten slag, impurities dissolve. The slag also floats on top of the reduced metal, protecting it from oxidation. Other nonmetal oxides, such as  $\text{P}_4\text{O}_{10}$ , can take the place of  $\text{SiO}_2$  giving slags of other formulas:  $\text{Ca}_3(\text{PO}_4)_2$ . In this way low-level impurities are removed from the metal.
3. (a) Paramagnetism indicates that atoms, molecules, or ions have one or more unpaired electrons. In ferromagnetism, the unpaired electrons on several adjacent atoms or ions align with each other, producing a stronger magnetic field.
- (b) Roasting refers to heating a concentrated ore, usually to convert hydroxides, carbonates, or sulfides to oxides. Refining is the process of purifying the crude metal that results from the reduction of the ore.
- (c) In hydrometallurgy, reactions in aqueous solution are used in concentration, reduction, and/or refining. In pyrometallurgy, the process of reduction and/or refining are carried out at high temperatures.
- (d) Chromate ion is  $\text{CrO}_4^{2-}$ , a good precipitating agent; dichromate ion is  $\text{Cr}_2\text{O}_7^{2-}$ , a good oxidizing agent.
4. (a)  $\text{Sc(OH)}_3$ , scandium hydroxide
- (b)  $\text{Cu}_2\text{O}$ , copper(I) oxide
- (c)  $\text{TiCl}_4$ , titanium(IV) chloride or titanium tetrachloride

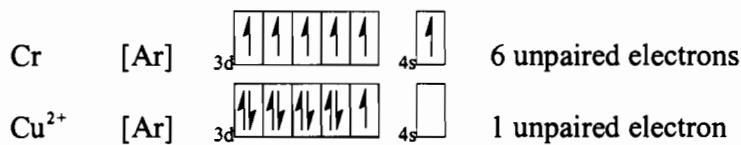
- (d)  $\text{V}_2\text{O}_5$ , vanadium(V) oxide  
(e)  $\text{K}_2\text{CrO}_4$ , potassium chromate  
(f)  $\text{K}_2\text{MnO}_4$ , potassium manganate
5. (a)  $\text{CrO}_3$ , chromium(VI) oxide (b)  $\text{FeSiO}_3$ , iron(II) silicate  
(c)  $\text{BaCr}_2\text{O}_7$ , barium dichromate (d)  $\text{CuCN}$ , copper(I) cyanide  
(e)  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , cobalt(II) chloride hexahydrate
6. (a) Pig iron is the iron obtained from the blast furnace. Once poured into molds it is called cast iron. "It contains about 95% Fe, 3% to 4% C, and various other impurities."  
(b) Ferromanganese is an alloy of iron and manganese, produced by reducing the mixed oxides of the two metals with carbon.  
(c) Chromite ore is the principal ore of chromium,  $\text{Fe}(\text{CrO}_2)_2$   
(d) Brass is a mixture of copper and zinc, with small quantities of Sn, Pb, and Fe.  
(e) Aqua regia is a mixture of three parts  $\text{HCl}(\text{aq})$  and one part  $\text{HNO}_3(\text{aq})$ . It is both strongly oxidizing acid can form complex ions with cations in solution, making it the only acid mixture that can dissolve sparingly soluble substances, such as Au and  $\text{HgS}$ .  
(f) Blister copper is the impure copper that results from the reduction process. The blisters are frozen bubbles of the  $\text{SO}_2(\text{g})$  that form during that process.  
(g) Stainless steel contains iron, and a significant proportion (about 10% each) of chromium and nickel. It is not ferromagnetic.
7. (a)  $\text{TiCl}_4(\text{g}) + 4 \text{Na}(\text{l}) \xrightarrow{\Delta} \text{Ti}(\text{s}) + 4\text{NaCl}(\text{l})$   
(b)  $\text{Cr}_2\text{O}_3(\text{s}) + 2\text{Al}(\text{s}) \xrightarrow{\Delta} 2 \text{Cr}(\text{l}) + \text{Al}_2\text{O}_3(\text{s})$   
(c)  $\text{Ag}(\text{s}) + \text{HCl}(\text{aq}) \rightarrow$  no reaction  
(d)  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq}) + 2\text{KOH}(\text{aq}) \rightarrow 2 \text{K}_2\text{CrO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
(e)  $\text{MnO}_2(\text{s}) + 2 \text{C}(\text{s}) \xrightarrow{\Delta} \text{Mn}(\text{l}) + 2\text{CO}(\text{g})$

8. (a) Oxidation:  $\{Fe_2S_3(s) + 6 OH^-(aq) \rightarrow 2Fe(OH)_3(s) + 3S(s) + 6e^-\} \times 2$   
 Reduction:  $\{O_2(g) + 2 H_2O(l) + 4e^- \rightarrow 4 OH^-(aq)\} \times 3$   
 Net:  $2 Fe_2S_3(s) + 3 O_2(g) + 6 H_2O(l) \rightarrow 4 Fe(OH)_3(s) + 6S(s)$
- (b) Oxidation:  $\{Mn^{2+}(aq) + 4 H_2O(l) \rightarrow MnO_4^-(aq) + 8 H^+(aq) + 5e^-\} \times 2$   
 Reduction:  $\{S_2O_8^{2-}(aq) + 2e^- \rightarrow 2 SO_4^{2-}(aq)\} \times 5$   
 Net:  $2 Mn^{2+}(aq) + 8 H_2O(l) + 5 S_2O_8^{2-}(aq) \rightarrow 2 MnO_4^-(aq) + 16 H^+(aq) + 10 SO_4^{2-}(aq)$
- (c) Oxidation:  $\{Ag(s) + 2 CN^-(aq) \rightarrow [Ag(CN)_2]^- (aq) + e^-\} \times 4$   
 Reduction:  $O_2(g) + 2 H_2O(l) + 4e^- \rightarrow 4 OH^-(aq)$   
 Net:  $4 Ag(s) + 8 CN^-(aq) + O_2(g) + 2 H_2O(l) \rightarrow 4 [Ag(CN)_2]^- (aq) + 4 OH^-(aq)$
9. (a)  $Cr(s) + 2HCl(aq) \rightarrow CrCl_2(aq) + H_2(g)$  Virtually any first period transition metal except Cu can be substituted for Cr, with a different metallic oxidation state, as well.  
 (b)  $Cr_2O_3(s) + 2 OH^-(aq) + 3 H_2O(l) \rightarrow 2 Cr(OH)_4^-(aq)$   
 The oxide must be amphoteric. Thus,  $Sc_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ , and  $ZnO$  could be substituted for  $Cr_2O_3$ .  
 (c)  $2 La(s) + 6 HCl(aq) \rightarrow 2 LaCl_3(aq) + 3 H_2(g)$   
 Any lanthanide or actinide element can be substituted for lanthanum.

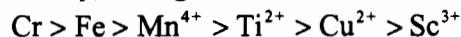
10. (a) Ti [Ar]  $3d$   (b)  $V^{3+}$  [Ar]  $3d$   4s   
 (c)  $Cr^{2+}$  [Ar]  $3d$   4s   
 (d)  $Mn^{4+}$  [Ar]  $3d$   4s   
 (e)  $Mn^{2+}$  [Ar]  $3d$   4s   
 (f)  $Fe^{3+}$  [Ar]  $3d$   4s 

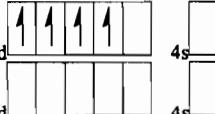
11. We first give the orbital diagram for each of the species, and then count the number of unpaired electrons.

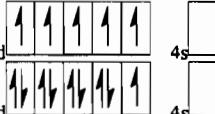
- Fe [Ar]  $3d$   4s  4 unpaired electrons
- $Sc^{3+}$  [Ar]  $3d$   4s  0 unpaired electrons
- $Ti^{2+}$  [Ar]  $3d$   4s  2 unpaired electrons
- $Mn^{4+}$  [Ar]  $3d$   4s  3 unpaired electrons

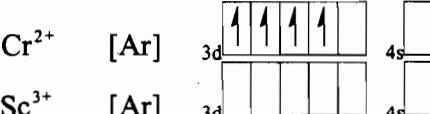


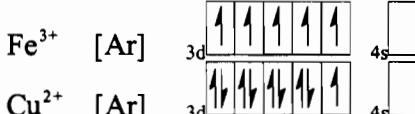
Finally, arrange in order of decreasing number of unpaired electrons:



- 12.** Transition metals tend to have higher melting points than representative metals. Because they are metals, transition elements have relatively low ionization energies. Ions of transition metals often are colored in aqueous solution. Because they are metals and thus readily form cations, they have negative standard reduction potentials. Their compounds often have unpaired electrons because of the diversity of *d*-electron configurations, and thus, they often are paramagnetic. Consequently, the correct answers are (c) and (e).
- 13.** Sc<sup>3+</sup> has the electron configuration of the preceding noble gas (Ar). This is obviously an electron configuration in which all electrons are paired, a diamagnetic species. All of the other species have at least one unpaired electron, as orbital diagrams show.
- $\text{Cr}^{2+}$  [Ar] 3d  4s

$\text{Fe}^{3+}$  [Ar] 3d  4s

$\text{Sc}^{3+}$  [Ar] 3d  4s

$\text{Cu}^{2+}$  [Ar] 3d  4s
- 14.** Ti should not display a +6 oxidation state, because in order for Ti to display a +6 oxidation state, two electrons would have to be removed from the noble gas electron configuration of Ar. This is quite unlikely.
- 15.** The ion that is the best oxidizing agent in aqueous solution is the ion that can most readily be reduced. And we can assess that property either by standard reduction potentials  
 $-E^\circ \{\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})\} = +0.800 \text{ V}$ ,  
 $E^\circ \{\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})\} = +0.337 \text{ V}$ ,  $E^\circ \{\text{Zn}^{2+}(\text{aq})|\text{Zn}(\text{s})\} = -0.763 \text{ V}$ ,  
 $E^\circ \{\text{Na}^+(\text{aq})|\text{Na}(\text{s})\} = -2.714 \text{ V}$ , with the most positive value indicating the best oxidizing agent, or from our own experience with the reverse reaction. We know that silver is the least likely of all the metals listed to be oxidized, and thus its ion is the most readily reduced.
- 16.** The +3 state probably is the most stable oxidation state of iron because in this oxidation state iron has a *d*<sup>5</sup> electron configuration. As we have seen before, an electron configuration containing a half-filled subshell is unexpectedly stable energetically, compared to other configurations with partially filled subshells. In the cases of cobalt and nickel, the ions with *d*<sup>5</sup> configurations are Co<sup>4+</sup> and Ni<sup>5+</sup>. The slight advantage of a *d*<sup>5</sup> configuration is not sufficient to stabilize ions with such high charges.

## EXERCISES

### Properties of the Transition Elements

- 17.** A given main group metal typically displays one oxidation state, usually equal to its family number in the periodic table. Exceptions are elements such as Tl (+1 and +3), Pb (+2 and +4), and Sn (+2 and +4) in which the lower oxidation state represents a pair of *s* electrons not being ionized (a so-called "inert pair").

Main group metals do not form a wide variety of complex ions, with  $\text{Al}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Pb}^{2+}$  being major exceptions. On the other hand, most transition metal ions form an extensive variety of complex ions. Most compounds of main group metals are colorless; exceptions occur when the anion is colored. On the other hand, many of the compounds of transition metal cations are colored, due to d-d electron transitions. Virtually every main group metal cation has no unpaired electrons and hence is diamagnetic. On the other hand, many transition metals cations have one or more unpaired electrons and therefore are paramagnetic.

- 19.** When an electron is added to a main group element to create the element of next highest atomic number, this electron is added to the outer shell of the atom, far from the nucleus. Thus, it has a major influence on the size of the atom. However, when an electron is added to a transition metal atom to create the atom of next highest atomic number, it is added to the electronic shell inside the outermost. The electron thus has been added to a position close to the nucleus to which it is attracted quite strongly and thus it has small effect on the size of the atom.
- 21.** Of the first transition series, manganese exhibits the greatest number of different oxidation states in its compounds, every state from +1 to +7. One possible explanation might be its  $3d^54s^2$  electron configuration. Removing one electron produces an electron configuration ( $3d^54s^1$ ) with two half-filled subshells, removing two produces one with a half-filled and an empty subshell. Then there is no point of semistability until the remaining five *d* electrons are removed. These higher oxidation states all are stabilized by being present in oxides ( $\text{MnO}_2$ ) or oxoanions (e.g.  $\text{MnO}_4^-$ ).
- 23.** The greater ease of forming lanthanide cations compared to forming transition metal cations, is due to the larger size of lanthanide atoms. The valence (outer shell) electrons of these larger atoms are much further from the nucleus, much less strongly attracted to the positive charge of the nucleus, and thus are removed much more readily.

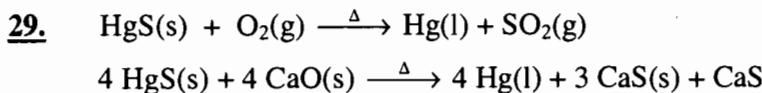
### Reactions of Transition Metals and Their Compounds

- 25.** (a)  $\text{Sc(OH)}_3(\text{s}) + 3\text{H}^+(\text{aq}) \rightarrow \text{Sc}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$   
(b)  $3\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{Fe}^{3+}(\text{aq}) + \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$

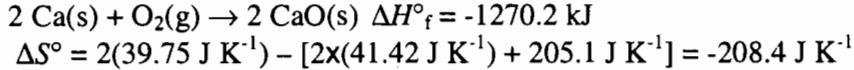
- (c)  $2 \text{KOH(l)} + \text{TiO}_2(\text{s}) \xrightarrow{\Delta} \text{K}_2\text{TiO}_3(\text{s}) + \text{H}_2\text{O(g)}$   
 (d)  $\text{Cu(s)} + 2 \text{H}_2\text{SO}_4(\text{conc, aq}) \rightarrow \text{CuSO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 2 \text{H}_2\text{O(l)}$

**27.** We write some of the following reactions as total equations rather than as net ionic equations so that the reagents used are indicated.

- (a)  $\text{FeS(s)} + 2 \text{HCl(aq)} \rightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2\text{S(g)}$   
 $4 \text{Fe}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 4\text{Fe}^{3+}(\text{aq}) + 2 \text{H}_2\text{O(l)}$   
 $\text{Fe}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq}) \rightarrow \text{Fe(OH)}_3(\text{s})$
- (b)  $\text{BaCO}_3(\text{s}) + 2 \text{HCl(aq)} \rightarrow \text{BaCl}_2(\text{aq}) + \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$   
 $2 \text{BaCl}_2(\text{aq}) + \text{K}_2\text{Cr}_2\text{O}_7(\text{aq}) + 2 \text{NaOH(aq)}$   
 $\rightarrow 2 \text{BaCrO}_4(\text{s}) + 2 \text{KCl(aq)} + 2 \text{NaCl(aq)} + \text{H}_2\text{O(l)}$



**31.** The plot of  $\Delta G^\circ$  versus T will consist of three lines of increasing positive slope. The first line is joined to the second line at the melting point for Ca(s), while the second line is joined to the third at the boiling point for Ca(l).



The graph should be similar to that for  $2 \text{Mg(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO(s)}$ . We expect a positive slope with slight changes in the slope after the melting point(839 °C) and boiling points(1484 °C) ,owing mainly to changes in entropy. The plot will always below the  $\Delta G^\circ$  line for  $2 \text{Mg(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO(s)}$  at all temperatures.

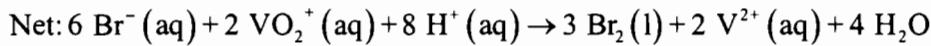
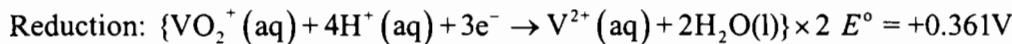
### Oxidation-reduction

- 33.** (a) Reduction:  $\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O(l)}$   
 (b) Oxidation:  $\text{Cr}^{2+}(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{e}^-$
- 35.** (a) First we need the reduction potential for the couple  $\text{VO}_2^+(\text{aq}) / \text{V}^{2+}(\text{aq})$ . We will use a method learned in Chapter 21 (see page 834).
- $$\text{VO}_2^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O(l)} \quad \Delta G^\circ = -1 \text{ F (+1.000 V)}$$
- $$\text{VO}^{2+}(\text{aq}) + 2 \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O(l)} \quad \Delta G^\circ = -1 \text{ F (+0.337 V)}$$
- $$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{V}^{2+}(\text{aq}) \quad \Delta G^\circ = -1 \text{ F (-0.255 V)}$$
- 
- $$\text{VO}_2^+(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{V}^{2+}(\text{aq}) + 2 \text{H}_2\text{O} \quad \Delta G^\circ = -3 \text{ F E}^\circ$$

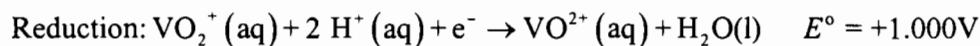
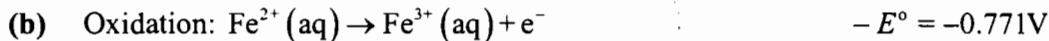
$$E^\circ = \frac{1.000 \text{ V} + 0.337 \text{ V} - 0.255 \text{ V}}{3} = +0.361 \text{ V}$$

We next analyze the oxidation-reduction reaction.

Oxidation:

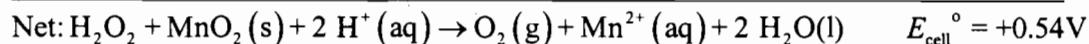
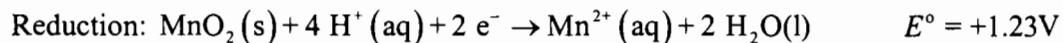
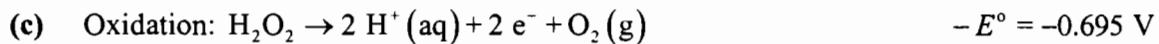


$$E_{\text{cell}}^\circ = -0.704 \text{ V} \quad \text{This reaction does not occur to a significant extent as written.}$$



$$E_{\text{cell}}^\circ = +0.229 \text{ V}$$

This reaction does occur to a significant extent under standard conditions.



This reaction does occur to a significant extent under standard conditions.

37. The reducing couple that we seek must have a half-cell potential of such a size and sign that a positive sum results when this half-cell potential is combined with  $E^\circ \{\text{VO}^{2+} (\text{aq})|\text{V}^{3+} (\text{aq})\} = 0.337 \text{ V}$  and a negative sum must be produced when this half-cell potential is combined with  $E^\circ \{\text{V}^{3+} (\text{aq})|\text{V}^{2+} (\text{aq})\} = -0.255 \text{ V}$ .

So,  $-E^\circ$  for the couple must be  $> -0.337 \text{ V}$  and  $< +0.255 \text{ V}$  (i.e. it cannot be more positive than  $0.255 \text{ V}$ , nor more negative than  $-0.337 \text{ V}$ )

Some possible reducing couples from Table 21-1 are:

$$-E^\circ \{\text{Sn}^{2+} (\text{aq})|\text{Sn}(\text{s})\} = +0.137 \text{ V}; -E^\circ \{\text{H}^+ (\text{aq})|\text{H}_2 (\text{g})\} = 0.000 \text{ V}$$

$-E^\circ \{\text{Pb}^{2+} (\text{aq})|\text{Pb}(\text{s})\} = +0.125 \text{ V}$ ; thus  $\text{Pb}(\text{s})$ ,  $\text{Sn}(\text{s})$ ,  $\text{H}_2(\text{g})$ , to name but a few, will do the job.

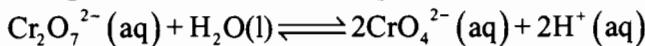
- 39.** Table D-4 contains the following data:  $\text{Cr}^{3+}/\text{Cr}^{2+}$  reduction potential = -0.424 V,  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  reduction potential = 1.33 V and  $\text{Cr}^{2+}/\text{Cr}$  reduction potential = -0.90 V. By using the additive nature of free energies and the fact that  $\Delta G^\circ = -nFE^\circ$ , we can determine the two unknown potentials and complete the diagram.

$$(i) \quad \text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{2+}: E^\circ = \frac{3(1.33 \text{ V}) - 0.424 \text{ V}}{4} = 0.892 \text{ V}$$

$$(ii) \quad \text{Cr}^{3+}/\text{Cr}: E^\circ = \frac{-0.424 \text{ V} + 2(-0.90) \text{ V}}{3} = -0.74 \text{ V}$$

## Chromium and Chromium Compounds

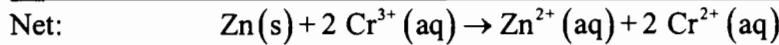
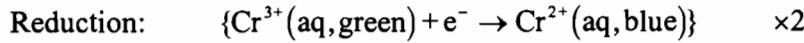
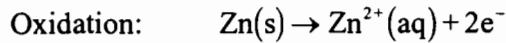
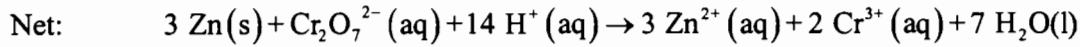
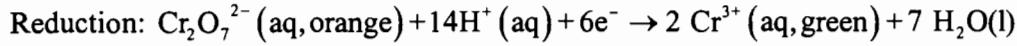
- 41.** Orange dichromate ion is in equilibrium with yellow chromate ion in aqueous solution.



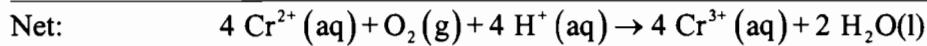
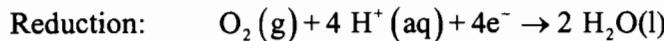
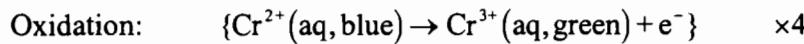
The chromate ion in solution then reacts with lead(II) ion to form a precipitate of yellow lead(II) dichromate.  $\text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightleftharpoons \text{PbCrO}_4(\text{s})$

$\text{PbCrO}_4(\text{s})$  will form until  $[\text{H}^+]$  from the first equilibrium increases to a significant value and both equilibria are simultaneously satisfied.

- 43.** Oxidation:  $\{\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-\}$  }  $\times 3$



The green color is most likely due to a chloro complex of  $\text{Cr}^{3+}$ , such as  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ .



- 45.** Simple substitution into expression (24.19) yields  $[\text{Cr}_2\text{O}_7^{2-}]$  in each case. In fact, the expression is readily solved for the desired concentration:

$[\text{Cr}_2\text{O}_7^{2-}] = 3.2 \times 10^{14} [\text{H}^+]^2 [\text{CrO}_4^{2-}]^2$ . In each case, we use the value of pH to determine  $[\text{H}^+] = 10^{-\text{pH}}$ .

(a)  $[\text{Cr}_2\text{O}_7^{2-}] = 3.2 \times 10^{14} (10^{-6.62})^2 (0.20)^2 = 0.74 \text{ M}$

(b)  $[\text{Cr}_2\text{O}_7^{2-}] = 3.2 \times 10^{14} (10^{-8.85})^2 (0.20)^2 = 2.6 \times 10^{-5} \text{ M}$

47. Each mole of chromium metal plated out from a chrome plating bath (i.e.,  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ ) requires six moles of electrons.

$$\text{mass Cr} = 1.00 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ hr}} \times \frac{3.4 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Cr}}{6 \text{ mol e}^-} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 1.10 \text{ g Cr}$$

49. Dichromate ion is the prevalent species in acidic solution. Oxoanions are better oxidizing agents in acidic solution because increasing the concentration of hydrogen ion favors formation of product. The half-equation

is:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$  Note that precipitation occurs most effectively in alkaline solution. In fact, adding an acid to a compound is often an effective way of dissolving a water-insoluble compound. Thus, we expect to see the form that predominates in alkaline solution be the most effective precipitating agent. Notice also that  $\text{CrO}_4^{2-}$  is smaller than is  $\text{Cr}_2\text{O}_7^{2-}$ , giving it a higher lattice energy in its compounds and making those compounds harder to dissolve.

51.  $4\text{Fe}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \quad E^\circ = 0.44 \text{ V}$

$$[\text{Fe}^{2+}] = [\text{Fe}^{3+}]; \text{ pH} = 3.25 \text{ or } [\text{H}^+] = 5.6 \times 10^{-4} \text{ and } P_{\text{O}_2} = 0.20 \text{ atm}$$

$$E = E^\circ - \frac{0.0592}{n} \log \left( \frac{[\text{Fe}^{3+}]^4}{[\text{Fe}^{2+}]^4 [\text{H}^+]^4 P_{\text{O}_2}} \right) = 0.44 \text{ V} - \frac{0.0592}{4} \log \left( \frac{\cancel{[\text{Fe}^{3+}]^4}}{\cancel{[\text{Fe}^{2+}]^4} [10^{-3.25}]^4 0.20} \right)$$

$$E = 0.24 \text{ V} \text{ (spontaneous under these conditions)}$$

53.  $\text{Fe}^{3+}(\text{aq}) + \text{K}_4^{[\text{III}]}[\text{Fe}(\text{CN})_6](\text{aq}) \rightarrow \text{K}^{[\text{III}]}[\text{Fe}(\text{CN})_6](\text{s}) + 3\text{K}^+(\text{aq})$

$$\text{Alternate formulation: } 4\text{Fe}^{3+} + 3[\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) + \text{Fe}_4^{[\text{III}]}[\text{Fe}(\text{CN})_6]_3$$

## Group 11 Metals

55. (a)  $\text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{aq})$   
 (b)  $\text{Au}^+(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Au}(\text{s}) + \text{Fe}^{3+}(\text{aq})$   
 (c)  $2\text{Cu}^{2+}(\text{aq}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Cu}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq})$

57. In the Integrative Example we determined that  $K_c = 1.2 \times 10^6 = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$  or

$$[\text{Cu}^{2+}] = 1.2 \times 10^6 [\text{Cu}^+]^2$$

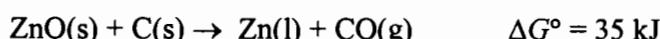
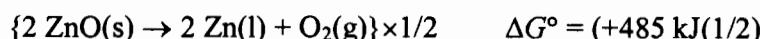
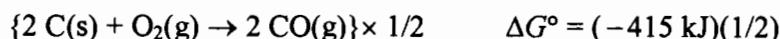
- (a) When  $[\text{Cu}^+] = 0.20 \text{ M}$ ,  $[\text{Cu}^{2+}] = 1.2 \times 10^6 (0.20)^2 = 4.8 \times 10^4 \text{ M}$ . This is an impossibly high concentration. Thus  $[\text{Cu}^+] = 0.20 \text{ M}$  can never be achieved.
- (b) When  $[\text{Cu}^+] = 1.0 \times 10^{-10} \text{ M}$ ,  $[\text{Cu}^{2+}] = 1.2 \times 10^6 (1.0 \times 10^{-10})^2 = 1.2 \times 10^{-14} \text{ M}$ . This is an entirely reasonable (even though small) concentration;  $[\text{Cu}^+] = 1.0 \times 10^{-10} \text{ M}$  can be maintained in solution.

## Group 12 Metals

59. Given:  $\text{Hg}^{2+}/\text{Hg}$  reduction potential = 0.854 V and  $\text{Hg}_2^{2+}/\text{Hg}$  reduction potential = 0.796 V  
 Using the additive nature of free energies and the fact that  $\Delta G^\circ = -nFE^\circ$ , we may determine the

$$\text{Hg}^{2+}/\text{Hg}_2^{2+} \text{ potential as } \frac{2(0.854 \text{ V}) - 0.796 \text{ V}}{1} = 0.912 \text{ V}$$

61. (a) Estimate  $K_p$  for  $\text{ZnO}(\text{s}) + \text{C}(\text{s}) \rightarrow \text{Zn}(\text{l}) + \text{CO}(\text{g})$  at 800 °C (Note:  $\text{Zn}(\text{l})$  boils at 907 °C)



Use  $\Delta G^\circ = -RT \ln K_{\text{eq}}$  where  $T = 800 \text{ }^\circ\text{C}$ ,  $K_{\text{eq}} = K_p$

- 63.** We calculate the wavelength of light absorbed in order to promote an electron across each band gap.

First a few relationships.  $E_{\text{mole}} = N_A E_{\text{photon}}$        $E_{\text{photon}} = h\nu$        $c = \nu\lambda$  or  $\nu = c/\lambda$

Then, some algebra.  $E_{\text{mole}} = N_A E_{\text{photon}} = N_A h\nu = N_A hc/\lambda$       or       $\lambda = N_A hc/E_{\text{mole}}$

$$\text{For ZnO, } \lambda = \frac{6.022 \times 10^{23} \text{ mol}^{-1} \times 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{290 \times 10^3 \text{ J mol}^{-1}} \times \frac{10^9 \text{ nm}}{1 \text{ m}}$$

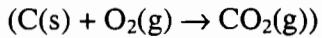
$$= \frac{1.196 \times 10^8 \text{ J mol}^{-1} \text{ nm}}{290 \times 10^3 \text{ J mol}^{-1}} = 413 \text{ nm} \quad \text{violet light}$$

$$\text{For CdS, } \lambda = \frac{1.196 \times 10^8 \text{ J mol}^{-1} \text{ nm}}{250 \times 10^3 \text{ J mol}^{-1}} = 479 \text{ nm blue light}$$

The blue light absorbed by CdS is subtracted from the white light incident on the surface of the solid. The remaining reflected light is colored, yellow in this case. When the violet light is subtracted from the white light incident on the ZnO surface, the reflected light appears white.

## Feature Problems

- 82. (a)** If  $\Delta n_{\text{gas}} = 0$ , then  $\Delta S^\circ \sim 0$  and  $\Delta G^\circ$  is essentially independent of temperature



If  $\Delta n_{\text{gas}} > 0$ , then  $\Delta S^\circ > 0$  and  $\Delta G^\circ$  will become more negative with increasing temperature, hence the graph has a negative slope ( $2 \text{ C(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{ CO(g)}$ )

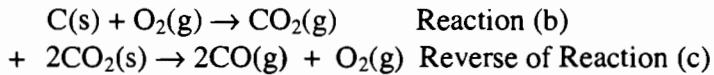
If  $\Delta n_{\text{gas}} < 0$ , then  $\Delta S^\circ < 0$  and  $\Delta G^\circ$  will become more positive with increasing temperature, hence the graph has a positive slope ( $2 \text{ CO(g)} + \text{O}_2(\text{g}) \rightarrow 2 \text{ CO}_2(\text{g})$ )

- (b)** The additional blast furnace reaction,  $\text{C(s)} + \text{CO}_2(\text{g}) \rightarrow 2 \text{ CO(g)}$ , has

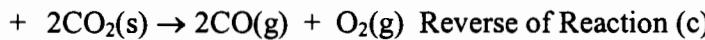
$$\Delta H^\circ = [2 \times -110.5 \text{ kJ}] - [-393.5 \text{ kJ} + 0 \text{ kJ}] = 172.5 \text{ kJ} \quad \text{and}$$

$$\Delta S^\circ = [2 \times 197.7 \text{ J K}^{-1}] - [1 \times 5.74 \text{ J K}^{-1} + 213.7 \text{ J K}^{-1}] = 176.0 \text{ J K}^{-1}$$

It can be obtained by adding reaction (b) to the reverse of reaction (c) (both appear in the provided figure)



*Net: C(s) + CO<sub>2</sub>(g) → 2 CO(g) (Additional Blast Furnace Reaction)*



Consequently, the plot of  $\Delta G^\circ$  for the *net* reaction as a function of temperature will be a straight line with a slope of  $-(\{\Delta S^\circ(\text{Rxn b})\} - \{\Delta S^\circ(\text{Rxn c})\})$  (in  $\text{kJ/K}$ ) and a y-intercept of  $[\{\Delta H^\circ(\text{Rxn b})\} - \{\Delta H^\circ(\text{Rxn c})\}]$  (in  $\text{kJ}$ ).

Since  $\Delta H^\circ(\text{Rxn b}) = -393.5 \text{ kJ}$ ,  $\Delta H^\circ(\text{Rxn c}) = -566 \text{ kJ}$ ,  $\Delta S^\circ(\text{Rxn b}) = 2.9 \text{ J/K}$  and  $\Delta S^\circ(\text{Rxn c}) = -173.1 \text{ J/K}$ , the plot of  $\Delta G^\circ$  vs.  $T$  for the reaction  $\text{C(s) + CO}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g})$  will follow the equation  $y = -0.176x + 172.5$

From the graph, we can see that the difference in  $\Delta G^\circ$  (line b – line c at  $1000^\circ\text{C}$ ) is  $\sim -40 \text{ kJ/mol}$ .  $K_p$  is readily calculated using this value of  $\Delta G^\circ$ .

$$\Delta G^\circ = -RT \ln K_p = -40 \text{ kJ} = -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(1273 \text{ K})(\ln K_p)$$

$$\ln K_p = 3.8 \quad \text{Hence, } K_p = 44$$

The equilibrium partial pressure for  $\text{CO}(\text{g})$  is then determined by using the  $K_p$  expression:

$$K_p = \frac{(P_{\text{CO}})^2}{(P_{\text{CO}_2})} = 44 = \frac{(P_{\text{CO}})^2}{(0.25 \text{ atm})} \quad \text{Hence, } (P_{\text{CO}})^2 = 11 \text{ and } P_{\text{CO}} = 3.3 \text{ atm or 3 atm.}$$

Alternatively, we can determine the partial pressure for  $\text{CO}_2$  at  $1000^\circ\text{C}$  via the calculated  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the reaction  $\text{C(s) + CO}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g})$  to find  $\Delta G^\circ$  at  $1000^\circ\text{C}$ , and ultimately  $K_p$  with the relationship  $\Delta G^\circ = -RT \ln K_p$  (here we are making the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are relatively constant over the temperature range  $298 \text{ K}$  to  $1273 \text{ K}$ ). The calculated values of  $H^\circ$  and  $\Delta S^\circ$  (using Appendix D) are given below:

$$\Delta H^\circ = [2 \times -110.5 \text{ kJ}] - [-393.5 \text{ kJ} + 0 \text{ kJ}] = 172.5 \text{ kJ}$$

$$\Delta S^\circ = [2 \times 197.7 \text{ J K}^{-1}] - [1 \times 5.74 \text{ J K}^{-1} + 213.7 \text{ J K}^{-1}] = 176.0 \text{ J K}^{-1}$$

To find  $\Delta G^\circ$  at  $1000^\circ\text{C}$ , we simply plug  $x = 1273 \text{ K}$  into the straight-line equation we developed above and solve for  $y$  ( $\Delta G^\circ$ ).

$$\text{So, } y = -0.176(1273 \text{ K}) + 172.5 ; y = -51.5 \text{ kJ}$$

Next we need to calculate the  $K_p$  for the reaction at  $1000^\circ\text{C}$ .

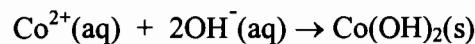
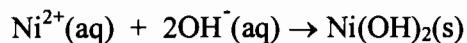
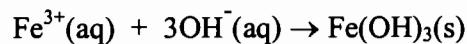
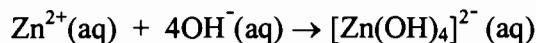
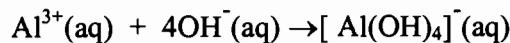
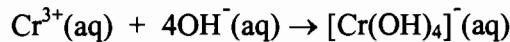
$$\Delta G^\circ = -RT \ln K_p = -51.5 \text{ kJ} = -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(1273 \text{ K})(\ln K_p)$$

$$\ln K_p = 4.87 \quad \text{Hence, } K_p = 1.3 \times 10^2$$

The equilibrium partial pressure for  $\text{CO}(\text{g})$  is then determined by using the  $K_p$  expression:

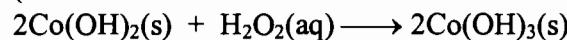
$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})} = 130 = \frac{(P_{CO})^2}{(0.25 \text{ atm})} \text{ Hence, } (P_{CO})^2 = 32.5 \text{ and } P_{CO} = 5.7 \text{ atm}$$

83. (a) The amphoteric cations are  $Al^{3+}$ ,  $Cr^{3+}$  and  $Zn^{2+}$ .

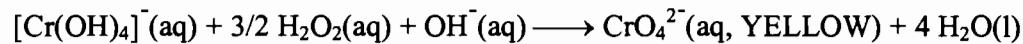


- (b) Of the three hydroxide precipitates, only  $Co^{2+}$  is easily oxidized:

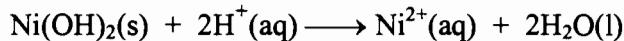
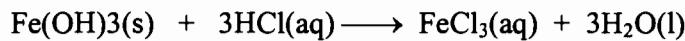
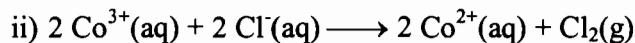
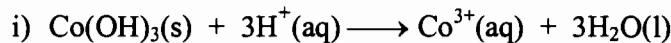
(refer to the Standard Reduction Potential table in Appendix D)



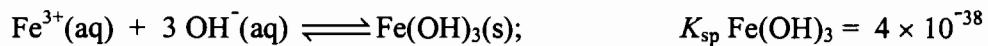
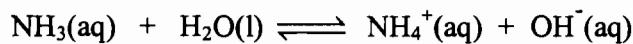
- (c) We know that the chromate ion is yellow. Thus,



- (d)  $Co^{3+}$  is reduced to  $Co^{2+}$  by the  $H_2O_2$  in solution. The other hydroxides simply dissolve in strong acid:



- (e) The  $Fe^{3+}(aq)$  ions in the presence of concentrated ammonia(6 M) form an insoluble precipitate with the hydroxide ions generated by the ammonia hydrolysis reaction:



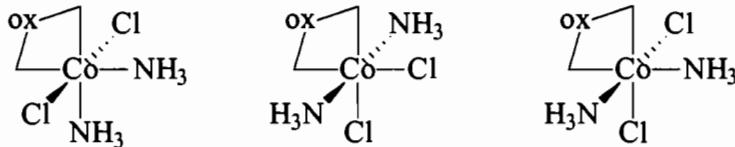
Both  $Co^{3+}$  and  $Ni^{2+}$  form soluble complex ions with ammonia ligands rather than hydroxide precipitates.

# CHAPTER 25

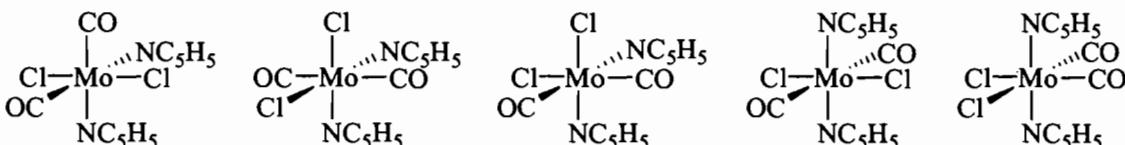
## COMPLEX IONS AND COORDINATION COMPOUNDS

### PRACTICE EXAMPLES

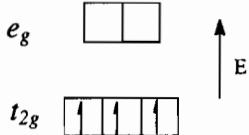
- 1A** There are two different kinds of ligands in this complex ion,  $\Gamma^-$  and  $\text{CN}^-$ . Both are monodentate ligands, that is, they each form only one bond to the central atom. Since there are five ligands in total for the complex ion, the coordination number is 5: C.N.=5. Each  $\text{CN}^-$  ligand has a charge of  $-1$ , as does the  $\Gamma^-$  ligand. Thus, the O.S. must be such that:  $\text{O.S.} + [(4+1) \times (-1)] = -3 = \text{O.S.} - 5$ . Therefore, O.S.=+2.
- 1B** The ligands are  $\text{CN}^-$ .  $\text{Fe}^{3+}$  is the central metal ion. The complex ion is  $[\text{Fe}(\text{CN})_6]^{3-}$ .
- 2A** There are six “ $\text{Cl}^-$ ” ligands (chloride), each with a charge of  $1-$ . Platinum is the metal ion with an oxidation state of  $+4$ . Thus, the complex ion is  $[\text{PtCl}_6]^{2-}$ , and we need two  $\text{K}^+$  to balance charge:  $\text{K}_2[\text{PtCl}_6]$
- 2B** The “ $\text{SCN}^-$ ” ligand is the thiocyanato group, with a charge of  $1-$ , bonding to the central metal ion through the sulfur atom. The “ $\text{NH}_3$ ” ligand is ammonia, a neutral ligand. There are five (penta) ammine ligands bonded to the metal. The oxidation state of cobalt is  $+3$ . The complex ion is not negatively charged, so its name does not end with “ate”. The name of the compound is pentaamminethiocyanato-S-cobalt(III) chloride
- 3A** The oxalato ligand must occupy two *cis*- positions. Either the two  $\text{NH}_3$  or the two  $\text{Cl}^-$  ligands can be coplanar with the oxalate ligand, leaving the other two ligands axial. The other isomer has one  $\text{NH}_3$  and one  $\text{Cl}^-$  ligand coplanar with the oxalate ligand. The structures are sketched below.



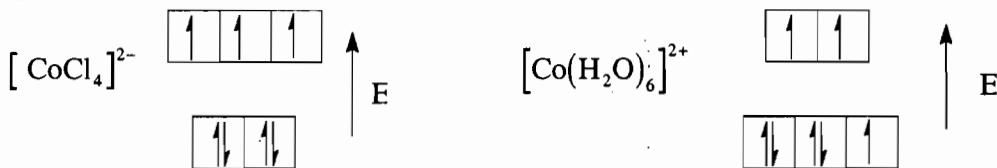
- 3B** We start out with the two pyridines,  $\text{C}_5\text{H}_5\text{N}$ , located *cis* to each other. With that imposed, we can have the two  $\text{Cl}^-$  ligands *trans* and the two CO ligands *cis*, the two CO ligands *trans* and the two  $\text{Cl}^-$  ligands *cis*, or both the  $\text{Cl}^-$  ligands and the two CO ligands *cis*. If we now consider the two pyridines *trans*, we can either have both other pairs *trans*, or both other pairs *cis*. There are five geometric isomers. They follow, in the order described.



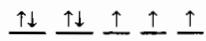
- 4A** The  $\text{F}^-$  ligand is a weak field ligand.  $[\text{MnF}_6]^{2-}$  is an octahedral complex.  $\text{Mn}^{4+}$  has three  $3d$  electrons. The ligand field splitting diagram for  $[\text{MnF}_6]^{2-}$  is sketched below. There are three unpaired electrons.



- 4B**  $\text{Co}^{2+}$  has seven  $3d$  electrons.  $\text{Cl}^-$  is a weak field ligand.  $\text{H}_2\text{O}$  is a moderate field ligand. There are three unpaired electrons in each case. The number of unpaired electrons has no dependence on geometry for either metal ion complex.

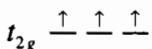


- 5A**  $\text{CN}^-$  is a strong field ligand.  $\text{Co}^{2+}$  has seven  $3d$  electrons. In the absence of a crystal field, all five  $d$  orbitals of the same energy, seven  $d$  electrons will result in three unpaired electrons. Thus, we need an orbital splitting diagram in which there are three orbitals of the same energy at the highest energy. This is the case with a tetrahedral orbital diagram.

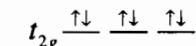
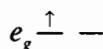


in absence of a

crystal field



Tetrahedral Geometry



Octahedral Geometry

Thus,  $[\text{Co}(\text{CN})_4]^{2-}$  must be tetrahedral (3 unpaired electrons) and not octahedral (1 unpaired electron) because the magnetic property would agree with the experimental observations (3 unpaired electrons).

- 5B**  $\text{NH}_3$  is a strong field ligand.  $\text{Cu}^{2+}$  has nine  $3d$  electrons. There is only one way to arrange nine electrons in five  $d$ -orbitals, that is, to have four fully occupied orbitals (two electrons in each orbital), and one half-filled orbital. Thus, the complex ion must be paramagnetic to the extent of one unpaired electron, regardless of the geometry the ligands adopt around the central metal ion.

- 6A** We are certain that  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is octahedral with a moderate field ligand. Tetrahedral  $[\text{CoCl}_4]^{2-}$  has a weak field ligand. The relative values of ligand field splitting for the same ligand are  $\Delta_t = 0.44 \Delta_o$ . Thus,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  absorbs light of higher energy, blue or green light, leaving a light pink as the complementary color we observe.  $[\text{CoCl}_4]^{2-}$  absorbs lower energy red light, leaving blue light to pass through and be seen.

**6B** In order, the two complex ions are  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ . We know that  $\text{CN}^-$  is a strong field ligand; it should give rise to a large value of  $\Delta_o$  and result in the absorption of light of the shorter wavelength. We would expect the cyano complex to absorb blue or violet light and thus  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$  should appear yellow. The compound  $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ , containing the weak field complex thus should be green, because the weak field would result in the absorption of light of long wavelength, namely, red light.

## REVIEW QUESTIONS

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1. (a) The coordination number of a complex refers to the number of ligand atoms that are attached directly to the central metal ion. If all ligands are monodentate, the coordination number equals the number of ligands attached to the central metal ion.  
(b)  $\Delta$  is the crystal field splitting energy: the energy difference between the lower- and higher-energy  $d$  orbitals in the crystal field splitting diagram.  
(c) An ammine complex is one with ammonia molecule(s) as the ligand(s).  
(d) An enantiomer is one of two optical isomers: molecules of identical formula and bonding which are nonsuperimposable mirror images of each other.
2. (a) The spectrochemical series is a listing of common ligands, ordered in terms of their ability to produce a splitting in the  $d$ -orbitals, ( $\Delta$ ), around a central metal ion.  
(b) Crystal field theory describes bonding in complexes in terms of electrostatic attractions between ligands and the central metal (both of which are assumed to be point charges). Particular attention is focused on the energies of the  $d$ -orbitals on the central metal.  
(c) Optical isomerism refers to two compounds that differ in physical and chemical properties only in the direction in which each rotates the plane of polarized light.  
(d) Structural isomerism refers to differences in the ligands that are bonded to the central atom, and in the ligand atoms that are directly attached to the central atom.
3. (a) The coordination number of a central metal atom is the total number of ligand atoms that are directly bonded to that central metal atom. It also is known as the secondary valence. The oxidation number, or primary valence, is equal to the charge of the isolated central metal ion.  
(b) A monodentate ligand is one that binds to the central metal atom using only one donor atom (lone pair). A monodentate ligand only occupies one position in the coordination sphere. A polydentate ligand is one that binds to the central metal atom using two or more donor atoms and occupies two or more positions in the coordination sphere of the complex.

- (c) In a *cis* isomer, two ligands have a small angular distance between their bonds to the central atom ( $\sim 90^\circ$ ). In a *trans* isomer, two ligands are on opposite sides of the central atom ( $\sim 180^\circ$ ).
- (d) Dextrorotatory and levorotatory isomers differ in the direction in which they rotate the plane of polarized light. A dextrorotatory isomer rotates this plane to the right (clockwise), while a levorotatory isomer rotates it to the left (counterclockwise).
- (e) In a high-spin complex, a weak crystal field splitting results in the *d* orbital electrons of the central atom to arrange themselves so as to maximize the number of unpaired electrons (pairing energy is comparable to crystal field splitting energy). Conversely, in a low-spin complex, a strong ligand field results in the *d* orbital electrons of the central atom to arrange themselves so as to minimize the number of unpaired electrons (pairing energy is small compared to crystal field splitting energy).

4. (a)  $[\text{CrCl}_4(\text{NH}_3)_2]^-$  diamminetetrachlorochromate(III) ion
- (b)  $[\text{Fe}(\text{CN})_6]^{3-}$  hexacyanoferrate(III) ion
- (c)  $[\text{Cr}(\text{en})_3]_2[\text{Ni}(\text{CN})_4]_3$  tris(ethylenediamine)chromium(III) tetracyanonickelate(II) ion
5. (a)  $[\text{Co}(\text{NH}_3)_6]^{2+}$  The coordination number of Co is 6; there are six monodentate  $\text{NH}_3$  ligands attached to Co. Since the  $\text{NH}_3$  ligand is neutral, the oxidation state of cobalt is +2, the same as that of the complex ion; hexaamminecobalt(III) ion
- (b)  $[\text{AlF}_6]^{3-}$  The coordination number of Al is six;  $\text{F}^-$  is monodentate. Each  $\text{F}^-$  has a 1- charge; thus the oxidation state of Al is +3; hexafluoroaluminate(III) ion
- (c)  $[\text{Cu}(\text{CN})_4]^{2-}$  The coordination number of Cu is 4;  $\text{CN}^-$  is monodentate.  $\text{CN}^-$  has a 1- charge; thus the oxidation state of Cu is +2; tetracyanocuprate(II) ion
- (d)  $[\text{CrBr}_2(\text{NH}_3)_4]^+$  The coordination number of Cr is 6;  $\text{NH}_3$  and  $\text{Br}^-$  are monodentate.  $\text{NH}_3$  has no charge;  $\text{Br}^-$  has a 1- charge. The oxidation state of chromium is +3; tetraamminedibromochromium(III) ion
- (e)  $[\text{Co}(\text{ox})_3]^{4-}$  The coordination number of Co is 6; oxalate is bidentate.  $\text{C}_2\text{O}_4^{2-}$  (ox) has a 2- charge; thus the oxidation state of cobalt is +2; trioxalatocobaltate(II) ion.
- (f)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  The coordination number of Ag is 2;  $\text{S}_2\text{O}_3^{2-}$  is monodentate.  $\text{S}_2\text{O}_3^{2-}$  has a 2- charge; thus the oxidation state of silver is +1; dithiosulfatoargentate(I) ion. (Although +1 is by far the most common oxidation state for silver in its compounds, stable silver(III) complexes are known. Thus, strictly speaking, silver is not a non-variable metal, and hence when naming silver compounds, the oxidation state(s) for the silver atom(s) should be specified).

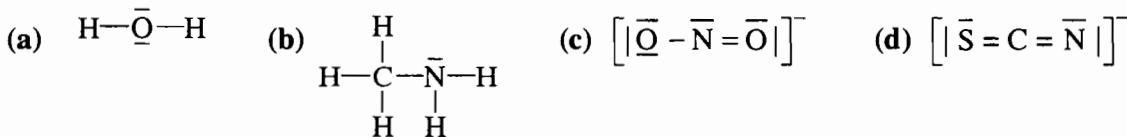
6. (a)  $[\text{AgI}_2]^-$  diidoargentate(I) ion  
 (b)  $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  pentaqua hydroxoaluminum(III) ion  
 (c)  $[\text{Zn}(\text{CN})_4]^{2-}$  tetracyanozincate(II) ion  
 (d)  $[\text{Pt}(\text{en})_2]^{2+}$  bis(ethylenediamine)platinum(II) ion  
 (e)  $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]^+$  tetraamminechloronitrito-*N*-cobaltate(III) ion

7. (a)  $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$  pentaamminebromocobalt(III) sulfate  
 (b)  $[\text{CoSO}_4(\text{NH}_3)_5]\text{Br}$  pentaamminesulfatocobalt(III) bromide  
 (c)  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  hexaamminechromium(III) hexacyanocobaltate(III)  
 (d)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  sodium hexanitrito-*N*-cobaltate(III)  
 (e)  $[\text{Co}(\text{en})_3]\text{Cl}_3$  tris(ethylenediamine)cobalt(III) chloride

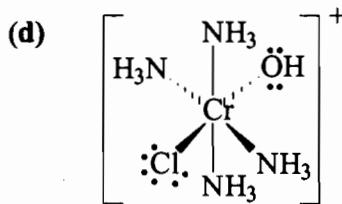
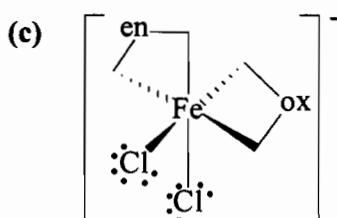
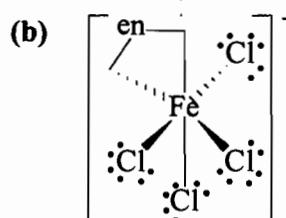
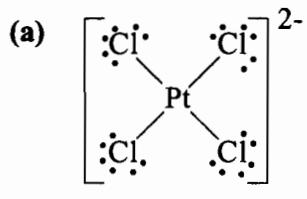
8. (a)  $[\text{Ag}(\text{CN})_2]^-$  dicyanoargentate(I) ion  
 (b)  $[\text{Pt}(\text{NO}_2)(\text{NH}_3)_3]^+$  triamminenitroplatinum(II) ion  
 (c)  $[\text{CoCl}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  aquachlorobis(ethylenediamine)cobalt(III) ion  
 (d)  $\text{K}_4[\text{Cr}(\text{CN})_6]$  potassium hexacyanochromate(II)

9. The Lewis structures are grouped together at the end.

- (a)  $\text{H}_2\text{O}$  has  $2 \times 1 + 6 = 8$  valence electrons, or 4 pairs.  
 (b)  $\text{CH}_3\text{NH}_2$  has  $4 + 3 \times 1 + 5 + 2 \times 1 = 14$  valence electrons, or 7 pairs.  
 (c)  $\text{ONO}^-$  has  $2 \times 6 + 5 + 1 = 18$  valence electrons, or 9 pairs. The structure has a 1 $-$  formal charge on the oxygen that is singly bonded to N.  
 (d)  $\text{SCN}^-$  has  $6 + 4 + 5 + 1 = 16$  valence electrons, or 8 pairs. This structure, appropriately, gives a 1 $-$  formal charge to N.

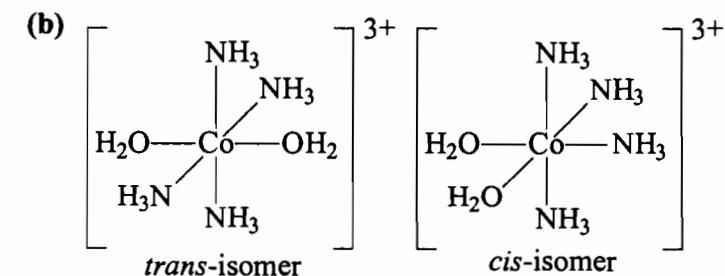
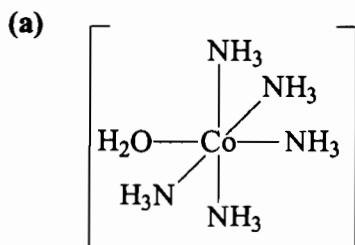


10. (a) manganese(II) sulfate hexahydrate,  $\text{MnSO}_4 \cdot 6 \text{H}_2\text{O}$  or  $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$   
 (b) potassium hexacyanochromate(II) trihydrate,  $\text{K}_4[\text{Cr}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$
11. (a)  $[\text{PtCl}_4]^{2-}$  tetrachloroplatinate(IV) ion  
 (b)  $[\text{FeCl}_4(\text{en})]^-$  tetrachloro(ethylenediamine)ferrate(III) ion  
 (c)  $cis-[\text{FeCl}_2(\text{ox})(\text{en})]^-$  *cis*-dichloro(ethylenediamine)(oxalato)ferrate(III) ion.  
 (d)  $trans-[\text{CrCl}(\text{OH})(\text{NH}_3)_4]^+$  *trans*-tetraamminechlorohydroxochromium(III) ion

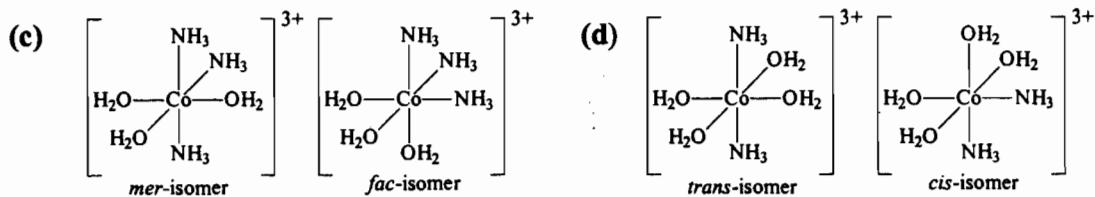


12. We assume that all of these complexes are octahedral in shape.

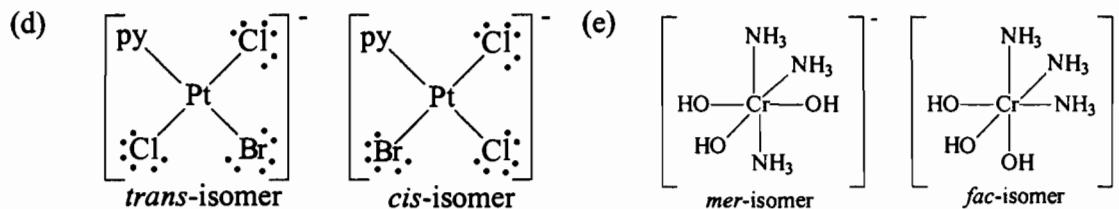
- (a)  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$  has just one isomer.  
 (b)  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{3+}$  has two isomers, a *cis*-isomer (drawn on the left following) and a *trans*-isomer (drawn on the right). The two  $\text{H}_2\text{O}$  ligands are  $90^\circ$  from each other (*cis*-) or  $180^\circ$  from each other (*trans*-).



- (c)  $[\text{Co}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$  has two isomers, a *fac*-isomer (in which the three  $\text{NH}_3$  ligands are  $90^\circ$  to each other, also called the *cis*-isomer) and a *mer*-isomer (in which two of the  $\text{NH}_3$  ligands are  $180^\circ$  from each other, on opposite sides of the central Co atom, also referred to as the *trans*-isomer).
- (d)  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{3+}$  has two isomers, a *cis*-isomer and a *trans*-isomer. In this case it is the two  $\text{NH}_3$  groups that are  $90^\circ$  from each other (*cis*-) or  $180^\circ$  from each other (*trans*-).



13. (a)  $[\text{Zn}(\text{NH}_3)_4][\text{CuCl}_4]$  can display coordination isomerism. Another isomer is  $[\text{Cu}(\text{NH}_3)_4][\text{ZnCl}_4]$ .
- (b)  $[\text{Fe}(\text{CN})_5\text{SCN}]^{4-}$  displays linkage isomerism. The other isomer is  $[\text{Fe}(\text{CN})_5\text{NCS}]^{4-}$
- (c)  $[\text{NiCl}(\text{NH}_3)_5]^+$  does not display isomerism.
- (d)  $[\text{PtBrCl}_2(\text{py})]^-$  displays geometric isomerism, because the complex is square planar.
- (e)  $[\text{Cr}(\text{OH})_3(\text{NH}_3)_3]^-$  displays geometric isomerism. There is a *fac*-isomer and a *mer*-isomer. These could also be labeled *cis*- and *trans*-, respectively.



14. A yellow color indicates that the complex absorbs blue light, while a blue color indicates that the complex absorbs red and yellow light. Blue light has more energy per photon than red and yellow light. The complex with the larger value of  $\Delta$  will absorb the higher energy light. The ethylenediamine ligand produces a larger crystal field splitting energy than does the aqua ligand, according to the spectrochemical series. Thus, the yellow complex is  $[\text{Co}(\text{en})_3]^{3+}$  and the blue complex is  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

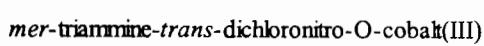
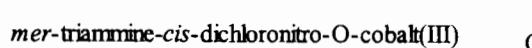
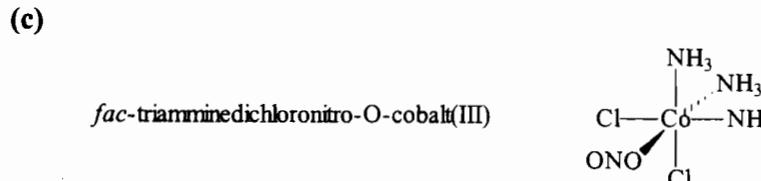
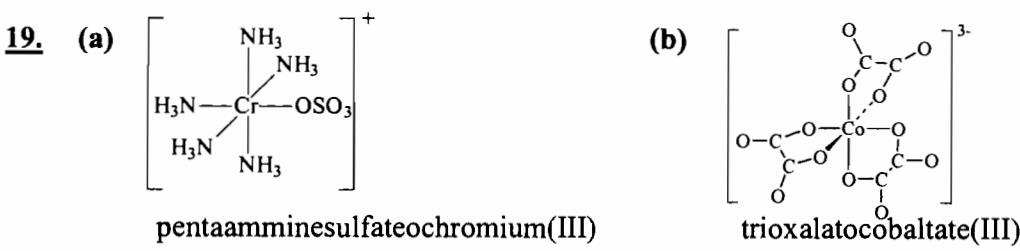
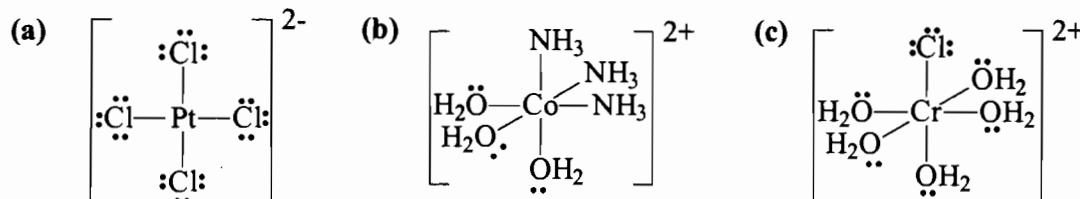
## EXERCISES

### Nomenclature

15. (a)  $[\text{Co}(\text{OH})(\text{H}_2\text{O})_4(\text{NH}_3)]^{2+}$  amminetetraaquahydroxocobalt(III) ion  
 (b)  $[\text{Co}(\text{ONO})_3(\text{NH}_3)_3]$  triamminetrinitrito-*O*-cobalt(III)  
 (c)  $[\text{Pt}(\text{H}_2\text{O})_4][\text{PtCl}_6]$  tetraaquaplatinum(II) hexachloroplatinate(IV)  
 (d)  $[\text{Fe}(\text{ox})_2(\text{H}_2\text{O})_2]^-$  diaquadioxalatoferrate(III) ion  
 (e)  $\text{Ag}_2[\text{HgI}_4]$  silver(I) tetraiodomercurate(II)

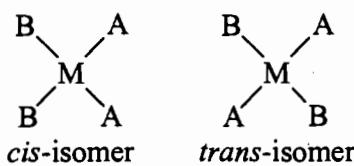
### Bonding and Structure in Complex Ions

17. We assume that  $[\text{PtCl}_4]^{2-}$  is square planar by analogy with  $[\text{PtCl}_2(\text{NH}_3)_2]$  in Figure 25-5. The other two complex ions are octahedral.

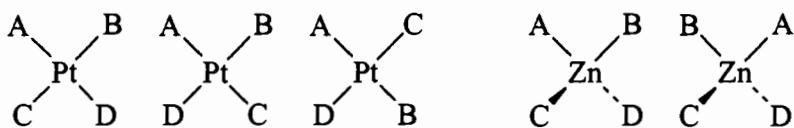


## Isomerism

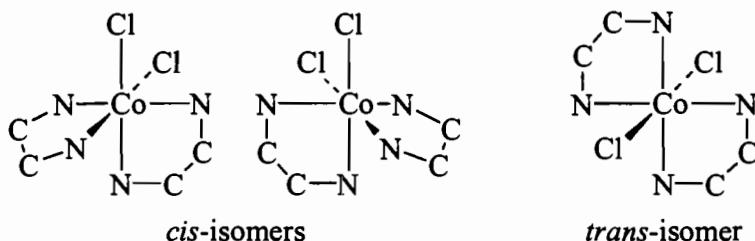
- 21.** (a) *cis-trans* isomerism cannot occur with tetrahedral structures because all of the ligands are separated by the same angular distance from each other. One ligand cannot be on the other side of the central atom from another.
- (b) Square planar structures can show *cis-trans* isomerism. Examples are drawn following, with the *cis*-isomer drawn on the left, and the *trans*-isomer drawn on the right.



- (c) Linear structures do not display *cis-trans* isomerism; there is only one way to bond the two ligands to the central atom.
- 23.** (a) There are three different square planar isomers, with D, C, and B, respectively, trans to the A ligand. They are drawn below.



- (b) Tetrahedral  $[\text{ZnABCD}]^{2+}$  does display optical isomerism. The two optical isomers are drawn above.
- 25.** The *cis*-dichlorobis(ethylenediamine)cobalt(III) ion is optically active. The two optical isomers are drawn below. The *trans*-isomer is not optically active: the ion and its mirror image are superimposable.

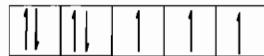


## Crystal Field Theory

- 27.** In crystal field theory, the five *d* orbitals of a central transition metal ion are split into two (or more) groups of different energies. The energy spacing between these groups often corresponds to the energy of a photon of visible light. Thus, the complex ion will absorb light with energy corresponding to this spacing. If white light is incident on the complex

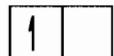
ion, the light remaining after absorption will be missing some of its components. Thus, light of certain wavelengths (corresponding to the energies absorbed) will no longer be present in the formerly white light. The resulting light is colored. For example, if blue light is absorbed from white light, the remaining light will be yellow in color.

29. We begin with the 7 electron *d*-orbital diagram for  $\text{Co}^{2+}$   $[\text{Ar}]$

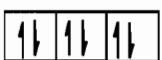


The strong field and weak field diagrams for octahedral complexes follow, along with the number of unpaired electrons in each case.

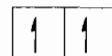
*Strong Field*



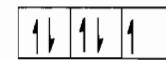
(1 unpaired electron)



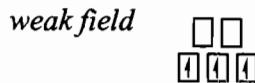
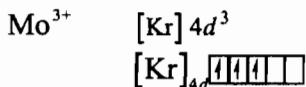
*Weak Field*



(3 unpaired electrons)

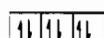


31. (a) Both of the central atoms have the same oxidation state, +3. We give the electron configuration of the central atom to the left, then the completed crystal field diagram in the center, and finally the number of unpaired electrons. The chloro ligand is a weak field ligand in the spectrochemical series.



3 unpaired electrons; paramagnetic

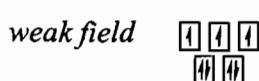
The ethylenediamine ligand is a strong field ligand in the spectrochemical series.



no unpaired electrons; diamagnetic

- (b) In  $[\text{CoCl}_4]^{2-}$  the oxidation state of cobalt is 2+. Chloro is a weak field ligand. The electron configuration of  $\text{Co}^{2+}$  is  $[\text{Ar}] 3d^7$  or  $[\text{Ar}] \boxed{\text{|||||}}$

The tetrahedral ligand field diagram is shown on the right.



3 unpaired electrons

33. The electron configuration of  $\text{Ni}^{2+}$  is  $[\text{Ar}] 3d^8$  or  $[\text{Ar}] \boxed{\text{I}\text{I}\text{I}\text{I}\text{I}\text{I}}$

Ammine is a strong field ligand. The ligand field diagrams follow, octahedral at left, tetrahedral in the center and square planar at right.

Octahedral



Tetrahedral

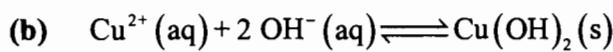
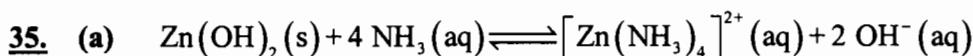


Square Planar

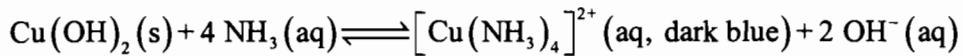


Since the octahedral and tetrahedral configurations have the same number of unpaired electrons (that is, 2 unpaired electrons), we cannot use magnetic properties to determine whether the ammine complex of nickel(II) is octahedral or tetrahedral. But we can determine if the complex is square planar, since the square planar complex is diamagnetic with zero unpaired electrons.

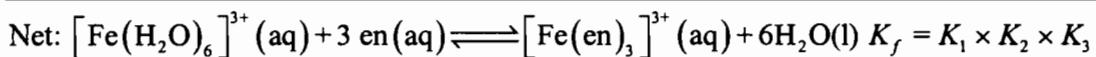
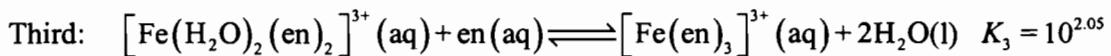
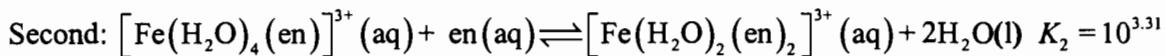
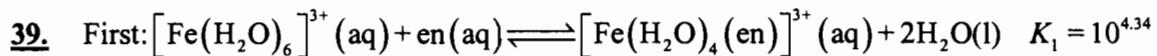
## Complex Ion Equilibria



The blue color is most likely due to some unreacted  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  (aq, pale blue)

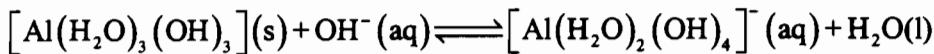


37.  $[\text{Co}(\text{en})_3]^{3+}$  should have the largest overall  $K_f$  value. We expect a complex ion with polydentate ligands to have a larger value for its formation constant than complexes that contain only monodentate ligands. This is an expression of the chelate effect. Once one end of a polydentate ligand becomes attached to the central metal, the attachment of the remaining electron pairs is relatively easy because they already are close to the central metal (and do not have to migrate in from a distant point in the solution).

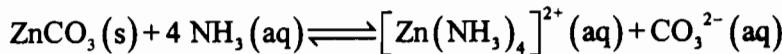


$$\log K_f = 4.34 + 3.31 + 2.05 = 9.70 \quad K_f = 10^{9.70} = 5.0 \times 10^9 = \beta_3$$

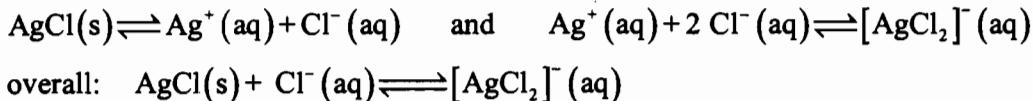
41. (a) Aluminum(III) forms a stable (and soluble) hydroxo complex but not a stable ammine complex.



- (b) Although zinc(II) forms a soluble stable ammine complex ion, its formation constant is not sufficiently large to dissolve highly insoluble ZnS. However, it is sufficiently large to dissolve the moderately insoluble ZnCO<sub>3</sub>. Said another way, ZnS does not produce sufficient [Zn<sup>2+</sup>] to permit the complex ion to form.

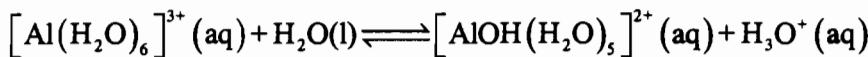


- (c) Chloride ion forms a stable complex ion with silver(I) ion, that dissolves the AgCl(s) that formed when [Cl<sup>-</sup>] is low.



## Acid-Base Properties

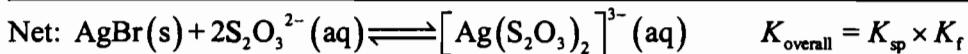
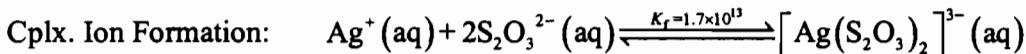
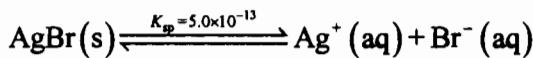
43.  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  is capable of releasing H<sup>+</sup>:



The value of its ionization constant ( $pK_a = 5.01$ ) approximates that of acetic acid.

## Applications

45. (a) Solubility:



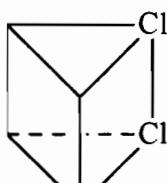
$$K_{\text{overall}} = 5.0 \times 10^{-13} \times 1.7 \times 10^{13} = 8.5$$

With a reasonably high  $[\text{S}_2\text{O}_3^{2-}]$ , this reaction will go essentially to completion.

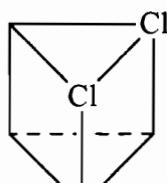
- (b) NH<sub>3</sub>(aq) cannot be used in the fixing of photographic film because of the relatively small value of  $K_f$  for  $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$ ,  $K_f = 1.6 \times 10^7$ . This would produce a value of  $K = 8.0 \times 10^{-6}$  in the expression above, too small to indicate a reaction that goes to completion.

## Feature Problems

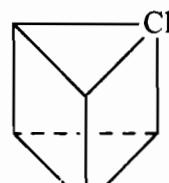
- 71. (a)** A trigonal prismatic structure predicts three geometric isomers for  $[\text{CoCl}_2(\text{NH}_3)_4]^+$ , which is one more than the actual number of geometric isomers found for this complex ion. All three geometric isomers arising from a trigonal prism are shown below.



(i)



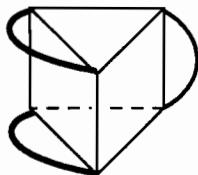
(ii)



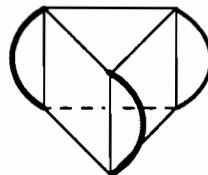
(iii)

The fact that the trigonal prismatic structure does not afford the correct number of isomers is a clear indication that the ion actually adopts some other structural form (i.e., the theoretical model is contradicted by the experimental result). We know now of course, that this ion has an octahedral structure and as a result, it can exist only in *cis* and *trans* configurations.

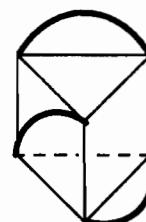
- (b)** All attempts to produce optical isomers of  $[\text{Co}(\text{en})_3]^{3+}$  based upon a trigonal prismatic structure are shown below. The ethylenediamine ligand appears as an arc in each diagram below:



(i)



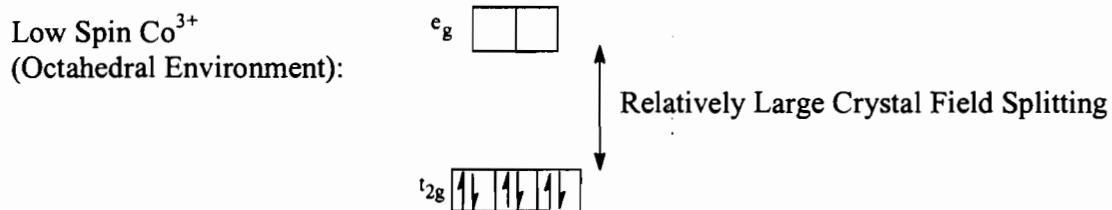
(ii)



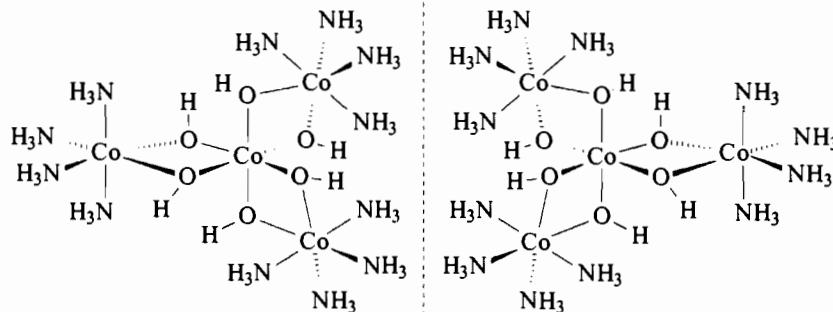
(iii)

Only structure (iii), which has an ethylenediamine ligand connecting the diagonal corners of a face can give rise to optical isomers. Structure (iii) is highly unlikely, however, because the ethylenediamine ligand is simply too short to effectively span the diagonal distance across the face of the prism. Thus, barring any unusual stretching of the ethylenediamine ligand, a trigonal prismatic structure cannot account for the optical isomerism that was observed for  $[\text{Co}(\text{en})_3]^{3+}$ .

72. Assuming that each hydroxide ligand bears its normal 1<sup>-</sup> charge, and that each ammonia ligand is neutral, the total contribution of negative charge from the ligands is 6<sup>-</sup>. Since the net charge on the complex ion is 6<sup>+</sup>, the average oxidation state for each Co atom must be +3 (i.e., each Co in the complex can be viewed as a  $\text{Co}^{3+} 3d^6$  ion surrounded by six ligands.) The five 3d orbitals on each Co are split by the octahedrally arranged ligands into three lower energy orbitals, called  $t_{2g}$  orbitals, and two higher energy orbitals, called  $e_g$  orbitals. We are told in the question that the complex is *low spin*. This is simply another way of saying that all six 3d electrons on each Co are paired up in the  $t_{2g}$  set as a result of the  $e_g$  and  $t_{2g}$  orbitals being separated by a relatively large energy gap (see below). Hence, there should be no unpaired electrons in the hexacation (i.e., the cation is expected to be diamagnetic).



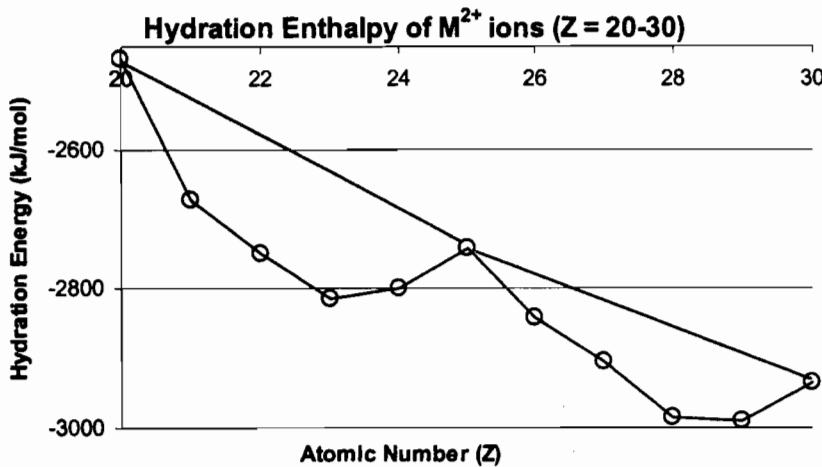
The Lewis structures for the two optical isomers are depicted below:



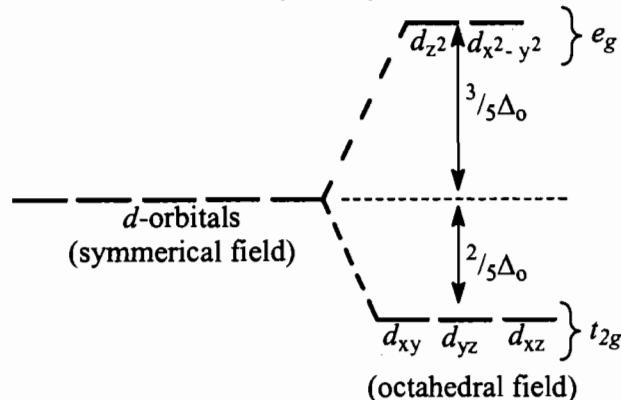
Non-superimposable mirror images of one another

73. The data used to construct a plot of hydration energy as a function of metal ion atomic number is collected in the table below. The graph of hydration energy (kJ/mol) versus metal ion atomic number is located beneath the table.

Metal Ion	Atomic number	Hydration Energy
$\text{Ca}^{2+}$	20	-2468 kJ/mol
$\text{Sc}^{2+}$	21	-2673 kJ/mol
$\text{Ti}^{2+}$	22	-2750 kJ/mol
$\text{V}^{2+}$	23	-2814 kJ/mol
$\text{Cr}^{2+}$	24	-2799 kJ/mol
$\text{Mn}^{2+}$	25	-2743 kJ/mol
$\text{Fe}^{2+}$	26	-2843 kJ/mol
$\text{Co}^{2+}$	27	-2904 kJ/mol
$\text{Ni}^{2+}$	28	-2986 kJ/mol
$\text{Cu}^{2+}$	29	-2989 kJ/mol
$\text{Zn}^{2+}$	30	-2936 kJ/mol



- (b) When a metal ion is placed in an octahedral field of ligands, the five  $d$ -orbitals are split into  $e_g$  and  $t_{2g}$  subsets, as shown in the diagram below:



Since water is a weak field ligand, the magnitude of the splitting is relatively small. As a consequence, high-spin configurations result for all of the hexaaqua complexes. The electron configurations for the metal ions in the high-spin hexaaqua complexes and their associated crystal field stabilization energies (CFSE) are provided below.

Metal Ion	Configuration	$t_{2g}$	$e_g$	# of unpaired $e^-$	CFSE( $\Delta_o$ )
$\text{Ca}^{2+}$	$3d^0$	0	0	0	0
$\text{Sc}^{2+}$	$3d^1$	1	0	1	$-\frac{2}{5}$
$\text{Ti}^{2+}$	$3d^2$	2	0	2	$-\frac{4}{5}$
$\text{V}^{2+}$	$3d^3$	3	0	3	$-\frac{6}{5}$
$\text{Cr}^{2+}$	$3d^4$	3	1	4	$-\frac{3}{5}$
$\text{Mn}^{2+}$	$3d^5$	3	2	5	0
$\text{Fe}^{2+}$	$3d^6$	4	2	4	$-\frac{2}{5}$
$\text{Co}^{2+}$	$3d^7$	5	2	3	$-\frac{4}{5}$
$\text{Ni}^{2+}$	$3d^8$	6	2	2	$-\frac{6}{5}$
$\text{Cu}^{2+}$	$3d^9$	6	3	1	$-\frac{3}{5}$
$\text{Zn}^{2+}$	$3d^{10}$	6	4	0	0

Thus, the crystal field stabilization energy is zero for  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ .

- (c) The lines drawn between those ions that have a CFSE = 0 show the trend for the enthalpy of hydration after the contribution from the crystal field stabilization energy has been subtracted from the experimental values. The Ca to Mn and Mn to Zn lines both have a negative slope. This trend shows that as one proceeds from left to right across the periodic table, the energy of hydration for dication becomes increasingly more negative. The hexaaqua complexes become progressively more stable because the  $Z_{\text{eff}}$  experienced by the bonding electrons in the valence shell of the metal ion steadily increases as we move further and further to the right. Put another way, the  $Z_{\text{eff}}$  climbs steadily as we move from left to right and this leads to the positive charge density on the metal becoming larger and larger, which results in the water ligands steadily being pulled closer and closer to the nucleus. Of course, the closer the approach of the water ligands to the metal, the greater is the energy released upon successful coordination of the ligand.
- (d) Those ions that exhibit crystal field stabilization energies greater than zero have heats of hydration that are more negative (i.e. more energy released) than the hypothetical heat of hydration for the ion with CFSE subtracted out. The heat of hydration without CFSE for a given ion falls on the line drawn between the two flanking ions with CFSE = 0 at a position directly above the point for the experimental hydration energy. The energy difference between the observed heat of hydration for the ion and the heat of hydration without CFSE is, of course, approximately equal to the CFSE for the ion.
- (e) As was mentioned in the answer to part (c), the straight line drawn between manganese and zinc (both ions with CFSE = 0) on the previous plot, describes the enthalpy trend after the ligand field stabilization energy has been subtracted from the experimental values for the hydration enthalpy. Thus,  $\Delta_o$  for  $\text{Fe}^{2+}$  in  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is approximately equal to  $5/2$  of the energy difference (in kJ/mol) between the observed hydration energy for  $\text{Fe}^{2+}(\text{g})$  and the point for  $\text{Fe}^{2+}$  on the line connecting  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ , which is the expected enthalpy of hydration after the CFSE has been subtracted out. Remember that the crystal field stabilization energy for  $\text{Fe}^{2+}$  that is obtained from the graph is not  $\Delta_o$ , but rather  $2/5\Delta_o$ , since the CFSE for a  $3d^6$  ion in an octahedral field is just  $2/5$  of  $\Delta_o$ . Consequently, to obtain  $\Delta_o$ , we must multiply the enthalpy difference by  $5/2$ . According to the graph, the high-spin CFSE for  $\text{Fe}^{2+}$  is  $-2843 \text{ kJ/mol} - (-2782 \text{ kJ/mol})$  or  $-61 \text{ kJ/mol}$ . Consequently,  $\Delta_o = 5/2(-61 \text{ kJ/mol}) = -153 \text{ kJ/mol}$ , or  $1.5 \times 10^2 \text{ kJ/mol}$  is the energy difference between the  $e_g$  and  $t_{2g}$  orbital sets.
- (f) The color of an octahedral complex is caused by the promotion of an electron on the metal from a  $t_{2g}$  orbital  $\rightarrow e_g$  orbital. The energy difference between the  $e_g$  and  $t_{2g}$  orbital sets is  $\Delta_o$ . As the metal-ligand bonding becomes stronger, the separation between the  $t_{2g}$  and  $e_g$  orbitals becomes larger. If the  $e_g$  set is not full, then the metal complex will exhibit an absorption band corresponding to a  $t_{2g} \rightarrow e_g$  transition. Thus, the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  complex ion should absorb electromagnetic radiation that has  $E_{\text{photon}} = \Delta_o$ . Since  $\Delta_o \approx 150 \text{ kJ/mol}$  (calculated in part (e) of this question) for a mole of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ,

$$E_{\text{photon}} = \frac{1.5 \times 10^2 \text{ kJ}}{1 \text{ mol} [\text{Fe}(\text{H}_2\text{O})_6]^{2+}} \times \frac{1 \text{ mol} [\text{Fe}(\text{H}_2\text{O})_6]^{2+}}{6.022 \times 10^{23} [\text{Fe}(\text{H}_2\text{O})_6]^{2+}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$
$$= 2.5 \times 10^{-19} \text{ J per ion}$$
$$\nu = \frac{E}{h} = \frac{2.5 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 3.8 \times 10^{14} \text{ s}^{-1}$$
$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{3.8 \times 10^{14} \text{ s}^{-1}} = 7.8 \times 10^{-7} \text{ m (780 nm)}$$

So, the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion will absorb radiation with a wavelength of 780 nm, which is red light in the visible part of the electromagnetic spectrum.

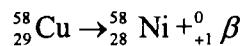
# CHAPTER 26

## NUCLEAR CHEMISTRY

### PRACTICE EXAMPLES

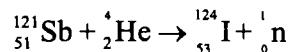
- 1A** A  $\beta^-$  has a mass number of zero and an “atomic number” of  $-1$ . Emission of this electron has the effect of transforming a neutron into a proton.  $^{241}_{94}\text{Pu} \rightarrow ^{241}_{95}\text{Am} + ^0_{-1}\beta$

- 1B**  $^{58}\text{Ni}$  has a mass number of 58 and an atomic number of 28. A positron has a mass number of 0 and an effective atomic number of  $+1$ . Emission of a positron has the seeming effect of transforming a proton into a neutron. The parent nuclide must be copper-58.

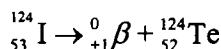


- 2A** The sum of the mass numbers ( $139 + 12 = ? + 147$ ) tells us that the other product species has  $A = 4$ . The atomic number of La is 57, that of C is 6, and that of Eu is 63. The atomic number sum ( $57 + 6 = ? + 63$ ) indicates that the atomic number of this product species is zero. Therefore, four neutrons must have been emitted.  $^{139}_{57}\text{La} + ^{12}_6\text{C} \rightarrow ^{147}_{63}\text{Eu} + ^4_1n$

- 2B** An alpha particle is  $^4_2\text{He}$  and a positron is  $^0_{+1}\beta$ . We note that the total mass number in the first equation is 125; the mass number of the additional product is 1. The total atomic number is 53; the atomic number of the additional product is 0; it is a neutron.



In the second equation, the positron has a mass number of 0, meaning that the mass number of the product is 124. Because the atomic number of the positron is  $+1$ , that of the product is 52; it is  $^{124}_{52}\text{Te}$ .



- 3A (a)** The decay constant is found from the 8.040-day half-life.

$$\lambda = \frac{0.693}{8.040 \text{ d}} = 0.0862 \text{ d}^{-1} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 9.98 \times 10^{-7} \text{ s}^{-1}$$

- (b)** The number of  $^{131}\text{I}$  atoms is used to find the activity.

$$\begin{aligned} \text{no.}^{131}\text{I atoms} &= 2.05 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol}^{131}\text{I}}{131 \text{ g}^{131}\text{I}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}^{131}\text{I}} \\ &= 9.42 \times 10^{18} \text{ atoms}^{131}\text{I} \end{aligned}$$

$$\text{Activity} = \lambda N = 9.98 \times 10^{-7} \text{ s}^{-1} \times 9.42 \times 10^{18} \text{ atoms} = 9.40 \times 10^{12} \text{ disintegrations/second}$$

- (c) We now determine the number of atoms remaining after 16 days. Because two half-lives elapse in 16 days, the number of atoms has halved twice, to one-fourth (25%) the original number of atoms.

$$N_t = 0.25 \times N_0 = 0.25 \times 9.42 \times 10^{18} \text{ atoms} = 2.36 \times 10^{18} \text{ atoms}$$

- (d) The rate after 14 days is determined by the number of atoms present.

$$\text{rate} = \lambda N_t = 9.98 \times 10^{-7} \text{ s}^{-1} \times 2.36 \times 10^{18} \text{ atoms} = 2.36 \times 10^{12} \text{ dis/s}$$

**3B** First we determine the value of  $\lambda$ :  $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{11.4 \text{ d}} = 0.0608 \text{ d}^{-1}$

Then we allow  $N_t = 1\% N_0 = 0.010 N_0$  in equation (26.12).

$$\ln \frac{N_t}{N_0} = -\lambda t = \ln \frac{0.010 N_0}{N_0} = \ln (0.010) = -4.61 = - (0.0608 \text{ d}^{-1}) t$$

$$t = \frac{-4.61}{-0.0608 \text{ d}^{-1}} = 75.8 \text{ d}$$

- 4A** The half-life of  $^{14}\text{C}$  is 5730 y and  $\lambda = 1.21 \times 10^{-4} \text{ y}^{-1}$ . The activity of  $^{14}\text{C}$  when the object supposedly stopped growing was 15 dis/min per g C. We use equation (26.12) with activities ( $\lambda N$ ) in place of numbers of atoms (N).

$$\ln \frac{A_t}{A_0} = -\lambda t = \ln \frac{8.5 \text{ dis/min}}{15 \text{ dis/min}} = - (1.21 \times 10^{-4} \text{ y}^{-1}) t = -0.568; t = \frac{0.57}{1.21 \times 10^{-4} \text{ y}^{-1}} = 4.7 \times 10^3 \text{ y}$$

- 4B** The half-life of  $^{14}\text{C}$  is 5730 y and  $\lambda = 1.21 \times 10^{-4} \text{ y}^{-1}$ . The activity of  $^{14}\text{C}$  when the object supposedly stopped growing was 15 dis/min per g C. We use equation (26.12) with activities ( $\lambda N$ ) in place of numbers of atoms (N).

$$\ln \frac{A_t}{A_0} = -\lambda t = \ln \frac{A_t}{15 \text{ dis/min}} = - (1.21 \times 10^{-4} \text{ y}^{-1}) (1100 \text{ y}) = -0.13$$

$$\frac{A_t}{15 \text{ dis/min}} = e^{-0.13} = 0.88, A_t = 0.88 \times 15 \text{ dis/min} = 13 \text{ dis/min (per gram of C)}$$

**5A** Mass defect. =  $145.913053 \text{ u} (^{146}\text{Sm}) - 141.907719 \text{ u} (^{142}\text{Nd}) - 4.002603 \text{ u} ({}^4\text{He}) = 0.002731 \text{ u}$

Then, from the text, we have  $931.5 \text{ MeV} = 1 \text{ u} E = 0.002731 \text{ u} \times \frac{931.5 \text{ MeV}}{1 \text{ u}} = 2.544 \text{ MeV}$

- 5B** Unfortunately, we cannot use the result of Example 26-5 ( $0.0045 \text{ u} = 4.2 \text{ MeV}$ ) because it is expressed to only two significant figures, and we begin with four significant figures. But, we essentially work backwards through that calculation. The last conversion factor is from Table 2-1.

$$E = 5.590 \text{ MeV} \times \frac{1.602 \times 10^{-13} \text{ J}}{1 \text{ MeV}} = 8.955 \times 10^{-13} \text{ J} = mc^2 = m(2.9979 \times 10^8 \text{ m/s})^2$$

$$m = \frac{8.955 \times 10^{-13} \text{ J}}{(2.9979 \times 10^8 \text{ m/s})^2} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1.0073 \text{ u}}{1.673 \times 10^{-24} \text{ g}} = 0.005999 \text{ u}$$

$$\text{Or we could use } m = 5.590 \text{ MeV} \times \frac{1 \text{ u}}{931.5 \text{ MeV}} = 0.006001 \text{ u}$$

- 6A** (a)  $^{88}\text{Sr}$  has an even atomic number (38) and an even neutron number (50); its mass number (88) is not too far from the average mass (87.6) of Sr. It should be stable.  
 (b)  $^{118}\text{Cs}$  has an odd atomic number (55) and a mass number (118) that is pretty far from the average mass of Cs (132.9). It should be radioactive.  
 (c)  $^{30}\text{S}$  has an even atomic number (16) and an even neutron number (14); but its mass number (30) is too far from the average mass of S (32.1). It should be radioactive.

- 6B** We know that  $^{19}\text{F}$  is stable, with approximately the same number of neutrons and protons: 9 protons, and 10 neutrons. Thus, nuclides of light elements with approximately the same number of neutrons and protons will be stable. In Practice Example 26-1 we saw that positron emission has the effect of transforming a proton into a neutron.  $\beta^-$  emission has the opposite effect: transforming a neutron into a proton. The mass number does not change in either case. Now let us analyze our two nuclides.

$^{17}\text{F}$  has 9 protons and 8 neutrons. Replacing a proton with a neutron would produce a more stable nuclide. Thus, we predict positron emission by  $^{17}\text{F}$  to produce  $^{17}\text{O}$ .

$^{22}\text{F}$  has 9 protons and 13 neutrons. Replacing a neutron with a proton would produce a more stable nuclide. Thus, we predict  $\beta^-$  emission by  $^{22}\text{F}$  to produce  $^{22}\text{Ne}$ .

## REVIEW QUESTIONS

- 1** (a)  $\alpha$  refers to an alpha particle, a helium-4 nucleus:  ${}_2^4\text{He}^{2+}$ .  
 (b)  $\beta^-$  refers to a beta particle, that is, an electron.  
 (c)  $\beta^+$  refers to a positron, identical in all respects to an electron but with opposite (positive) charge.  
 (d)  $\gamma$  refers to gamma radiation, electromagnetic radiation with energy measured in MeV per photon. In contrast, visible light has energies measured in eV per photon.  
 (e)  $t_{1/2}$  indicates half-life, the time needed for half of a sample to decay radioactively.

2. (a) A radioactive decay series is the series of successive products resulting from one nuclide, which decays to a second nuclide, which in turn decays to yet a third, and so forth, until a stable nuclide is produced.
- (b) A charged-particle accelerator is a device that produces particles of very high speeds. It imparts energy and thus speed to these particles by using the influence of either an electric field or a magnetic field on the charge of the particle.
- (c) The neutron-to-proton ratio is the quotient of the number of neutrons divided by the number of protons. It is a general indication of the stability of a nuclide (when combined with atomic number). Certainly, for light elements (up to about  $Z = 20$ ), a neutron-to-proton ratio of 1-to-1 is that of a stable nuclide.
- (d) The mass-energy relationship was first promulgated by Einstein:  $E = mc^2$ .
- (e) Background radiation is that radiation consistently present on earth from natural sources: cosmic rays, radioactive elements in the soil and the air, etc.
3. (a) Both electrons and positrons have the same mass, about 0.00055 u. However, the electron is negatively charged, while the positron has the same magnitude of charge but a positive one.
- (b) The half-life,  $t_{1/2}$ , of a radioactive nuclide is the time necessary for half of a sample to decay. The decay constant is the rate constant for that first-order decay process:  $\lambda = 0.693 / t_{1/2}$ .
- (c) The mass defect is the difference between the mass sum of the protons, neutrons, and electrons that constitute a nuclide and the nuclidic mass. The binding energy is that defect expressed as an energy.
- (d) Nuclear fission refers to the process in which the nucleus of an atom is split into smaller fragments, usually with the release of energy. Nuclear fusion refers to the process in which two lighter nuclei are combined to give a heavier nucleus.
- (e) Primary ionization refers to those ions created by collision of the radiation with the atoms of the sample. However, when these atoms ionize, they give off electrons, which often are energetic enough to produce further ionization, called secondary ionization, in the sample.
4. (a)  $\gamma$  rays penetrate through matter the greatest distance, largely because they are uncharged and thus do not interact with matter extensively.
- (b)  $\alpha$  particles have the greatest ionizing power, principally because they have the largest charge and mass.
- (c)  $\beta$  particles are deflected the most in a magnetic field, because of their small mass and relatively large charge, that is, because they have the largest charge-to-mass ratio.

5. (a)  $^{160}_{74}\text{W} \rightarrow ^{156}_{72}\text{Hf} + ^4_2\text{He}$  (b)  $^{38}_{17}\text{Cl} \rightarrow ^{38}_{18}\text{Ar} + ^0_{-1}\beta$   
 (c)  $^{214}_{83}\text{Bi} \rightarrow ^{214}_{84}\text{Po} + ^0_{-1}\beta$  (d)  $^{32}_{17}\text{Cl} \rightarrow ^{32}_{16}\text{S} + ^0_{+1}\beta$
6. (a)  $^{23}_{11}\text{Na} + ^2_1\text{H} \rightarrow ^{24}_{11}\text{Na} + ^1_1\text{H}$  (b)  $^{59}_{27}\text{Co} + ^1_0\text{n} \rightarrow ^{56}_{25}\text{Mn} + ^4_2\text{He}$   
 (c)  $^{238}_{92}\text{U} + ^2_1\text{H} \rightarrow ^{240}_{94}\text{Pu} + ^0_{-1}\beta$  (d)  $^{246}_{96}\text{Cm} + ^{13}_6\text{C} \rightarrow ^{254}_{102}\text{No} + 5 ^1_0\text{n}$   
 (e)  $^{238}_{92}\text{U} + ^{14}_7\text{N} \rightarrow ^{246}_{99}\text{Es} + 6 ^1_0\text{n}$
7. (a)  $^{214}_{88}\text{Ra} \rightarrow ^{210}_{86}\text{Rn} + ^4_2\text{He}$  (b)  $^{205}_{85}\text{At} \rightarrow ^{205}_{84}\text{Po} + ^0_{+1}\beta^+$   
 (c)  $^{212}_{87}\text{Fr} + ^0_{-1}\text{e} \rightarrow ^{212}_{86}\text{Rn}$  (d)  $^2_1\text{H} + ^2_1\text{H} \rightarrow ^3_2\text{He} + ^1_0\text{n}$   
 (e)  $^{241}_{95}\text{Am} + ^4_2\text{He} \rightarrow ^{243}_{97}\text{Bk} + 2 ^1_0\text{n}$
8. (a) Since the decay constant is inversely related to the half-life, the nuclide with the smallest half-life also has the largest value of its decay constant. This is the nuclide  $^{214}_{84}\text{Po}$  with a half-life of  $1.64 \times 10^{-4}$  s.  
 (b) The nuclide that displays a 75% reduction in its radioactivity has passed through two half-lives in a period of one month. Thus, this is the nuclide with a half-life of approximately two weeks. This is the nuclide  $^{32}_{15}\text{P}$ , with a half-life of 14.3 days.  
 (c) If more than 99% of the radioactivity is lost, less than 1% remains. Thus  $(\frac{1}{2})^n < 0.010$ . Now, when  $n = 7$ ,  $(\frac{1}{2})^7 = 0.0078$ . Thus, seven half-lives have elapsed in one month, and each half-life approximates 4.3 days. The longest lived nuclide that fits this description is  $^{222}_{86}\text{Rn}$ , which has a half-life of 3.823 days. Of course, all other nuclides with shorter half-lives also meet this criterion, specifically the following nuclides:  $^{13}_8\text{O}(8.7 \times 10^{-3}$  s),  $^{28}_{12}\text{Mg}(21$  h),  $^{80}_{35}\text{Br}(17.6$  min), and  $^{214}_{84}\text{Po}(1.64 \times 10^{-4}$  s).
9. Since  $16 = 2^4$ , four half-lives have elapsed in 18.0 h, and each half-life equals 4.50 h. The half-life of isotope B thus is  $2.5 \times 4.50$  h = 11.25 h. Now, since  $32 = 2^5$ , five half-lives must elapse before the decay rate of isotope B falls to  $\frac{1}{32}$  of its original value. Thus, the time elapsed for this amount of decay is:

$$\text{time elapsed} = 5 \text{ half lives} \times \frac{11.25}{1 \text{ half life}} = 56.3 \text{ h}$$

- 10.** We use expression (26.12), substituting the disintegration rate for the number of atoms, since we recognize that in this first-order reaction the rate is directly proportional to the amount of reactant, that is, the number of atoms. (All radioactive decay processes follow first-order kinetics.) We also use equation (26.13), rearranged to  $\lambda = \frac{0.693}{t_{1/2}}$ . Thus

$$\ln \frac{N_t}{N_0} = -\frac{0.693 t}{t_{1/2}}.$$

$$(a) \quad \ln \frac{253 \text{ dis/min}}{1.00 \times 10^3 \text{ dis/min}} = -\frac{0.693 t}{87.9 \text{ d}} = -1.374; \quad t = \frac{1.374 \times 87.9 \text{ d}}{0.693} = 174 \text{ d}$$

$$(b) \quad \ln \frac{104 \text{ dis/min}}{1.00 \times 10^3 \text{ dis/min}} = -\frac{0.693 t}{87.9 \text{ d}} = -2.263; \quad t = \frac{2.263 \times 87.9 \text{ d}}{0.693} = 287 \text{ d}$$

$$(c) \quad \ln \frac{52 \text{ dis/min}}{1.00 \times 10^3 \text{ dis/min}} = -\frac{0.693 t}{87.9 \text{ d}} = -2.96; \quad t = \frac{2.96 \times 87.9 \text{ d}}{0.693} = 375 \text{ d}$$

- 11.** The principal equation that we shall employ is  $E = mc^2$ , along with conversion factors.

$$(a) \quad E = 6.02 \times 10^{-23} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times (3.00 \times 10^8 \text{ m/s})^2 = 5.42 \times 10^{-9} \text{ kg m}^2 \text{ s}^{-2} = 5.42 \times 10^{-9} \text{ J}$$

$$(b) \quad E = 4.0015 \text{ u} \times \frac{931.5 \text{ MeV}}{1 \text{ u}} = 3727 \text{ MeV}$$

$$\begin{aligned} \underline{12.} \quad \text{Mass of individual particles} &= \left( 47 \text{ p} \times \frac{1.0073 \text{ u}}{1 \text{ p}} \right) \times \left( 60 \text{ n} \times \frac{1.0087 \text{ u}}{1 \text{ n}} \right) \\ &= 47.3431 \text{ u} + 60.5220 \text{ u} = 107.8651 \text{ u} \end{aligned}$$

$$\text{Binding energy} = \frac{107.8651 \text{ u} - 106.879289 \text{ u}}{107 \text{ nucleons}} \times \frac{931.5 \text{ MeV}}{1 \text{ u}} = 8.58 \text{ MeV/nucleon}$$

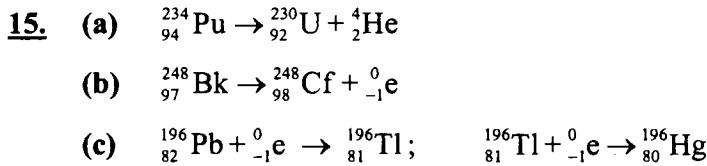
- 13. (c)**  $^{80}\text{Br}$  does not occur naturally; it has an odd number of protons (35) and an odd number of neutrons (45).  
**(d)**  $^{132}\text{Cs}$  also does not occur naturally, for the same reason.

- 14. (a)** A radioisotope with a long half-life gives off few disintegrations per second, and thus is not exceedingly hazardous unless a large quantity of it is present. Radioisotopes with short half-lives, however, give off large quantities of radiation in a short time, but they also "burn themselves out" quickly and thus are hazardous for only a short time. On the other hand, radioisotopes with an intermediate half-life are both giving off reasonably large quantities of radiation and are in existence for relatively long times.

- (b) The radioisotopes that are hazardous from a distance are those that give off  $\gamma$  or high energy  $\beta$  radiation, radiation with a large or moderate penetrating power. On the other hand,  $\alpha$  particles are not hazardous at long distances because of their short penetrating power, but they are highly ionizing, and thus do significant damage when they are encountered at short distances.
- (c) Potassium-40 is a radioisotope that decays by electron capture to argon-40. This accounts for a large majority of the argon in the atmosphere. Helium-4 is also produced by radioactive decay, but it is so light that it escapes from the atmosphere at a much faster rate than does argon-40.
- (d) Francium is produced by radioactive decay. It is quite short-lived and thus there is not much present on the Earth at any one time.
- (e) Fusion involves joining positively charged nuclei together. Such a process requires quite energetic nuclei. This, in turn, means that the nuclei must be at very high temperatures.

## EXERCISES

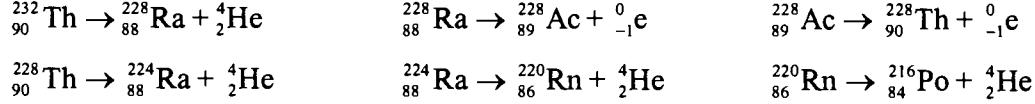
### Radioactive Processes



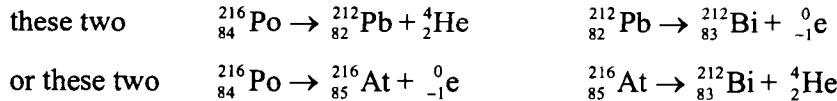
17. We would expect a neutron:proton ratio that is closer to 1:1 than that of  $^{14}\text{C}$ . This would be achieved if the product were  $^{14}\text{N}$ , which will be the result of  $\beta^-$  decay:  
 $^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^0_{-1}\text{e}$ .

### Radioactive Decay Series

19. We first write conventional nuclear reactions for each step in the decay series.

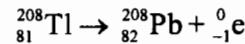
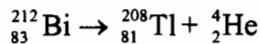


Now for a branch in the series

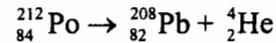
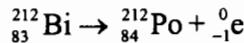


And now a second branch

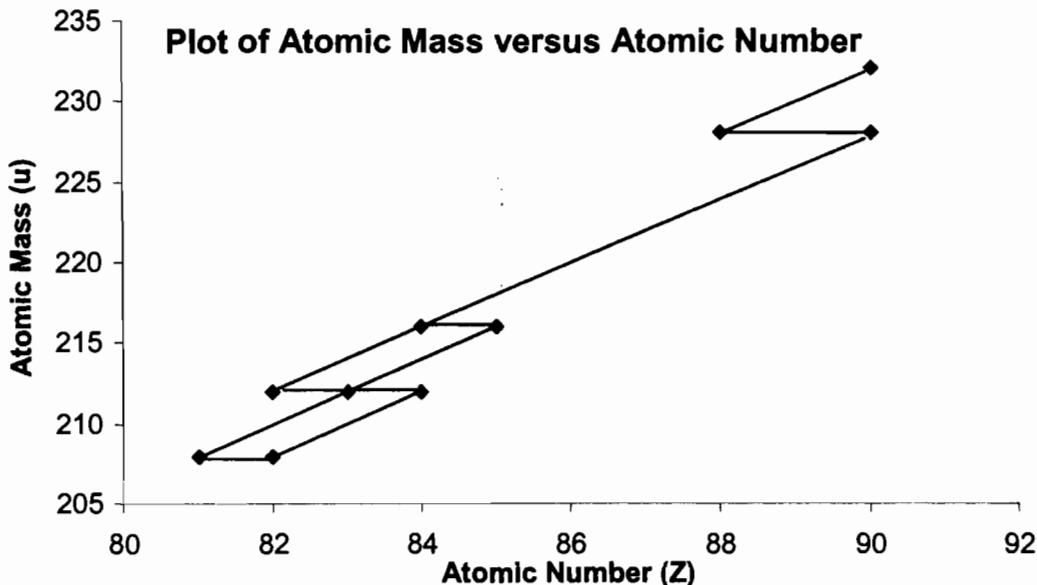
these two



or these two

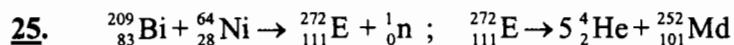
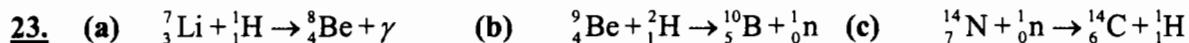


Both branches end with the isotope  $^{208}_{82}\text{Pb}$ . The graph, similar to Figure 26-2, is drawn below.



21. In Figure 26-2, only the following mass numbers are represented: 206, 210, 214, 218, 222, 226, 230, 234, and 238. We see that these mass numbers are separated from each other by 4 units. The first of them, 206, equals  $(4 \times 51) + 2$ , that is  $4n + 2$ , where  $n = 51$ .

## Nuclear Reactions



## Rate of Radioactive Decay

27. We use expression (26.13) to determine  $\lambda$  and then expression (26.11) to determine the number of atoms.

$$\lambda = \frac{0.693}{5.2 \text{ y}} \times \frac{1 \text{ y}}{365.25 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ h}} = 1.5 \times 10^{-5} \text{ h}^{-1}$$

$$N = \frac{\text{rate of decay}}{\lambda} = \frac{6740 \text{ atoms/h}}{1.5 \times 10^{-5} \text{ h}^{-1}} = 4.4 \times 10^8 \text{ }^{60}_{27}\text{Co atoms}$$

29. Let us use the first and the last values to determine the decay constant.

$$\ln \frac{R_t}{R_0} = -\lambda t = \ln \frac{138 \text{ cpm}}{1000 \text{ cpm}} = -\lambda 250 \text{ h} = -1.981 \quad \lambda = \frac{1.981}{250 \text{ h}} = 0.00792 \text{ h}^{-1}$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.00792 \text{ h}^{-1}} = 87.5 \text{ h}$$

A slightly different value of  $t_{1/2}$  may result from other combinations of  $R_0$  and  $R_t$ .

31.  $^{32}_{15}\text{P}$  half-life = 14.3 d. We need to determine the time necessary to get to the detectable

$$\text{limit, } \frac{1}{1000} \text{ of the initial value. Use } \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3 \text{ d}} = 0.0485 \text{ d}^{-1}$$

$$\ln \left( \frac{1}{1000} \right) = -0.0485 \text{ d}^{-1}(t) \quad t = 142 \text{ days}$$

## Radiocarbon Dating

33. Again we use expression (26.12) and (26.13) to determine the time elapsed. The initial rate of decay is about 15 dis/min. First we compute the decay constant.

$$\lambda = \frac{0.693}{5730 \text{ y}} = 1.21 \times 10^{-4} \text{ y}^{-1}$$

$$\ln \frac{10 \text{ dis/min}}{15 \text{ dis/min}} = -0.40_s = -\lambda t; \quad t = \frac{0.40_s}{1.21 \times 10^{-4} \text{ y}^{-1}} = 3.35 \times 10^3 \text{ y}$$

The object is a bit more than 3000 years old, probably not dating from the pyramid era, about 3000 B.C.

35. First we determine the decay constant.  $\lambda = \frac{0.693}{1.39 \times 10^{10} \text{ y}} = 4.99 \times 10^{-11} \text{ y}^{-1}$

Then we can determine the ratio of  $(N_t)$ , the number of thorium atoms after  $2.7 \times 10^9$  y, to  $(N_0)$ , the initial number of thorium atoms:

$$\ln \frac{N_t}{N_0} = -kt = -\left(4.99 \times 10^{-11} \text{ y}^{-1}\right)\left(2.7 \times 10^9 \text{ y}\right) = -0.13 \quad \frac{N_t}{N_0} = 0.88$$

Thus, for every mole of  $^{232}\text{Th}$  present initially, after  $2.7 \times 10^9 \text{ y}$  there are

0.88 mol  $^{232}\text{Th}$  and 0.12 mol  $^{208}\text{Pb}$ . From this information, we can compute the mass ratio.

$$\frac{0.12 \text{ mol } ^{208}\text{Pb}}{0.88 \text{ mol } ^{232}\text{Th}} \times \frac{1 \text{ mol } ^{232}\text{Th}}{232 \text{ g } ^{232}\text{Th}} \times \frac{208 \text{ g } ^{208}\text{Pb}}{1 \text{ mol } ^{208}\text{Pb}} = \frac{0.12 \text{ g } ^{208}\text{Pb}}{1 \text{ g } ^{232}\text{Th}}$$

## Energetics of Nuclear Reactions

37. The mass defect is the difference between the mass of the nuclide and the sum of the masses of its constituent particles. The binding energy is this mass defect expressed as an energy.

$$\begin{aligned} \text{Particle mass} &= 9p + 10n + 9e = 9(p + n + e) + n \\ &= 9(1.0073 + 1.0087 + 0.0005486) \text{ u} + 1.0087 \text{ u} = 19.1576 \text{ u} \end{aligned}$$

$$\text{mass defect} = 19.1576 \text{ u} - 18.998403 \text{ u} = 0.1592 \text{ u}$$

$$\text{binding energy per nucleon} = \frac{0.1592 \text{ u} \times \frac{931.5 \text{ MeV}}{1 \text{ u}}}{19 \text{ nucleons}} = 7.805 \text{ MeV/nucleon}$$

39. mass defect =  $(10.01294 \text{ u} + 4.00260 \text{ u}) - (13.00335 \text{ u} + 1.00783 \text{ u}) = 0.00436 \text{ u}$

$$\text{energy} = 0.00436 \text{ u} \times \frac{931.5 \text{ MeV}}{1 \text{ u}} = 4.06 \text{ MeV}$$

41. 1 neutron  $\approx$  1 amu  $= 1.66 \times 10^{-27} \text{ kg}$

$$E = mc^2 = 1.66 \times 10^{-27} \text{ kg} (2.998 \times 10^8 \text{ m s}^{-1})^2 = 1.49 \times 10^{-10} \text{ J (1 neutron)}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J},$$

$$\text{Hence, 1 neutron} = 1.49 \times 10^{-10} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 9.30 \times 10^8 \text{ eV or } 930. \text{ MeV}$$

$$6.75 \times 10^6 \text{ MeV} \times \frac{1 \text{ neutron}}{930 \text{ MeV}} = 7.26 \times 10^3 \text{ neutrons}$$

## Nuclear Stability

43. (a) We expect  $^{20}\text{Ne}$  to be more stable than  $^{22}\text{Ne}$ . A neutron-to-proton ratio of 1-to-1 is associated with stability for elements of low atomic number (with  $Z \leq 20$ ).
- (b) We expect  $^{18}\text{O}$  to be more stable than  $^{17}\text{O}$ . An even number of protons and an even number of neutrons are associated with a stable isotope.
- (c) We expect  $^7\text{Li}$  to be more stable than  $^6\text{Li}$ . Both isotopes have an odd number of protons, but only  $^7\text{Li}$  has an even number of neutrons.
45.  $\beta^-$  emission has the effect of “converting” a neutron to a proton.  $\beta^+$  emission, on the other hand, has the effect of “converting” a proton to a neutron.
- (a) The most stable isotope of phosphorus is  $^{31}\text{P}$ , with a neutron-to-proton ratio of close to 1-to-1 and an even number of neutrons. Thus,  $^{29}\text{P}$  has “too few” neutrons, or too many protons. It should decay by  $\beta^+$  emission. In contrast,  $^{33}\text{P}$  has “too many” neutrons, or “too few” protons. Therefore,  $^{33}\text{P}$  should decay by  $\beta^-$  emission.
- (b) Based on the atomic mass of I (126.90447), we expect the isotopes of iodine to have mass numbers close to 127. This means that  $^{120}\text{I}$  has “too few” neutrons and therefore should decay by  $\beta^+$  emission, whereas  $^{134}\text{I}$  has “too many” neutrons (or “too few” protons) and therefore should decay by  $\beta^-$  emission.
47. A “doubly magic” nuclide is one in which the atomic number is a magic number (2, 8, 20, 28, 50, 82, 114) and the number of neutrons also is a magic number (2, 8, 20, 28, 50, 82, 126, 184). Nuclides that fit this description are given below.

nuclide	$^4\text{He}$	$^{16}\text{O}$	$^{40}\text{Ca}$	$^{56}\text{Ni}$	$^{208}\text{Pb}$
no. of protons	2	8	20	28	82
no. of neutrons	2	8	20	28	126

## Fission and Fusion

49. We use the conversion factor between number of curies and mass of  $^{131}\text{I}$  which was developed in the Summarizing Example.

$$\text{no. g I-131} = 170 \text{ curies} \times \frac{18.8 \text{ g I-131}}{2.33 \times 10^6 \text{ curie}} = 1.37 \times 10^{-3} \text{ g} = 1.37 \text{ mg}$$

## Effect of Radiation on Matter

51. The term “rem” is an acronym for “radiation equivalent-man,” and takes into account the quantity of biological damage done by a given dosage of radiation. On the other hand, the rad is the dosage which places 0.010 J of energy into each kg of irradiated matter. Thus, for living tissue, the rem provides a good idea of how much tissue damage a certain kind

and quantity of radiation damage will do. But for nonliving materials, the rad is often preferred, and indeed is often the only unit of utility.

- 53.** One reason why  $^{90}\text{Sr}$  is hazardous is because strontium is in the same family of the periodic table as calcium, and hence often reacts in a similar fashion to calcium. One site where calcium is incorporated into the body is in bones, where it resides for a long time. Strontium is expected to behave in a similar fashion. Thus, it will be retained in the body for a long time. Bone is an especially dangerous place for a radioisotope to be present—even if it has low penetrating power, as do  $\beta^-$  rays—because blood cells are produced in bone marrow.

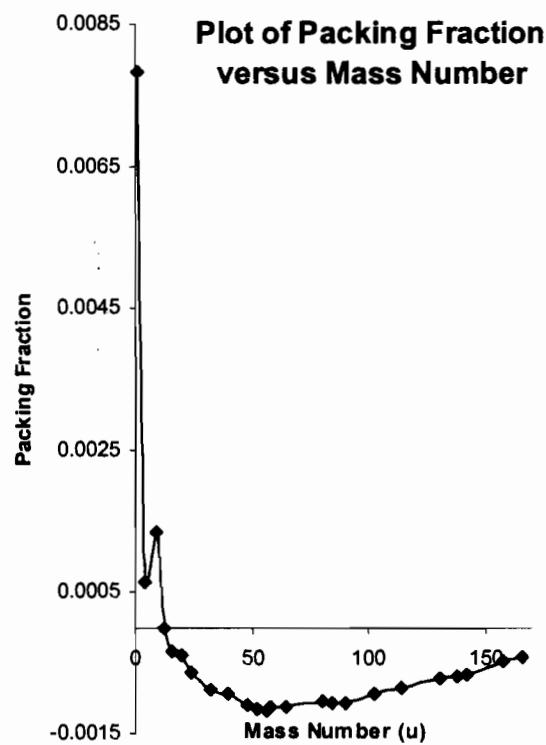
### Application of Radioisotopes

- 55.** Mix a small amount of tritium with the  $\text{H}_2(\text{g})$  and detect where the radioactivity appears.
- 57.** The recovered sample will be radioactive. When  $\text{NaCl}(\text{s})$  and  $\text{NaNO}_3(\text{s})$  are dissolved in solution, the ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ ) are free to move throughout the solution. A given anion does not remain associated with a particular cation. Thus, all the anions and cations are shuffled and some of the radioactive  $^{24}\text{Na}$  will end up in the crystallized  $\text{NaNO}_3$ .

## Feature Problems

75. First tabulate the isotopes symbols, the mass of isotope and its associated packing fraction.

Isotope Symbol	Mass of Isotope (u)	Packing Fraction
<sup>1</sup> H	1.007825	0.007825
<sup>4</sup> He	4.002603	0.000651
<sup>9</sup> Be	9.012186	0.001354
<sup>12</sup> C	12	0
<sup>16</sup> O	15.994915	-0.000318
<sup>20</sup> Ne	19.992440	-0.000378
<sup>24</sup> Mg	23.985042	-0.000623
<sup>32</sup> S	31.972074	-0.000873
<sup>40</sup> Ar	39.962384	-0.000940
<sup>40</sup> Ca	39.962589	-0.000935
<sup>48</sup> Ti	47.947960	-0.001084
<sup>52</sup> Cr	51.940513	-0.001144
<sup>56</sup> Fe	55.934936	-0.001162
<sup>58</sup> Ni	57.935342	-0.001115
<sup>64</sup> Zn	63.929146	-0.001107
<sup>80</sup> Se	79.916527	-0.001043
<sup>84</sup> Kr	83.911503	-0.001054
<sup>90</sup> Zr	89.904700	-0.001059
<sup>102</sup> Ru	101.904348	-0.000938
<sup>114</sup> Cd	113.903360	-0.000848
<sup>130</sup> Te	129.906238	-0.000721
<sup>138</sup> Ba	137.905000	-0.000688
<sup>142</sup> Nd	141.907663	-0.000650
<sup>158</sup> Gd	157.924178	-0.000480
<sup>166</sup> Er	165.932060	-0.000409



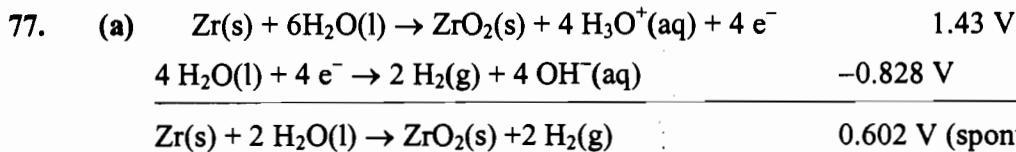
Data plotted above

This graph and Fig. 26-6 are almost the inverse of one another, with the maxima of one being the minima of the other. Actual nuclidic mass is often a number slightly less than the number of nucleons (mass number). This difference divided by the number of nucleons (packing fraction) is proportional to the negative of the mass defect per nucleon.

76. (a) The rate of decay depends on both the half-life and on the number of radioactive atoms present. In the early stages of the decay chain, the larger number of radium-226 atoms multiplied by the very small decay constant is still larger than the product of the very small number of radon-222 atoms and its much larger decay constant. Only after some time has elapsed, does the rate of decay of radon-222 approach the rate at which it is formed from radium-226 and the amount of radon-222 reaches a maximum. Beyond this point, the rate of decay of radon-222 exceeds its rate of formation.

$$(b) \frac{dD}{dt} = \lambda_p P - \lambda_d D = \lambda_p P_0 e^{-\lambda_p t} - \lambda_d D$$

- (c) The number of radon-222 atoms at various times are  $2.90 \times 10^{15}$  atoms after 1 day;  $1.26 \times 10^{16}$  after 1 week;  $1.75 \times 10^{16}$  after 1 year;  $1.68 \times 10^{16}$  after one century; and  $1.13 \times 10^{16}$  after 1 millennium. The actual maximum comes after about 2 months, but the amount after 1 year is only slightly smaller.



Yes, Zr can reduce water under standard conditions.

$$(b) E^\circ = \frac{0.0592}{n} \log K_{\text{eq}} \quad 0.602 \text{ V} = \frac{0.0592}{4} \log K_{\text{eq}} \quad K_{\text{eq}} = 5 \times 10^{40}$$

$$(c) \text{pH} = 7 \text{ Therefore, } [\text{OH}^-] = [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

$$E_{\text{ox}} = E_{\text{ox}}^\circ - \frac{0.0592}{n} \log Q = 1.43 \text{ V} - \frac{0.0592}{4} \log(1.0 \times 10^{-7})^4 = 1.84 \text{ V}$$

$$E_{\text{red}} = E_{\text{red}}^\circ - \frac{0.0592}{n} \log Q = -0.828 \text{ V} - \frac{0.0592}{4} \log(1 \times 10^{-7})^4 = -0.414 \text{ V}$$

$$E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}} = 1.84 + (-0.414) = 1.43 \text{ V (spontaneous)}$$

- (b) Zr may be the culprit responsible for the  $\text{H}_2\text{(g)}$  formation. In the Chernobyl accident the reaction of carbon with superheated steam played a major role.  
 Reaction:  $\text{H}_2\text{O(g)} + \text{C(s)} \rightarrow \text{CO}_{\text{(g)}} + \text{H}_2\text{(g)}$



$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = 2.25 \quad \frac{^{86}\text{Sr}}{^{88}\text{Sr}} = 0.119 \quad \frac{^{84}\text{Sr}}{^{88}\text{Sr}} = 0.007 \quad \text{Given: } 15.5 \text{ ppm Sr}$$

$$\text{Let } x = ^{86}\text{Sr}, y = ^{88}\text{Sr}, z = ^{87}\text{Sr}, w = ^{84}\text{Sr} \quad x + y + z + w = 15.5 \text{ ppm}$$

$$\frac{z}{x} = 2.25, \quad \frac{x}{y} = 0.119, \quad \frac{w}{y} = 0.007$$

$$\text{Hence, } z = 2.25x; \quad y = \frac{x}{0.119}; \quad w = 0.007; \quad y = \frac{x}{0.119} \cdot 0.007$$

$$x + y + z + w = 15.5 \text{ ppm} = x + \frac{x}{0.119} + 2.25x + 0.007 \left( \frac{x}{0.119} \right)$$

$$11.712x = 15.5 \text{ ppm}$$

$x = 1.32 \text{ ppm} = ^{86}\text{S}$ . Plugging into the ratios above, we find:

$y = 11.1 \text{ ppm} = {}^{88}\text{Sr}$ ;  $z = 2.97 \text{ ppm} = {}^{87}\text{Sr}$ ;  $w = 0.08 \text{ ppm} = {}^{84}\text{Sr}$ ;  
 % abundance in sample and isotopic mass are tabulated below:

1.32 ppm of  ${}^{86}\text{Sr} \rightarrow 8.52\% \text{ } 85.909 \text{ u}$

2.97 ppm of  ${}^{87}\text{Sr} \rightarrow 19.2\% \text{ } 86.909 \text{ u}$

11.1 ppm of  ${}^{88}\text{Sr} \rightarrow 71.6\% \text{ } 87.906 \text{ u}$

0.08 ppm of  ${}^{84}\text{Sr} \rightarrow 0.5\% \text{ } 83.913 \text{ u}$

Atomic mass

$$= 8.52\% (85.909 \text{ u}) + 19.2\% (86.909 \text{ u}) + 71.6\% (87.906 \text{ u}) + 0.5\% (83.913 \text{ u})$$

$$\text{Average Atomic mass} = 87.4 \text{ u}$$

(b) Original Rb in rock?

Currently 265.4 ppm for Rb, however,  $\frac{{}^{87}\text{Rb}}{{}^{85}\text{Rb}} = 0.330$

Let  $x = {}^{87}\text{Rb}$ , therefore,  $\frac{x}{265.4 - x} = 0.330$  (Solve for  $x$ )

$$x = 87.582 - 0.330x \text{ or } 1.330x = 87.582$$

$$x = 65.85 \text{ ppm} = {}^{87}\text{Rb} \text{ and thus, } {}^{85}\text{Rb} = 199.6 \text{ ppm}$$

Original  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}} = 0.700$  ( Since the half-life for strontium-86 is very long, we can assume that the concentration of strontium-86 has remained essentially constant)

$${}^{86}\text{Sr} = 1.32 \text{ ppm, hence, } {}^{87}\text{Sr} = 0.700(1.32 \text{ ppm}) = 0.924 \text{ ppm}$$

$$\text{The original Rb concentration is } 265.4 \text{ ppm} + 0.924 \text{ ppm} = 266.3 \text{ ppm}$$

$$(c) \% {}^{87}\text{Rb decayed} = \left( \frac{0.924 \text{ ppm}}{0.924 \text{ ppm} + 65.85 \text{ ppm}} \right) 100\% = 1.38\%$$

$$(d) \ln(0.9862) = -\lambda t \quad (\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.8 \times 10^{10} \text{ y}} = 1.44 \times 10^{-11} \text{ y}^{-1})$$

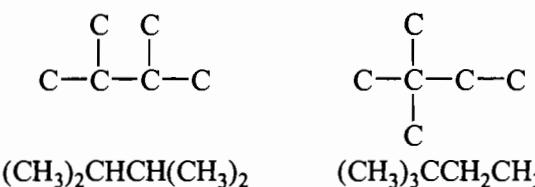
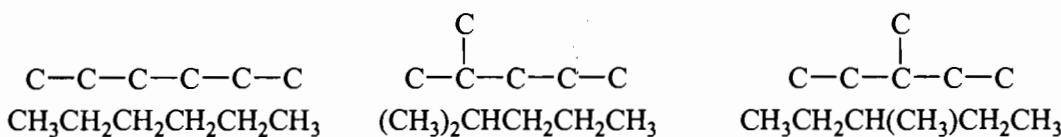
$$\ln(0.9862) = -1.44 \times 10^{-11} \text{ y}^{-1} t; \quad t = 9.65 \times 10^8 \text{ years}$$

# CHAPTER 27

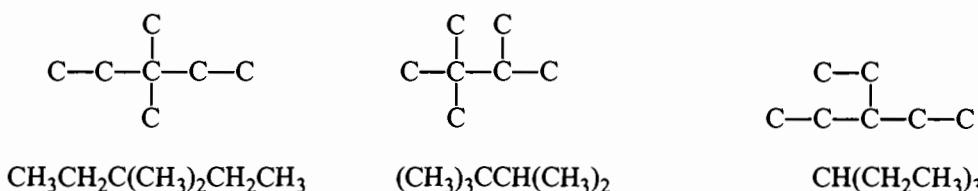
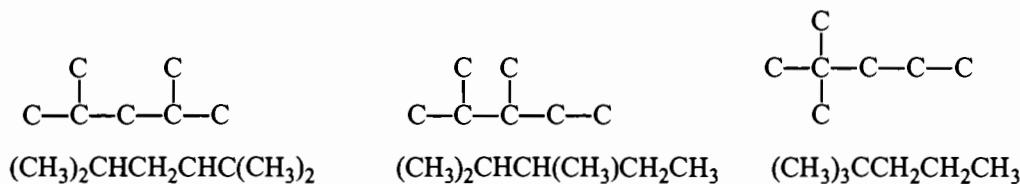
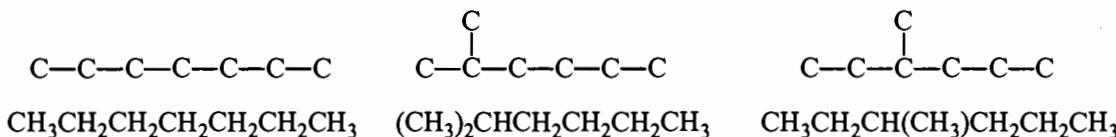
## ORGANIC CHEMISTRY

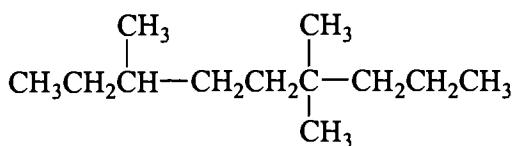
### PRACTICE EXAMPLES

- 1A** We show only the C atoms and the bonds between them. Remember that there are four bonds to each C atom; the remaining bonds not shown are to H atoms. First we realize there is only one isomer with all six C atoms in one line. Then we draw the isomers with one 1-C branch. These are the center two structures below. The isomers with two 1-C branches can have them both on the same atom or on different atoms, as in the rightmost two structures. This accounts for all five isomers.



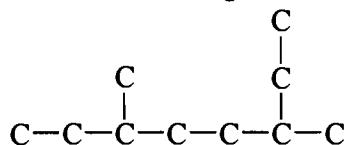
- 1B** We show only the C atoms and the bonds between them. Remember that there are four bonds to each C atom; the remaining bonds not shown are to H atoms.



**2A**

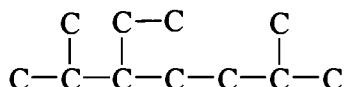
Numbering starts from the left and goes right so that the substituents appear with the lowest numbers possible. This is 3,6,6-trimethylnonane.

**2B** In the structural formula we show only the C atoms and the bonds between them. Remember that there are four bonds to each C atom; the remaining bonds not shown are to H atoms. The longest chain has 8 C atoms, making this an octane.



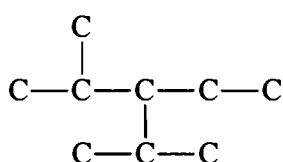
There are two methyl groups on the chain. The IUPAC name is 3,6-dimethyloctane.

**3A** We write the structural formula as before, showing only the C skeleton. The main chain is 7 C's long; we number it from left to right. Methyl groups are 1 carbon chains, an ethyl group is on carbon 2.



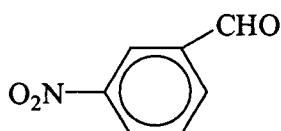
condensed structural formula:  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$

**3B** Pentane is a five-carbon chain. There is a  $-\text{CH}_3$  group on carbon 2, a sec-butyl group on carbon 3.



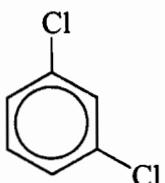
Condensed structural formula:  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}(\text{CH}_3)_2)\text{CH}_2\text{CH}_3$

**4A** The aldehyde group is a meta director. Thus, the product of the mononitration of benzaldehyde should be the compound whose structure is drawn below:

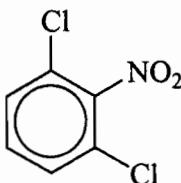


*m*-nitrobenzaldehyde or 3-nitrobenzaldehyde.

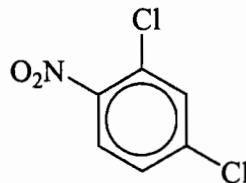
- 4B** — Cl is an ortho, para director. The possible products are 1,3-dichloro-2-nitrobenzene and 2,4-dichloro-1-nitrobenzene.



1,3-dichlorobenzene

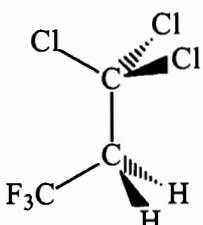


1,3-dichloro-2-nitrobenzene



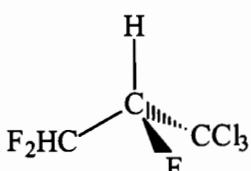
2,4-dichloro-1-nitrobenzene

- 5A** (a)



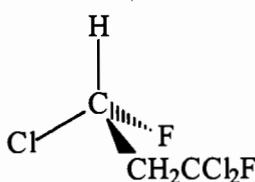
All three carbon atoms in this molecule are attached to at least two groups of the same type; thus, the molecule is achiral

- (b)



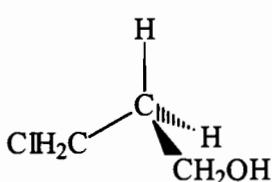
This molecule contains a carbon atom that is bonded to four different groups; consequently, the molecule is chiral.

- (c)



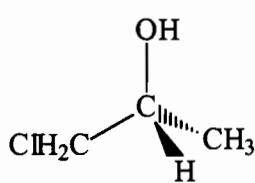
This molecule contains a carbon atom that is bonded to four different groups; consequently, the molecule is chiral.

- 5B** (a)



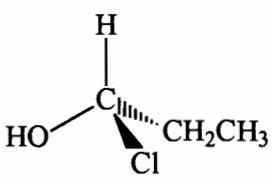
None of the three carbon atoms in this alcohol are bonded to four different groups; consequently the molecule is achiral

- (b)

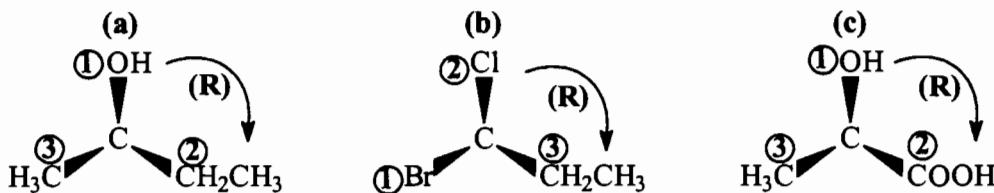
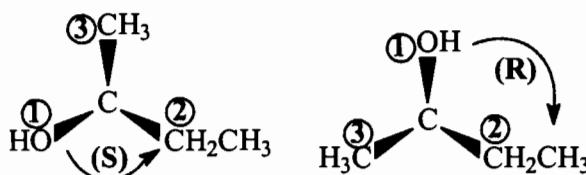


This molecule contains a carbon atom that is bonded to four different groups; consequently, the molecule is chiral.

- (c)

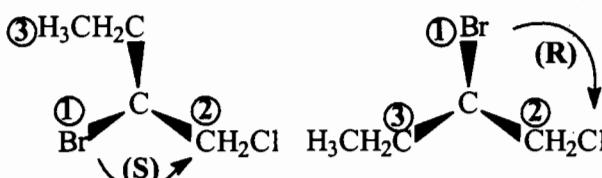


This molecule contains a carbon atom that is bonded to four different groups; consequently, the molecule is chiral.

6A6B

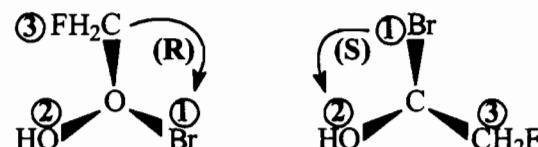
Thus, the structures are enantiomers.

(b)



Thus, the structures are enantiomers.

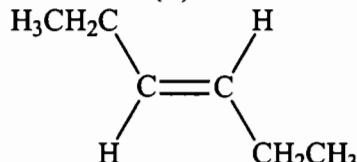
(c)



Thus, the structures are enantiomers.

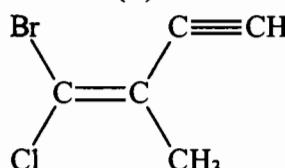
7A

(a) This is the (E) stereoisomer



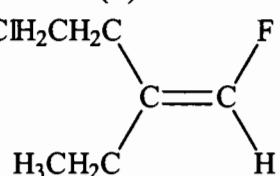
(b)

This is the (Z) stereoisomer



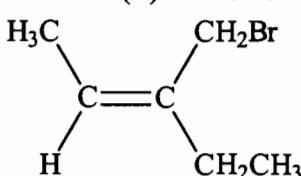
(c)

This is the (Z) stereoisomer

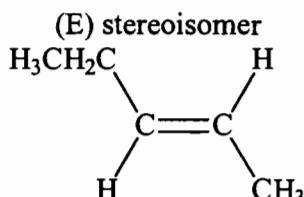
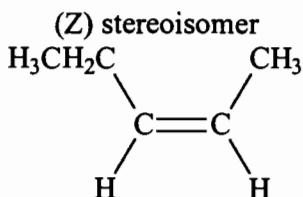


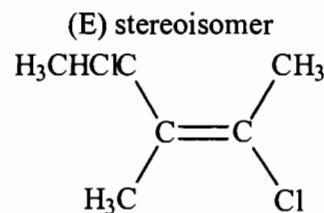
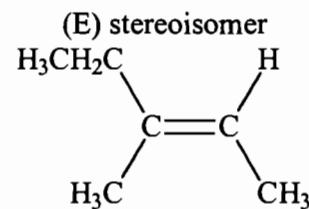
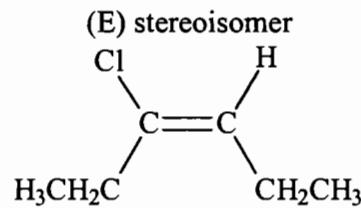
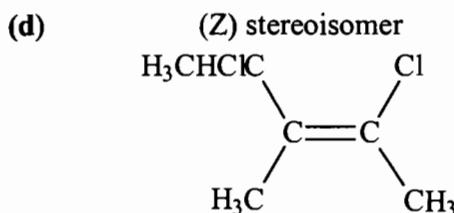
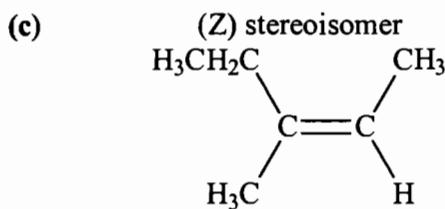
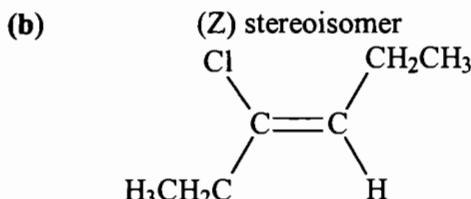
(d)

This is the (Z) stereoisomer

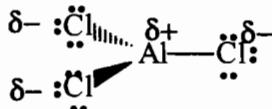
7B

(a)





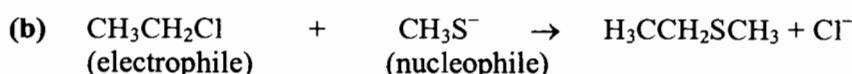
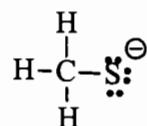
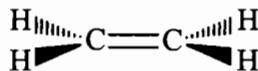
- 8A** The hydride ion is a nucleophile because it has a lone pair of electrons that can be shared with another atom.



Ethylene can be viewed as a nucleophile because it has a pair of pi-electrons that can be shared with another atom

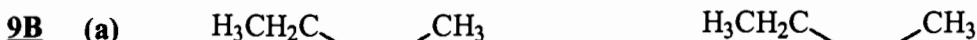
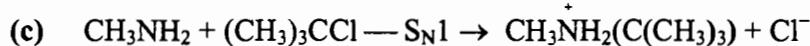
The central Al atom is electron deficient. Thus,  $\text{AlCl}_3$  is an electrophile.

The negatively charged S atom possesses three lone pairs of electrons that can potentially be shared with other atoms. Thus methylthiolate anion is a nucleophile.





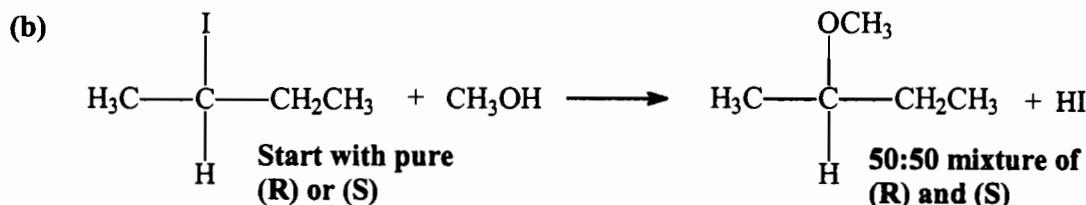
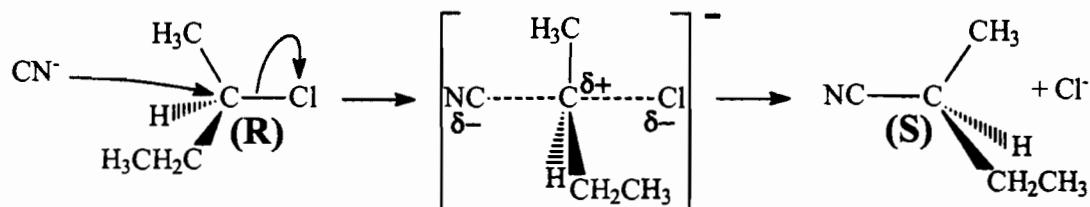
The nucleophile in this reaction is  $\text{Cl}^-$  while the leaving group is the  $\text{CN}^-$  ion. The  $\text{CN}^-$  ion is a much stronger nucleophile than  $\text{Cl}^-$ , so the equilibrium will strongly favor the reactants. In other words, no reaction is expected.



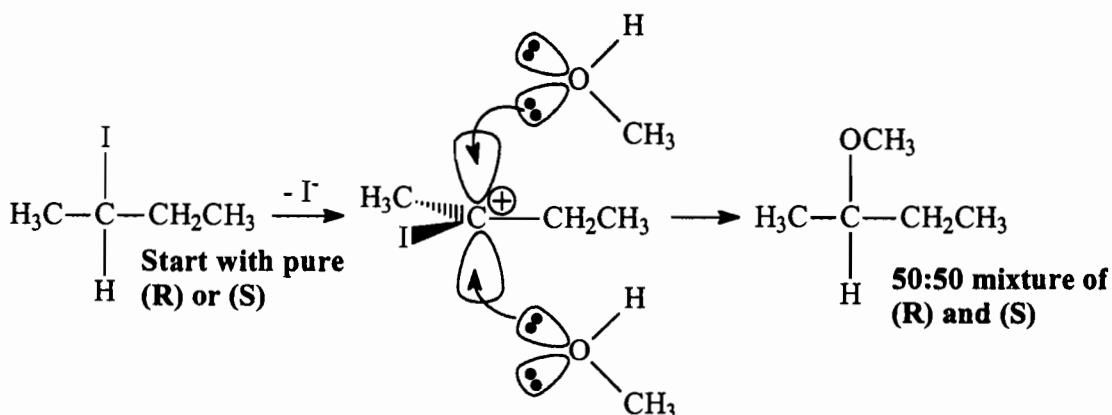
(R)-2-chlorobutane

(S)-2-cyanobutane

Because the configuration at the stereogenic carbon has undergone an inversion, we can conclude that the reaction has occurred via an  $\text{S}_{\text{N}}2$  mechanism.



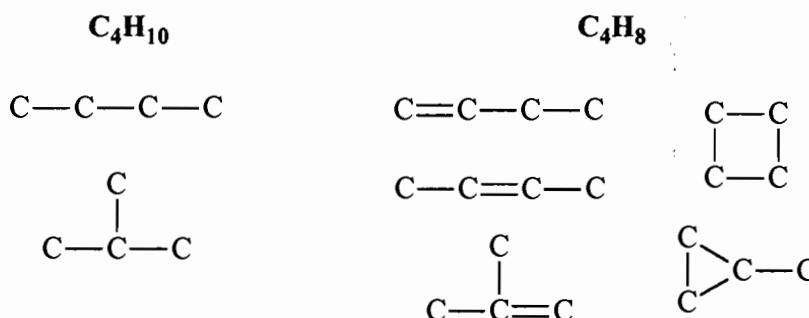
Clearly, since a racemic mixture forms, the reaction must occur via an  $\text{S}_{\text{N}}1$  mechanism.



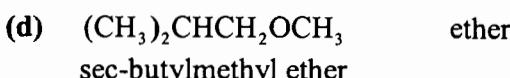
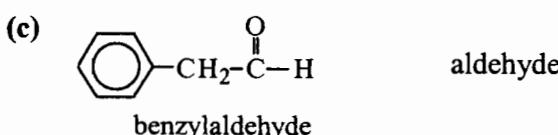
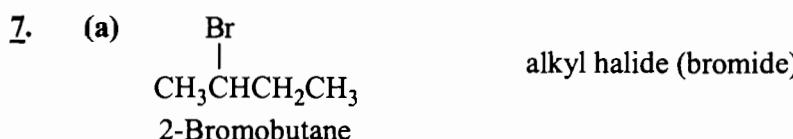
## REVIEW QUESTIONS

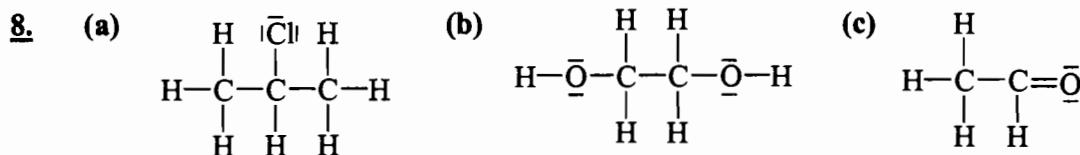
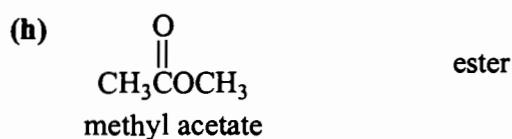
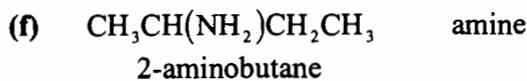
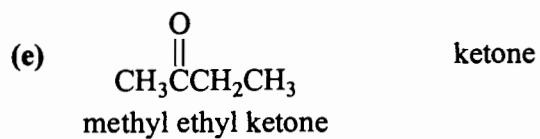
1. (a)  $t$  is the symbol for tertiary; it refers to a carbon atom to which three other carbon atoms are singly bonded.  
(b)  $R-$  is the symbol for an alkyl group, a carbon-hydrogen chain with no multiple bonds.  
(c) A hexagon with an inscribed circle is the symbol for a benzene ring, the molecule with formula  $C_6H_6$ .  
(d) A carbonyl group is the  $C=O$  moiety that is a characteristic feature in aldehydes, ketones, esters, amides and carboxylic acids.  
(e) A primary amine is a compound that contains the  $\text{--NH}_2$  functional group.
2. (a) In a substitution reaction, one atom or group of atoms replaces another atom or group of atoms.  
(b) The octane rating of gasoline is a measure of its quality. Gasoline's octane number is equal to the percent of isooctane in an isooctane-*n*-heptane mixture that has the same combustion characteristics as the gasoline.  
(c) Stereoisomerism refers to isomers (same chemical formula) that have exactly the same bonding arrangements, only differing in the three dimensional spatial orientation of the atoms. Geometric and optical isomerism are two examples of stereoisomerism.  
(d) An ortho, para director is a substituent on an aromatic ring that guides substitution reactions to occur preferentially at positions ortho- and para- to it.  
(e) Step reaction (condensation) polymerization occurs when the monomers join the polymer chain by the reaction of two functional groups and the elimination of a small molecule such as water.
3. (a) An alkane is a hydrocarbon in which there are no multiple bonds; in an alkene there is at least one double bond in the hydrocarbon.  
(b) An aliphatic compound is an alkane, a compound of carbon and hydrogen in which all bonds are single bonds and in which the carbon skeleton consists of straight or branched chains. In an aromatic compound there is at least one planar, cyclic arrangement of carbon atoms held together by both  $\sigma$ -bonds and delocalized  $\pi$ -bonds.  
(c) An alcohol has an  $-\text{OH}$  (hydroxyl) functional group attached to an aliphatic ( $sp^3$  hybridized) carbon atom. In phenols, the  $-\text{OH}$  group is attached to a benzene ring.  
(d) An ether has a  $\text{C}-\text{O}-\text{C}$  linkage. An ester has a  $\text{C}-\text{O}-\overset{\text{O}}{\underset{||}{\text{C}}}-$  linkage.  
(e) An amine contains  $\text{N}-\text{C}$  bond; ammonia is  $\text{NH}_3$ .

4. (a) Structural (or skeletal) isomers differ in how the atoms are joined together.
- (b) Positional isomers differ in the location of a functional group along the carbon chain of the molecule.
- (c) *cis*-, *trans*- isomers differ in the arrangement of atoms around a double bond.
- (d) *ortho*-, *meta*-, and *para*- isomers differ in the location of substituent groups on an aromatic ring.
5. Just in terms of straight and branched chains,  $C_4H_{10}$  has more isomers than  $C_4H_8$ , as shown by the structures below, in which the  $C_4H_8$  structures are at right. In addition, only  $C_4H_8$  can form rings: one four-membered ring isomer and one three-membered ring isomer.

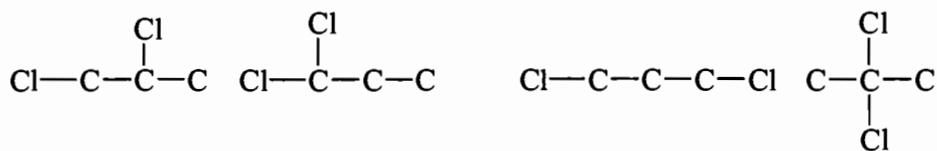


6. Cyclobutane has the formula  $C_4H_8$ ; there is one carbon for every two hydrogens.  $CH_3CH=CHCH_3$  has the formula  $C_4H_8$ , and  $CH_3C \equiv CCH_3$  has the formula  $C_4H_6$ . Only in  $CH_3CH=CHCH_3$  is there the same carbon-to-hydrogen ratio as in cyclobutane.





9. We draw only the carbon and chlorine atoms in each structure. Remember that there are four bonds to each carbon atom; the bonds not shown in these structures are C—H bonds.

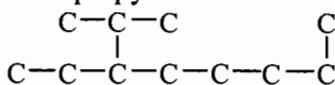


10. (a) These are not isomers, because they have different formulas:  $\text{C}_4\text{H}_{10}$  and  $\text{C}_4\text{H}_8$ .  
 (b) These two compounds are structural isomers. (Only the carbon skeleton is shown below).  
 $\begin{array}{ccccc} \text{C} & & & \text{C} & \\ | & & & | & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} & & & \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ | & & & | & \\ \text{C} & & & \text{C} & \end{array}$   
 (c) The compounds are not isomers; they have different formulas:  $\text{C}_4\text{H}_9\text{Cl}$  and  $\text{C}_5\text{H}_{11}\text{Cl}$ .  
 (d) These two compounds are identical; simply rotated.  
 (e) These two compounds are identical; simply rotated.  
 (f) These are two ortho-para isomers, ortho-nitrophenol on the left, and para-nitrophenol on the right.

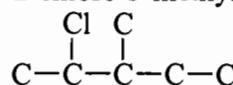
11. (a) The longest chain is eight carbons long, the two substituent groups are methyl groups, and they are attached to the number 3 and number 5 carbon atom. This is 3,5-dimethyloctane.
- (b) The longest carbon chain is three carbons long, the two substituent groups are methyl groups, and they are both attached to the number 2 carbon atom. This is 2,2-dimethylpropane.
- (c) The longest carbon chain is 7 carbon atoms long, there are two chloro groups attached to carbon atom 3, and an ethyl group attached to carbon 5. This is 3,3-dichloro-5-ethylheptane.
12. (a) There are 2 chloro groups at the 1 and 3 positions on a benzene ring. This is 1,3-dichlorobenzene or, more appropriately, meta-dichlorobenzene.
- (b) There is a methyl group at position 1 on a benzene ring, and a nitro group at position 3. This is 3-nitrotoluene or meta-nitrotoluene.
- (c) There is a —COOH group at position 1 on the benzene ring, and a —NH<sub>2</sub> group at position 4, or para to the —COOH group. This is 4-aminobenzoic acid or *p*-aminobenzoic acid.

13. In the structural formulas drawn below, we omit the hydrogen atoms. Remember that there are four bonds to each C atom. The bonds that are not shown are C—H bonds.

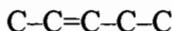
(a) 3-isopropyloctane



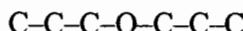
(b) 2-chloro-3-methylpentane



(c) 2-pentene



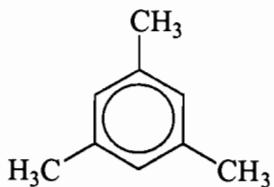
(d) dipropyl ether

(e) *p*-bromophenol

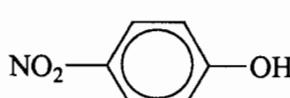
14. (a) isopropyl alcohol CH<sub>3</sub>CH(OH)CH<sub>3</sub>

(b) 1,1,1-chlorodifluoroethane CClF<sub>2</sub>CH<sub>3</sub>(c) 2-methyl-1,3-butadiene CH<sub>2</sub> = C(CH<sub>3</sub>)CH = CH<sub>2</sub>

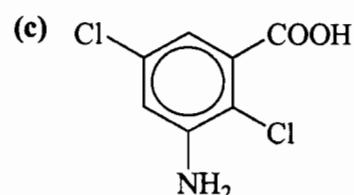
15. (a)



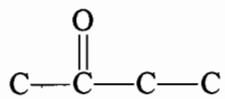
- (b)



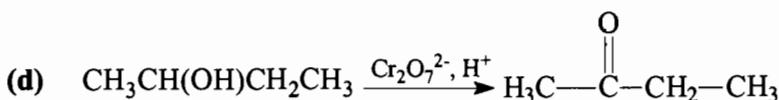
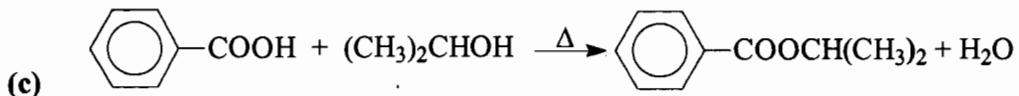
- (c)



16. Methyl ethyl ketone has the abbreviated structure shown on the right. Thus, the alcohol from which it is produced must have an —OH group on carbon 2 and it must be a four-carbon-atom straight-chain alcohol. Of the alcohols listed, 2-butanol satisfies these criteria.

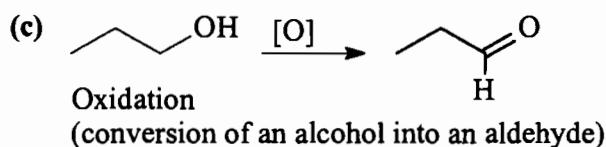
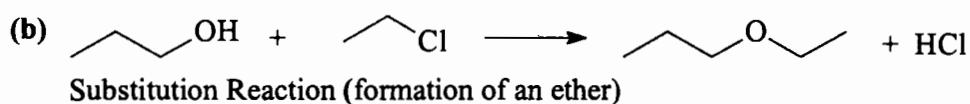
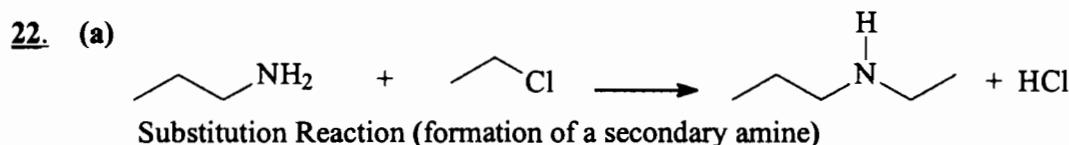
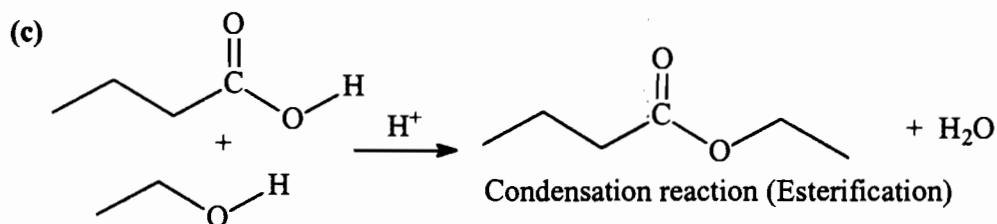
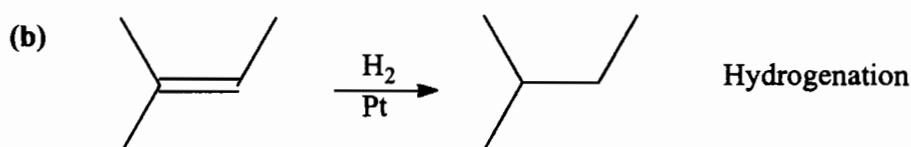
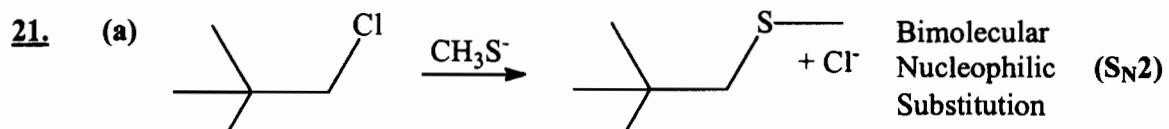


17. (a)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{H}_2\text{O}, \text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- (b)  $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \xrightarrow{h\nu} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CHClCH}_3$   
+ other polychlorinated propanes



18. (a)  $\text{C}_6\text{H}_6$  would have a higher boiling point than  $\text{C}_6\text{H}_{12}$  because its London forces are stronger;  $\text{C}_6\text{H}_6$  has many  $\pi$  electrons which interact with each other. There are no dipole-dipole forces or hydrogen bonds between these molecules.
- (b) Both  $\text{C}_3\text{H}_7\text{OH}$  and  $\text{C}_7\text{H}_{15}\text{OH}$  are alcohols that can hydrogen bond, but  $\text{C}_7\text{H}_{15}\text{OH}$  has a much longer nonpolar hydrocarbon chain, interfering with its aqueous solubility.  $\text{C}_3\text{H}_7\text{OH}$  is more water soluble.
- (c) Functional groups determine acidity of these two otherwise alike molecules. The aldehyde hydrogen is not notably acidic while the carboxylic hydrogen is.  $\text{C}_6\text{H}_5\text{COOH}$  is more acidic in aqueous solution.

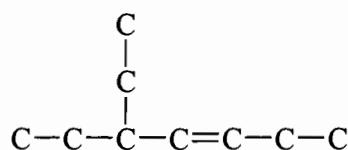
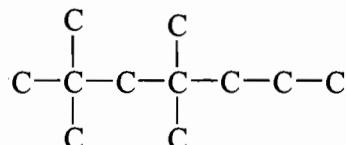
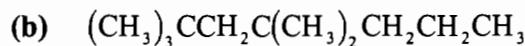
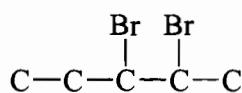
19. (a)  $:\text{NH}_3$  (nucleophile, possesses a chemically active lone pair)
- (b)  $\text{CH}_3\text{Cl}$  (electrophile, the polar C-Cl bond makes the molecule an electrophile)
- (c)  $\text{Br}^-$  (nucleophile, possesses chemically active lone pairs)
- (d)  $\text{CH}_3\text{OH}$  (nucleophile: lone pairs on oxygen can be used to form dative bonds)
- (e)  $\text{CH}_3\text{NH}_3^+$  (neither: though positively charged, this cation will not accept any additional electron pairs).
20. (a)  $\text{N}_3^-$  (nucleophile, possesses lone pairs of electrons that can be used to form dative bonds)
- (b)  $\text{NH}_4^+$  (neither: though positively charged, this cation will not accept any additional electron pairs)
- (c)  $\text{CH}_3\text{CHClCH}_3$  (electrophile: the polar C-Cl bond makes the molecule an electrophile)
- (d)  $\text{OH}^-$  (nucleophile: lone pairs on oxygen can be used to form dative bonds)
- (e)  $\text{H}_2\text{C}=\text{O}$  (both: as a nucleophile via the oxygen, donating a pair of electrons or as an electrophile via the carbon accepting a pair of electrons from a nucleophile).



## EXERCISES

### Organic Structures

- 23.** In the following structural formulas, the hydrogen atoms are omitted for simplicity. Remember that there are four bonds to each carbon atom. The missing bonds are C—H bonds.

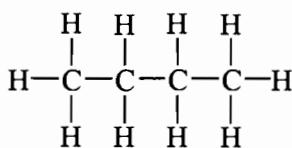


- 25. (a)** Each carbon atom is  $sp^3$  hybridized. All of the C—H bonds in the structure (drawn below) are sigma bonds, between the  $1s$  orbital of H and the  $sp^3$  orbital of C. The C—C bond is between  $sp^3$  orbitals on each C atom.

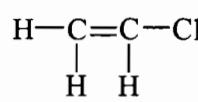
- (b)** Both carbon atoms are  $sp^2$  hybridized. All of the C—H bonds in the structure (drawn below) are sigma bonds between the  $1s$  orbital of H and the  $sp^2$  orbital of C. The C—Cl bond is between the  $sp^2$  orbital on C and the  $3p$  orbital on Cl. The C=C double bond is composed of a sigma bond between the  $sp^2$  orbitals on each C atom and a pi bond between the  $2p_z$  orbitals on the two C atoms.

- (c)** The left-most C atom (in the structure drawn below) is  $sp^3$  hybridized, and the C—H bonds to that C atom are between the  $sp^3$  orbitals on C and the  $1s$  orbital on H. The other two C atoms are  $sp$  hybridized. The right-hand C—H bond is between the  $sp$  orbital on C and the  $1s$  orbital on H. The  $\text{C} \equiv \text{C}$  triple bond is composed of one sigma bond formed by overlap of  $sp$  orbitals, one from each C atom, and two pi bonds, each formed by the overlap of two  $2p$  orbitals, one from each C atom (that is a  $2p_y$ — $2p_y$  overlap and a  $2p_z$ — $2p_z$  overlap).

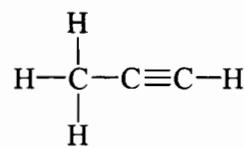
(a)



(b)



(c)

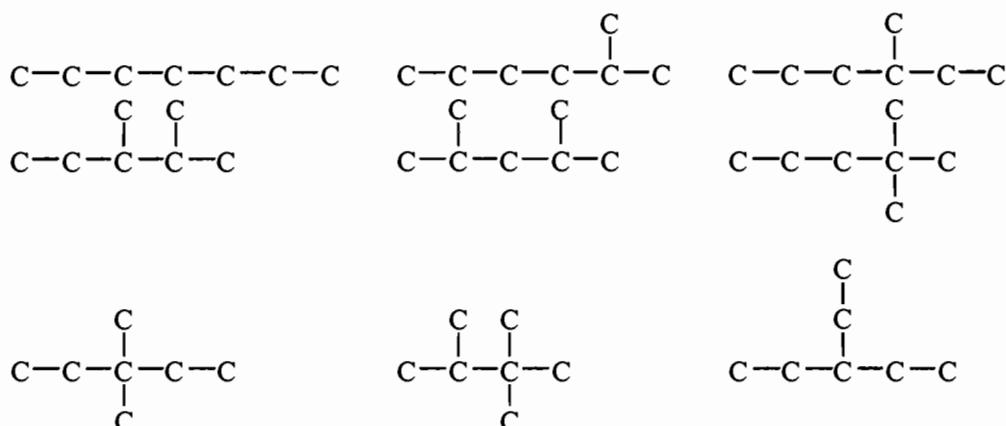


## Isomers

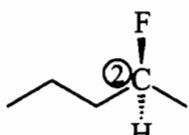
**27.** Structural (skeletal) isomers differ from each other in the length of their carbon atom chains and in the length of the side chains. The carbon skeleton differs between these isomers. Positional isomers differ in the location or position where functional groups are attached to the carbon skeleton. Geometric isomers differ in whether two substituents are on the same side of the molecule or on opposite sides of the molecule from each other; usually they are on opposite sides or the same side of a double bond.

- (a) The chloro group is attached to the terminal carbon in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  and to the central carbon atom in  $\text{CH}_3\text{CHClCH}_3$ . These are positional isomers.
- (b)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ , methylbutane, and  $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ , pentane, are structural isomers.
- (c) Ortho-aminotoluene and meta-aminotoluene differ in the position of the  $-\text{NH}_2$  group on the benzene ring. They are positional isomers.

**29.** We show only the carbon atom skeleton in each case. Remember that there are four bonds to carbon. The bonds that are not indicated in these structures are  $\text{C}-\text{H}$  bonds.

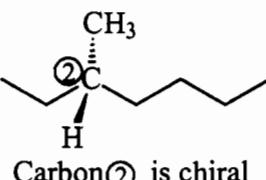


**31.** (a)



Carbon ② is chiral

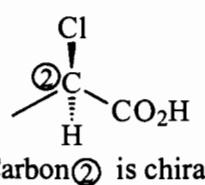
(b) There are no chiral carbon atoms in compound (b)



Carbon ② is chiral

(c)

**33.** (a)



Carbon ② is chiral

(b)

Carbon ② is chiral

(c) There are no chiral carbon atoms in compound (c)

## Functional Groups

35. (a) A carbonyl group is  $\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---}$ , while a carboxyl group is  $\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---OH}$

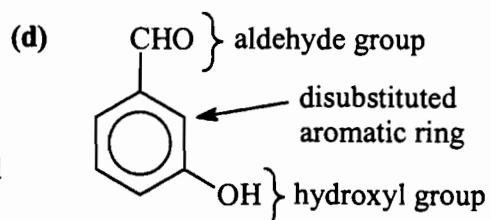
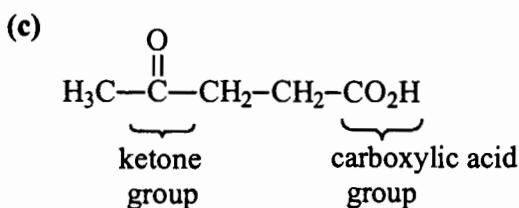
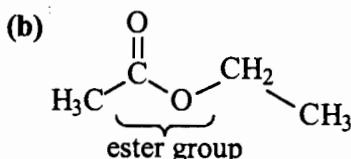
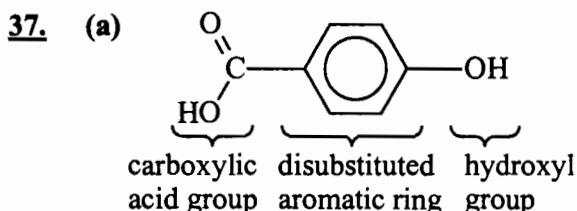
The essential difference between them is the hydroxyl group,  $\text{---OH}$ .

(b) An aldehyde has a carbonyl group at the end of a molecule,  $\text{R---}\overset{\text{O}}{\parallel}\text{C---H}$

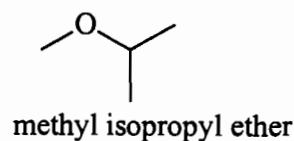
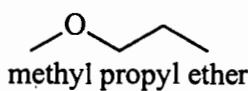
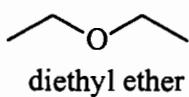
In a ketone,  $\text{R---}\overset{\text{O}}{\parallel}\text{C---R'}$ , the carbonyl group is in the center of the molecule.

(c) Acetic acid is  $\text{H}_3\text{C---}\overset{\text{O}}{\parallel}\text{C---OH}$ , while an acetyl group is  $\text{H}_3\text{C---}\overset{\text{O}}{\parallel}\text{C---}$

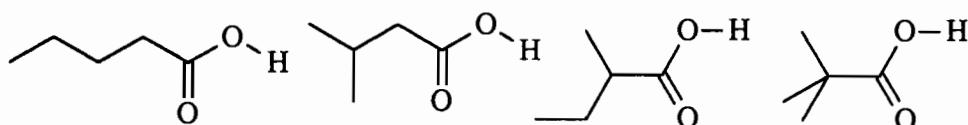
The essential difference is the presence of the  $\text{---OH}$  group in acetic acid.

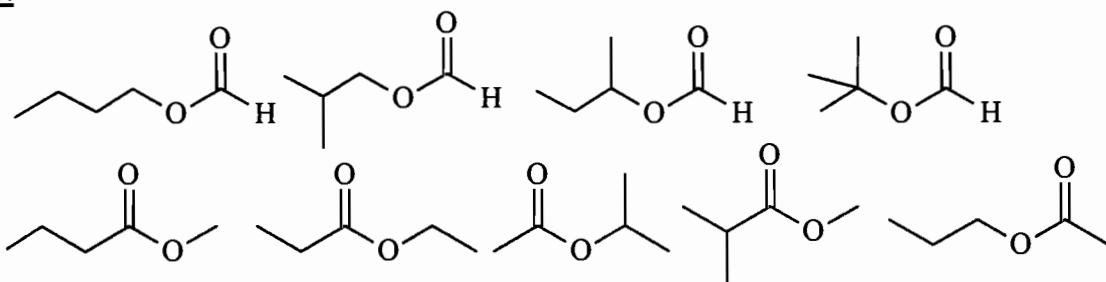
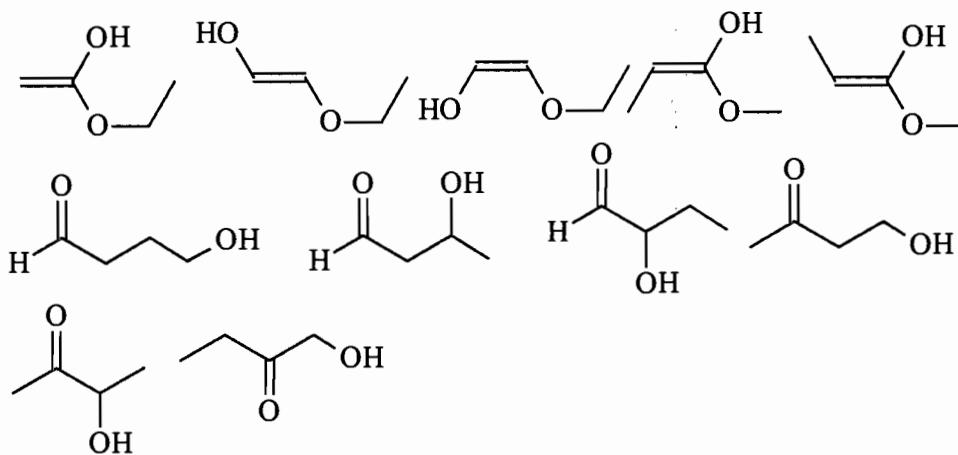


39.



41.



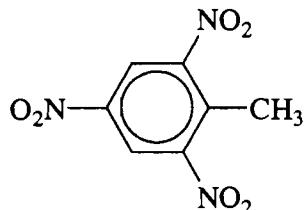
**43.****45.**

### Nomenclature and Formulas

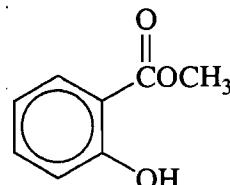
- 47.** (a) The longest carbon chain has four carbon atoms and there are 2 methyl groups attached to carbon 2. This is 2,2-dimethylbutane.
- (b) The longest chain is three carbons long, there is a double bond between carbons 1 and 2, and a methyl group attached to carbon 2. This is 2-methylpropene.
- (c) Two methyl groups are attached to a three-carbon ring. This is 1,2-dimethylcyclopropane.
- (d) The longest chain is 5 carbons long, there is a triple bond between carbons 2 and 3 and a methyl group attached to carbon 4. This is 4-methyl-2-pentyne.
- (e) The longest chain is 5 carbons long. There is an ethyl group on carbon 2 and a methyl group on carbon 3. This compound is 2-ethyl-3-methylpentane.
- (f) The longest carbon chain containing the double bond is 5 carbons long. The double bond is between carbons 1 and 2. There is a propyl group on carbon 2, and carbons 3 and 4 each have one methyl group. This is 3,4-dimethyl-2-propyl-1-pentene.
- 49.** (a) The name pentene is insufficient. 1-pentene is  $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$ , and 2-pentene is  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$ .
- (b) The name butanone is sufficient. There is only one four-carbon ketone.

- (c) The name butyl alcohol is insufficient. There are numerous butanols. 1-butanol is  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , 2-butanol is  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ , isobutanol is  $\text{HOCH}_2\text{CH}(\text{CH}_3)_2$ , and t-butanol is  $(\text{CH}_3)_3\text{COH}$ .
- (d) The name methylaniline is insufficient. It specifies  $\text{CH}_3-\text{C}_6\text{H}_4-\text{NH}_2$ , with no relative locations for the  $-\text{NH}_2$  and  $-\text{CH}_3$  substituents.
- (e) The name methylcyclopentane is sufficiently precise. It does not matter where on a five-carbon ring with only C–C single bonds a methyl group is placed.
- (f) Dibromobenzene is insufficient. It specifies  $\text{Br}-\text{C}_6\text{H}_4-\text{Br}$ , with no indication of the relative locations of the two bromo groups on the ring.

**51.** (a) 2,4,6-trinitrotoluene:



(b) methylsalicylate:



- (c) 2-hydroxy-1,2,3-propanetricarboxylic acid:  $\text{HOOCCH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$

**53.** (a)  $\text{HN}(\text{CH}_2\text{CH}_3)_2$

*N,N*-diethylamine

(b)  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$

p-aminonitrobenzene

(c)  $\text{NH}-\text{CH}_2-\text{CH}_3$

*N*-ethyl-*N*-cyclopentylamine

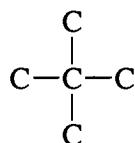
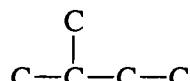
(d)  $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_3$

diethylmethylamine

## Alkanes

- 55.** The general formula of an alkane is  $\text{C}_n\text{H}_{2n+2}$ . Thus an alkane with a molecular mass of 72 u has the molecular formula  $\text{C}_5\text{H}_{12}$ .

- (a) If the compound forms four different monochlorination products, there must be four different kinds of carbons in the molecule, each with H atoms attached. This compound is 2-methylbutane, on the left.

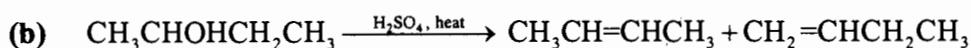
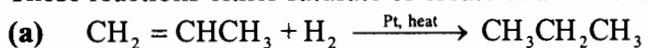


- (b) If the compound forms but one monochlorination product, every carbon atom in the molecule with H atoms attached must be the same. This compound is 2,2-dimethylpropane, the compound above and to the right.

## Alkenes

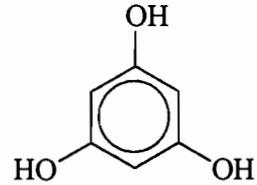
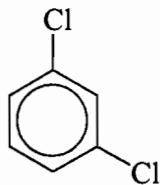
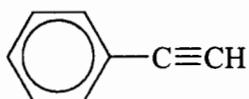
- 57.** In the case of ethene there are only two carbon atoms between which there can be a double bond. Thus, specifying the compound as 1-ethene is unnecessary. In the case of propene, there can be a double bond only between the central carbon atom and a terminal carbon atom. Thus here also, specifying the compound as 1-propene is unnecessary. The case of butene is different, however, since 1-butene,  $\text{CH}_2 = \text{CHCH}_2\text{CH}_3$ , is distinct from 2-butene,  $\text{CH}_3\text{CH} = \text{CHCH}_3$ .

- 59.** These reactions either saturate or create double bonds.



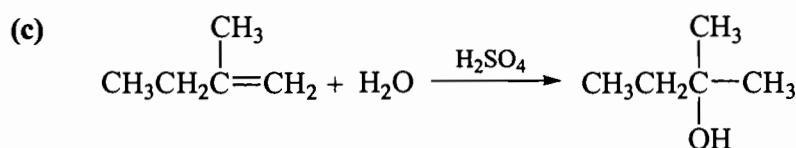
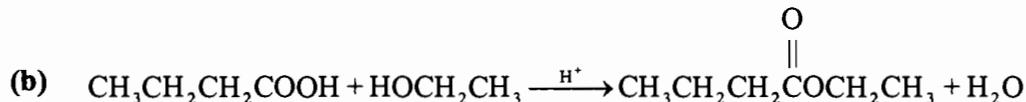
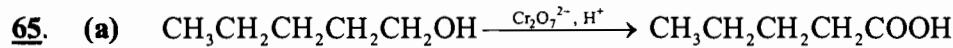
## Aromatic Compounds

- 61.** (a) phenylacetylene      (b) meta-dichlorobenzene      (c) 3,5-dihydroxyphenol

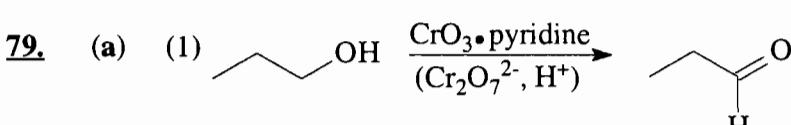
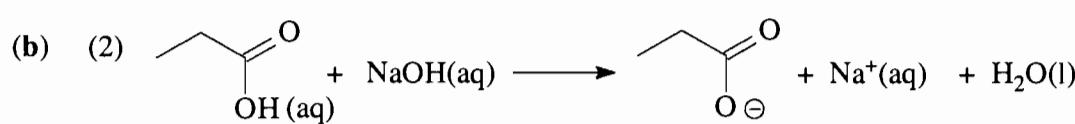
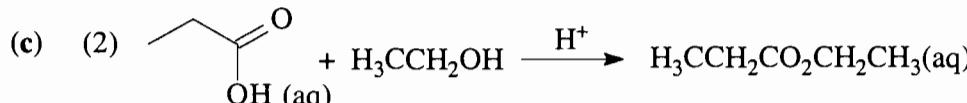


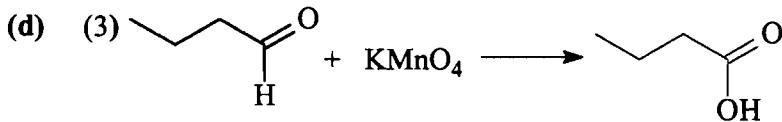
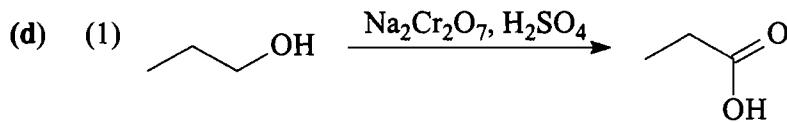
## Organic Reactions

- 63.** (a) In an aliphatic substitution reaction, an atom (usually H) of an alkane molecule is replaced by another atom or group of atoms. An example is equation (27.4).
- (b) In an aromatic substitution reaction, an atom (usually H) of a phenyl group is replaced by another atom or group of atoms. Examples are in equations (27.12) and (27.13).
- (c) In an addition reaction, a small molecule breaks apart into two fragments each of which bond to one of the adjacent atoms in a molecule that are engaged in multiple bonding (i.e. C=C, C=O, C≡C to name a few). An example is equation (27.10).
- (d) In an elimination reaction, two groups from within the same molecule join to form a small molecule—such as  $\text{H}_2$  or  $\text{H}_2\text{O}$ —and are eliminated from the larger molecule. Often a multiple bond results as well. An example is equation (27.6).



67. (a)  $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{Ether}} \text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$   
 (b)  $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{Cl}_2 \xrightarrow{\text{Ether}} \text{H}_3\text{C}-\text{CHCl}-\text{CH}_2\text{Cl}$   
 (c)  $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{HCN} \longrightarrow \text{H}_3\text{C}-\text{CH}(\text{CN})-\text{CH}_3$   
 (d)  $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{HCl} \longrightarrow \text{H}_3\text{C}-\text{CHCl}-\text{CH}_3$   
 (e)  $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_3\text{O}^+} \text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_3$
69. (a)  $\text{H}_3\text{CCH}_2\text{CO}_2^-(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{H}_3\text{CCH}_2\text{CO}_2\text{H}(\text{aq}) + \text{Cl}^-(\text{aq})$   
 (b)  $\text{H}_3\text{CCH}_2\text{CO}_2\text{CH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{CCH}_2\text{CO}_2\text{H}(\text{aq}) + \text{HOCH}_3(\text{aq})$   
 (c)  $\text{H}_3\text{CCH}_2\text{CO}_2\text{CH}_2\text{CH}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{H}_3\text{CCH}_2\text{CO}_2\text{Na}(\text{aq}) + \text{HOCH}_2\text{CH}_3(\text{aq})$
71. (a)  $\text{H}_3\text{CCO}_2\text{H} + \text{NH}_3 \longrightarrow \text{H}_3\text{CC}(\text{O})\text{NH}_2 + \text{H}_2\text{O}$   
 (b)  $\text{H}_3\text{CCH}_2\text{CONH}_2 \xrightarrow{\Delta} \text{H}_3\text{CCH}_2\text{C}\equiv\text{N} + \text{H}_2\text{O}$   
 (c)  $\text{H}_3\text{CCH}_2\text{C}(\text{O})\text{NH}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{H}_3\text{CCH}_2\text{C}(\text{O})\text{ONa}(\text{aq}) + \text{NH}_3(\text{aq})$
73. (a)  $\text{CH}_3\text{COO}^-(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{Cl}^-(\text{aq})$   
 (b)  $\text{H}_3\text{CCH}_2\text{C}(\text{O})\text{OCH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{H}_3\text{CCH}_2\text{C}(\text{O})\text{OH}(\text{aq})$   
 (c)  $\text{H}_3\text{CCH}_2\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{H}_3\text{CCH}_2\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$
75.  $\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$   

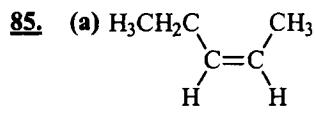
$$K_b = \frac{[\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+] [\text{OH}^-]}{[\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{NH}_2]}$$
77. (a)  $\text{H}_3\text{CCH}_2\text{NH}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{H}_3\text{CCH}_2\text{NH}_3^+\text{Cl}^-(\text{aq})$   
 (b)  $(\text{CH}_3)_3\text{N}(\text{aq}) + \text{HBr}(\text{aq}) \rightarrow (\text{CH}_3)_3\text{NH}^+\text{Br}^-(\text{aq})$   
 (c)  $\text{H}_3\text{CCH}_2\text{NH}_3^+(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightarrow \text{No Reaction}$   
 (d)  $\text{H}_3\text{CCH}_2\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_3\text{CCH}_2\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
79. (a) (1)   
 (b) (2)   
 (c) (2) 



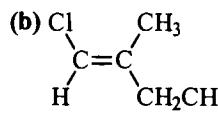
(e) None of the compounds (1) - (3) can be dehydrated to an alcohol

81. (a) Identical molecules (Both are achiral)  
 (b) Identical molecules (Both are the *R* enantiomers)  
 (c) Structural isomers (one is optically active, the other is not)  
 (d) Enantiomers (*R* and *S* optical isomers)  
 (e) Identical molecules (Both are the *R* enantiomers)  
 (f) Identical molecules (Both are the *R* enantiomers)

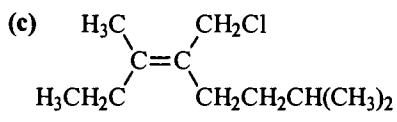
83. (a) (*S*)-3-bromo-2-methylpentane  
 (b) (*S*)-1,2-dibromopentane  
 (c) (*R*)-3-bromomethyl-5-chloro-*n*-pentan-3-ol  
 (d) (*S*)-1-bromo-*n*-propan-2-ol



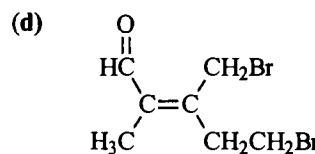
(Z)-2-pentene



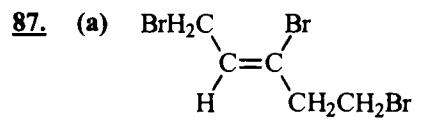
(E)-1-chloro-2-methyl-1-butene



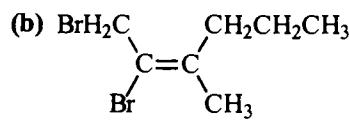
(E)-3-7-dimethyl-4-chloromethyl-3-octene



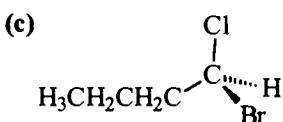
(Z)-5-bromo-3-bromomethyl-2-methylpent-2-enal



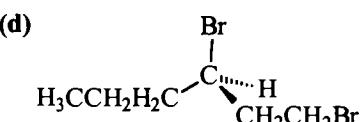
(Z)-1,3,5-tribromo-2-pentene



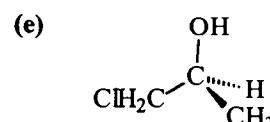
(E)-1,2-dibromo-3-methyl-2-hexene



(S)-1-bromo-1-chlorobutane



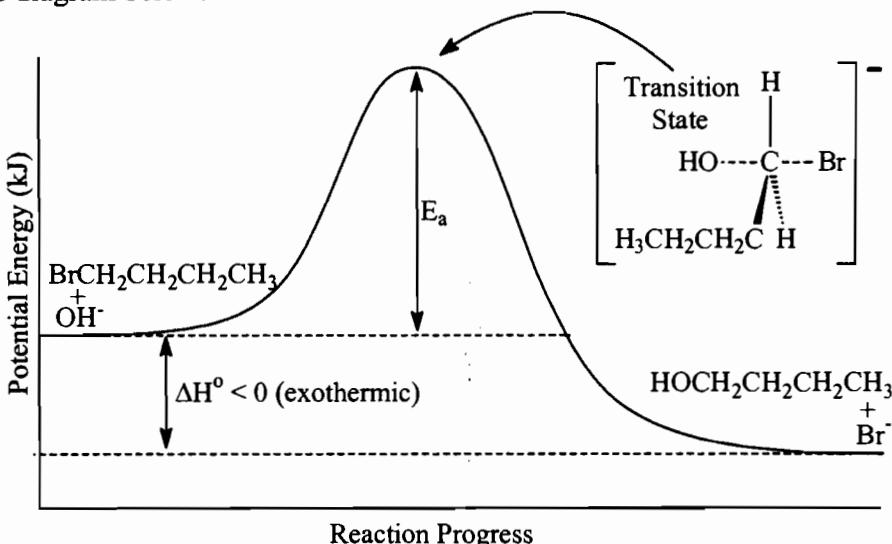
(R)-1,3-dibromohexane



(S)-1-chloro-2-propanol

89. (a) Reaction rate =  $k_{\text{obs}}[\text{OH}^-][\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3]$  ( $\text{S}_{\text{N}}2$  mechanism)

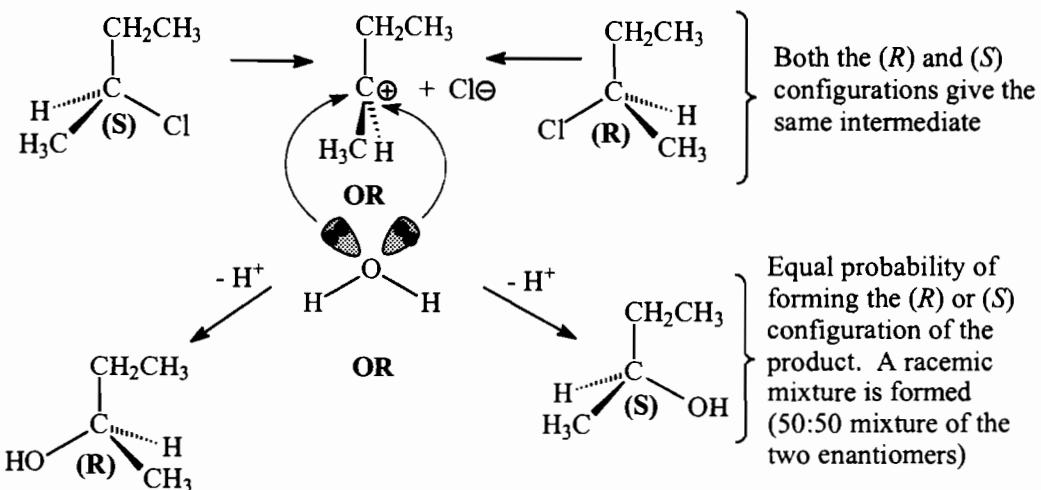
(b) See diagram below:



- (c) If the concentration of n-butyl bromide were doubled, the reaction rate would increase two fold
- (d) If the concentration of hydroxide ion were halved, the reaction rate would decrease by a factor of two.

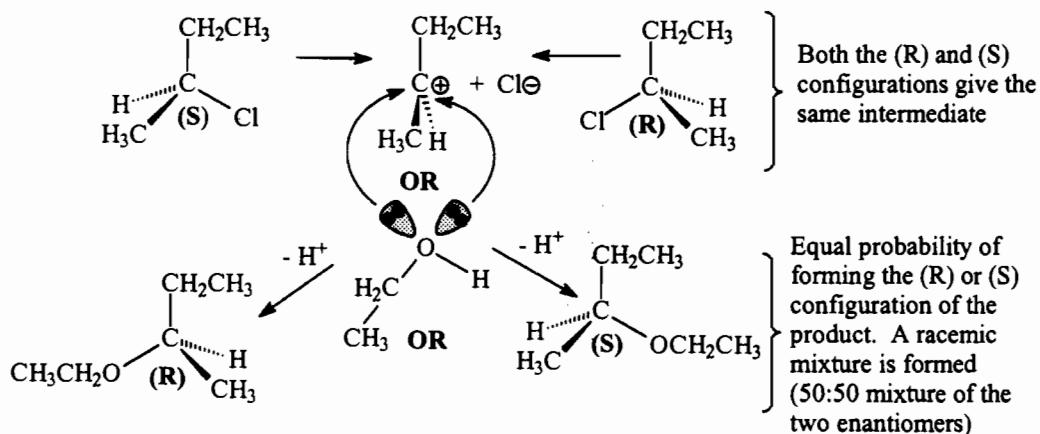
91. (a)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaBr}(\text{aq}) + \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{aq})$
- (b)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{aq}) + \text{NaC}\equiv\text{N}(\text{aq}) \rightarrow \text{NaBr}(\text{aq}) + \text{N}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{aq})$
- (c)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{Br}^-(\text{aq}) + {}^+\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{aq})$
- (d)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Na}^+\text{-O-CH}_2\text{CH}_3 \rightarrow \text{NaBr} + \text{H}_3\text{CH}_2\text{C-O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

93. (a)



- (b) Since the resulting product solution is optically inactive, we can conclude that a racemic mixture has been formed and hence, the reaction has occurred via an  $S_N1$  mechanism.

95. (a)

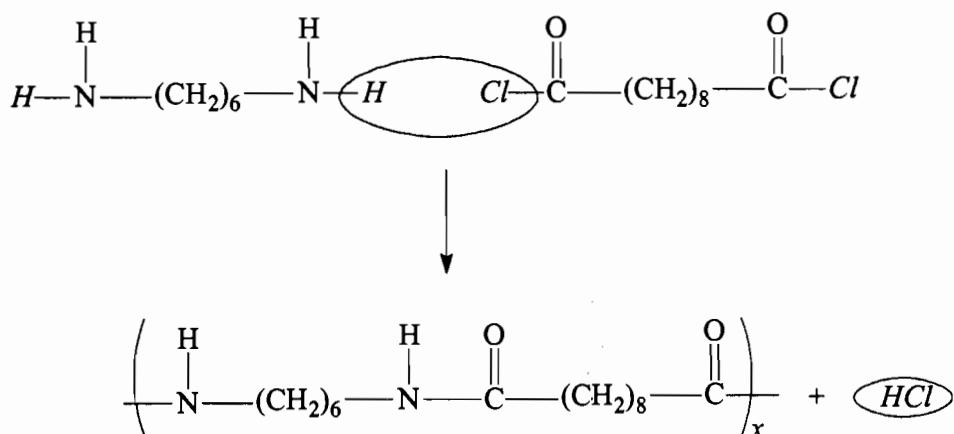


- (b) Since the resulting product solution is optically inactive. We can conclude that a racemic mixture has been formed and hence, the reaction has occurred via an  $S_N1$  mechanism.

## Polymerization Reactions

97. In a simple molecular substance like benzene, all molecules are identical ( $C_6H_6$ ). No matter how many of these molecules are present in one sample, any other sample with the same number of molecules has the same mass. The mass in grams of one mole of molecules—the molar mass—is a unique quantity. In a polymer the situation is quite different. The number of monomer units in a polymer chain is not a constant number but is widely variable. Thus individual polymer molecules differ very much in mass. Thus, a mass of a mole of their molecules also is quite variable. However, when we take a sample for analysis, we obtain many molecules of each chain length or molecular mass. The resulting determination of molar mass obtains the average mass of all of these different sized polymer molecules.

- 99.** The polymerization of 1,6-hexanediamine with sebacyl chloride proceeds in the following manner. The italicized H and Cl atoms are removed in this condensation reaction.



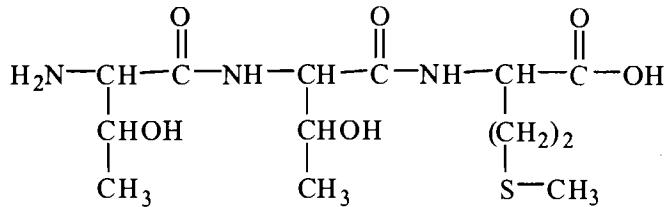
## FEATURE PROBLEMS

- 129. (a)**  $\text{HC(O)H} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-Mg-Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
(non-aqueous reaction of Grignard, followed by acid/water work-up of final product)
- (b)**  $\text{CH}_3\text{MgBr} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C(O)H} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH(OH)CH}_3$  or  
 $\text{CH}_3\text{C(O)H} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-Mg-Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH(OH)CH}_3$  (non-aqueous reaction of Grignard, followed by acid/water work-up of final product)
- (c)**  $\text{CH}_3\text{-Mg-Br} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C(O)CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C(OH)(CH}_3)_2$  or  
 $\text{CH}_3\text{C(O)CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-Mg-Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C(OH)(CH}_3)_2$   
(non-aqueous reaction of Grignard, followed by acid/water work-up of final product)
- (d)**  $\text{C}_6\text{H}_5\text{-Mg-Cl} + \text{CH}_3\text{C(O)CH}_3 \rightarrow \text{C}_6\text{H}_5\text{C(OH)(CH}_3)_2$   
Alternatively, this product can be prepared as follows:  
 $\text{C}_6\text{H}_5\text{C(O)CH}_3 + \text{CH}_3\text{-Mg-Cl} \rightarrow \text{C}_6\text{H}_5\text{C(OH)(CH}_3)_2$   
(non-aqueous reaction of Grignard, followed by acid/water work-up of final product)
- (e)**  $\text{CH}_3\text{CH}_2\text{-Mg-Br} + \text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{Br-Mg-C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3$
- (f)**  $\text{CH}_3\text{CH}_2\text{-Mg-Br} + \text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{Br-Mg-C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3$   
then,  $\text{Br-Mg-C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{HC(O)H} \rightarrow \text{HOH}_2\text{CC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$   
(non-aqueous reaction of Grignard, followed by acid/water work-up of final product)

# CHAPTER 28

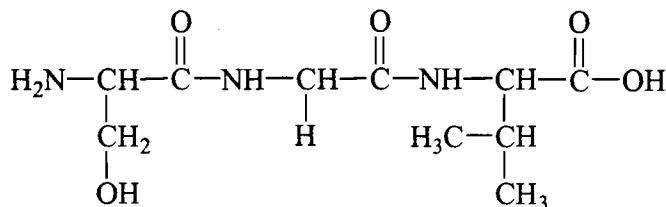
## CHEMISTRY OF THE LIVING STATE

### PRACTICE EXAMPLES

**1A**

The amino acids are threonine, threonine, and methionine. This tripeptide is dithreonylmethionine.

**1B** The amino acids are: serine, glycine, and valine. The N terminus is first.



**2A** Because it is a pentapeptide and five amino acids have been identified, no amino acid is repeated. The sequences fall into place, as follows.

	Gly	Cys			
	fragment		second		
	Cys	Val	third fragment		
	Val	Phe	first fragment		
	Phe	Tyr	fourth fragment		
pentapeptide sequence	Gly	Cys	Val	Phe	Tyr

**2B** Because it is a hexapeptide and there are five distinct amino acids, one amino acid must appear twice. The fragmentation pattern indicates that the doubled amino acid is glycine. The sequences fall into place if we begin with the N-terminal end.

	Ser	Gly	Gly			
	fragment	Gly	Gly	Ala	third fragment	
				Ala	Val	second
				Val	Trp	fourth fragment
				Trp	Val	first fragment
hexapeptide sequence	Ser	Gly	Gly	Ala	Val	Trp

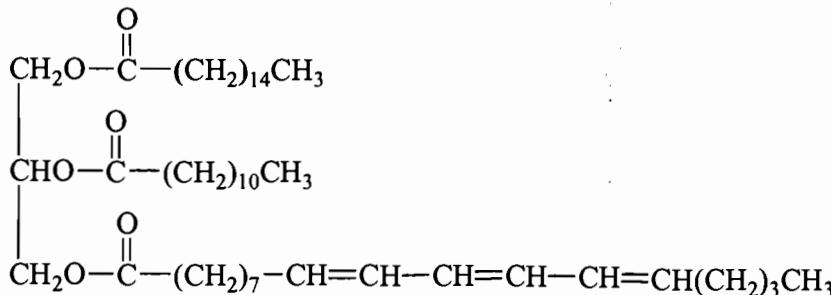
## REVIEW QUESTIONS

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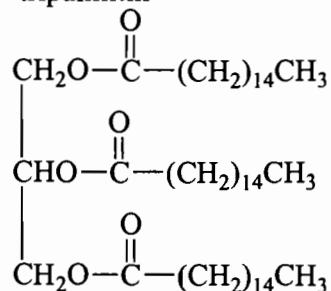
1. (a) (+) is another way of designating a dextrorotatory compound.
- (b) L indicates that, in the Fisher projection of the compound, the — OH group on the penultimate carbon atom is to the left and the — H group is to the right.
- (c) A sugar is a carbohydrate that is either a monosaccharide or an oligosaccharide.
- (d) An  $\alpha$  -amino acid is a carboxylic acid that has an amine group on the carbon next to the — COOH group, that is, on the  $\alpha$  carbon atom. Glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) is the simplest  $\alpha$  -amino acid.
- (e) The pH at which the zwitterion form of an amino acid predominates in solution is known as the isoelectric point. The isoelectric point of glycine is  $\text{pI} = 6.03$ .
2. (a) Saponification is the hydrolysis of a triglyceride in alkaline solution to produce glycerol and soaps: salts of fatty acids.
- (b) A chiral carbon atom is one that exhibits optical isomerism, one to which four different groups are attached.
- (c) A racemic mixture is one composed of equal amounts of an optically active compound and its enantiomer. Since these two compounds rotate polarized light by the same amount but in opposite directions, such a mixture does not rotate the plane of polarized light.
- (d) The denaturation of a protein is the process in which the protein is treated with somewhat harsh conditions and loses at least some of its secondary or tertiary structure, temporarily or permanently, leading to a loss of biological activity.
3. (a) A fat is a triglyceride in which the fatty acid chains are predominantly saturated hydrocarbon chains. Fats are solids at room temperature. An oil is a triglyceride in which the fatty acid chains are to predominantly unsaturated. Oils are liquids at room temperature.
- (b) Enantiomers are optically active isomers of a compound that are mirror images of each other. Diastereomers are optically active isomers that are not mirror images.
- (c) The primary structure of a protein refers to the sequence of amino acids. The secondary structure describes the shape of that polypeptide chain.
- (d) DNA is deoxyribonucleic acid, RNA is ribonucleic acid. They differ by an O atom. DNA is found in the cell nucleus, RNA in the cytoplasm.
- (e) ADP is adenosine diphosphate, ATP is adenosine triphosphate. They differ by a phosphate group.

4. (a)  $C_{15}H_{31}COOH$  is palmitic acid.  $C_{17}H_{29}COOH$  is linolenic acid or eleosteric acid.  $C_{11}H_{23}COOH$  is lauric acid. Thus, the given compound is glyceryl palmitolinolenolaurate or glyceryl palmitoleoleosteroesterolaurate.
- (b)  $C_{17}H_{33}COOH$  is oleic acid. Thus, the compound is glyceryl trioleate or triolein.
- (c)  $C_{13}H_{27}COOH$  is myristic acid. Thus, the compound is sodium myristate.

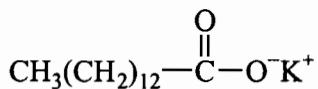
5. (a) glyceryl palmitolauroeleosteroesterate



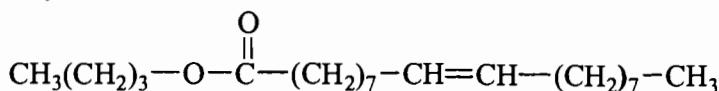
- (b) tripalmitin



- (c) potassium myristate

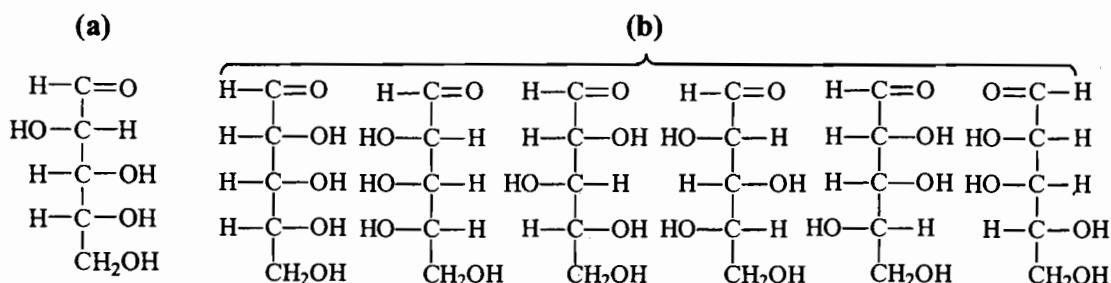


- (d) butyl oleate

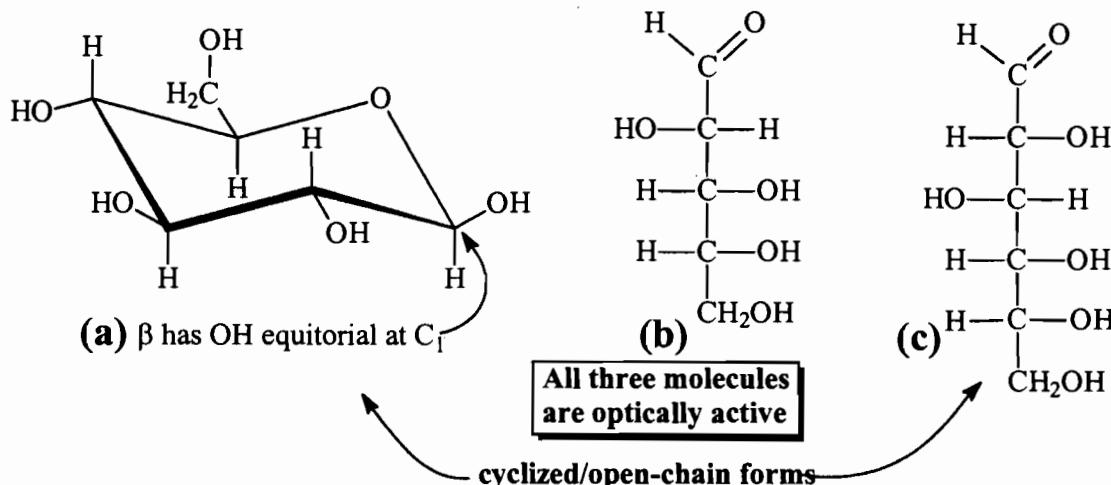


6. A DL mixture contains equal amounts of both enantiomers. This is also known as a racemic mixture. The optical activities of the two enantiomers cancel each other out, and the mixture rotates the plane of polarized light neither to the right nor to the left. Thus, statement (4) is the most appropriate.

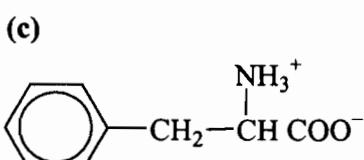
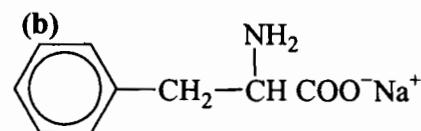
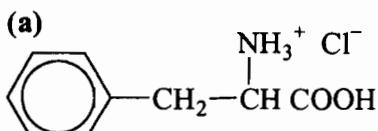
7. (a) D-(-)-arabinose is the optical isomer of L-(+)-arabinose. Its structure is shown below.
- (b) A diastereomer of L-(+)-arabinose is a molecule that is its optical isomer, but not its mirror image. There are several such diastereomers, some of which follows, at right.

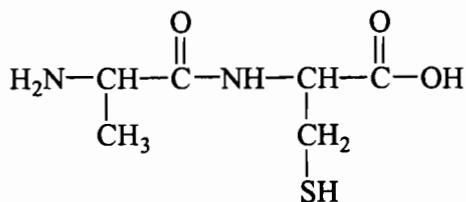


8.

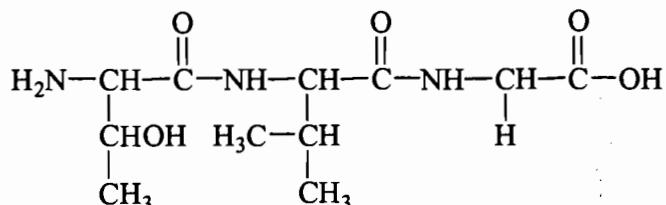
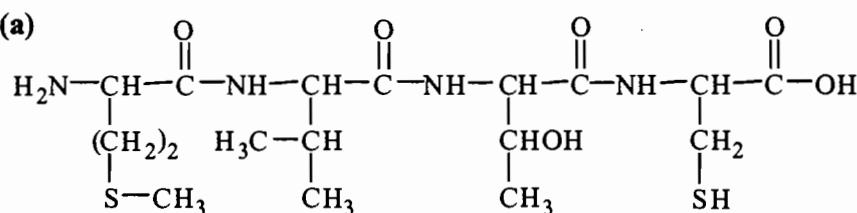


9. The pI of phenylalanine is 5.74. Thus, phenylalanine is in the form of a cation in 1.0 M HCl (pH = 0.0), in the form of an anion in 1.0 M NaOH (pH = 14.0), and in the form of a zwitterion at pH = 5.7. These three structures follow.



10. (a) alanylcytisteine

## (b) threonylvalylglycine

11.

## (b) methionylvalylthreonylcytisteine

12. The bases are on the right side of the Figure. From the top down, they are: adenine (purine), uracil (pyrimidine), guanine (purine), and cytosine (pyrimidine). The pentose sugars have five-membered rings as their carbon skeletons; they are ribose sugars, and hence this is a chain of RNA. The phosphate groups are five-membered groups centered on P atoms and surrounded by O atoms.

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**EXERCISES**

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**Structure and Composition of the Cell**

13. The volume of a cylinder is given by  $V = \pi r^2 h = \pi d^2 h / 4$ .

$$V = \left[ 3.14159 (1 \times 10^{-6} \text{ m})^2 (2 \times 10^{-6} \text{ m}) / 4 \right] \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 1.6 \times 10^{-15} \text{ L}$$

The volume of the solution in the cell is  $V_{\text{soln}} = 0.80 \times 1.6 \times 10^{-15} \text{ L} = 1.3 \times 10^{-15} \text{ L}$ .

$$(a) [\text{H}^+] = 10^{-6.4} = 4 \times 10^{-7} \text{ M}$$

$$\begin{aligned} \text{no. H}_3\text{O}^+ \text{ ions} &= 1.3 \times 10^{-15} \text{ L} \times \frac{4 \times 10^{-7} \text{ mol H}^+ \text{ ions}}{1 \text{ L soln}} \times \frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol ions}} \\ &= 3 \times 10^2 \text{ H}_3\text{O}^+ \text{ ions} \end{aligned}$$

(b) no.  $K^+$  ions =  $1.3 \times 10^{-15} \text{ L} \times \frac{1.5 \times 10^{-4} \text{ mol } K^+ \text{ ions}}{1 \text{ L soln}} \times \frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol ions}}$   
no.  $K^+$  ions =  $1.2 \times 10^5 K^+ \text{ ions}$

15. mass of protein in cytoplasm =  $0.15 \times 0.90 \times 2 \times 10^{-12} \text{ g} = 2.7 \times 10^{-13} \text{ g.}$

no. of protein molecules =  $2.7 \times 10^{-13} \text{ g} \times \frac{1 \text{ mol protein}}{3 \times 10^4 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol protein}}$   
=  $5 \times 10^6$  protein molecules

## Lipids

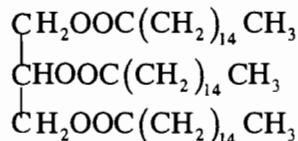
17. (a)

Trilaurin	Trilinolein
$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{CH}_2-\text{O}-\text{C}-\text{C}_{11}\text{H}_{23} \\    \\  \text{CH}-\text{O}-\text{C}-\text{C}_{11}\text{H}_{23} \\    \\  \text{O} \\  \parallel \\  \text{CH}_2-\text{O}-\text{C}-\text{C}_{11}\text{H}_{23}  \end{array}  $	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{CH}_2-\text{O}-\text{C}-\text{C}_{17}\text{H}_{31} \\    \\  \text{CH}-\text{O}-\text{C}-\text{C}_{17}\text{H}_{31} \\    \\  \text{O} \\  \parallel \\  \text{CH}_2-\text{O}-\text{C}-\text{C}_{17}\text{H}_{31}  \end{array}  $
A triglyceride or glycerol ester	A triglyceride or glycerol ester
Saturated triglyceride -made using saturated acid	Unsaturated triglyceride -made using unsaturated acid
A fat (usually solid at room temperature)	An oil (usually liquid at room temperature)

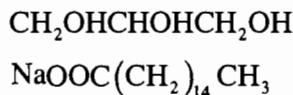
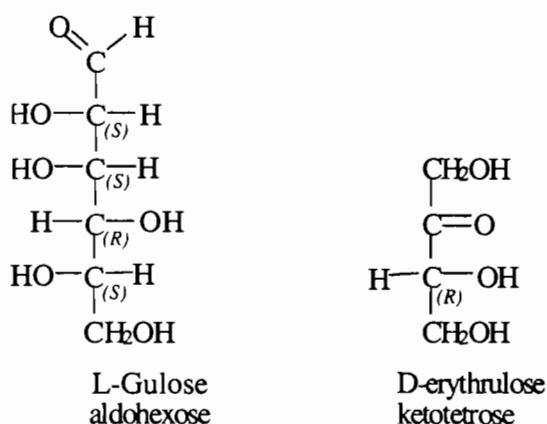
(b) Soaps: salt of fatty acids (from saponification of triglycerides)

Phospholipids: derived from glycerols, fatty acids, phosphoric acid and a nitrogen containing base (Both have hydrophilic heads and hydrophobic tails)

19. Polyunsaturated fatty acids are characterized by a large number of  $C=C$  double bonds in their hydrocarbon chain. Stearic acid has no  $C=C$  double bonds and therefore is not unsaturated, let alone polyunsaturated. But eleostearic acid has three  $C=C$  double bonds and thus is polyunsaturated. Polyunsaturated fatty acids are recommended in dietary programs since saturated fats are linked to a high incidence of heart disease. Of the lipids listed in Table 28-2, safflower oil has the highest percentage of unsaturated fatty acids, predominately linoleic acid, an unsaturated fatty acid with two  $C=C$  bonds.

**21.** tripalmitin

saponification products of tripalmitin:  
sodium palmitate and glycerol

**Carbohydrates****23.**

- 25. (a)** A dextrorotatory compound rotates the plane of polarized light to the right: clockwise.
- (b)** A levorotatory compound is one that rotates the plane of polarized light to the left: counterclockwise.
- (c)** A racemic mixture has equal amounts of an optically active compound and its enantiomer. Since these two compounds rotate polarized light by the same amount but in opposite directions, such a mixture does not rotate the plane of polarized light.
- (d)** (R) In organic nomenclature, this designation is given to a chiral carbon atom. First, we must assign priorities to the four substituents on the chiral carbon atom. With the lowest priority group pointing directly away from the viewer, we say that the stereogenic center has an R-configuration if a curved arrow from the group of highest priority through to the one of lowest priority is drawn in a clockwise direction.

- 27.** A reducing sugar has a sufficient amount of the straight-chain form present in equilibrium with its cyclic form such that the sugar will reduce  $\text{Cu}^{2+}(\text{aq})$  to insoluble, red  $\text{Cu}_2\text{O}(\text{s})$ . Only free aldehyde groups are able to reduce the copper(II) ion down to copper (I).

Next, we need to calculate the mass of  $\text{Cu}_2\text{O}$  expected when 0.500 g of glucose is oxidized in the reducing sugar test:

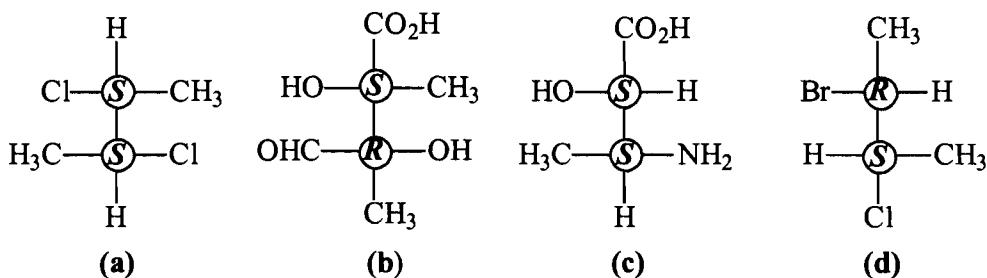
$$\text{Mass Cu}_2\text{O} (\text{g}) = \frac{1 \text{ mol glucose}}{180.2 \text{ g glucose}} \times \frac{2 \text{ mol Cu}^{2+}}{1 \text{ mol glucose}} \times \frac{1 \text{ mol Cu}_2\text{O}}{2 \text{ mol Cu}^{2+}} \times \frac{143.1 \text{ g Cu}_2\text{O}}{1 \text{ mol Cu}_2\text{O}} = 0.397 \text{ g Cu}_2\text{O}$$

- 29.** Enantiomers are alike in all respects, including in the degree to which they rotate polarized light. They differ only in the direction in which this rotation occurs. Since  $\alpha$ -glucose and  $\beta$ -glucose rotate the plane of polarized light by different degrees, and in the same direction, they are not enantiomers, but rather diastereomers.

### Fischer Projections and *R,S* Nomenclature

- 31.** a) Enantiomers: *S*-config. (leftmost structure), *R*-config. (rightmost structure)  
 b) Same molecule: both *R*-configuration  
 c) Diastereomers: *S,R* config. (leftmost structure-top to bottom),  
     *S,S*-config. (rightmost structure)  
 d) Diastereomers: *R,R*-config (leftmost structure-top to bottom),  
     *R, S*-config. (rightmost structure-top to bottom)

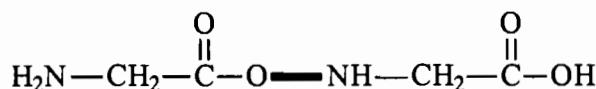
**33.**



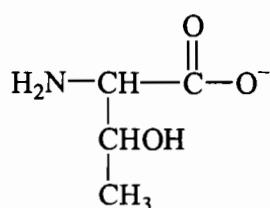
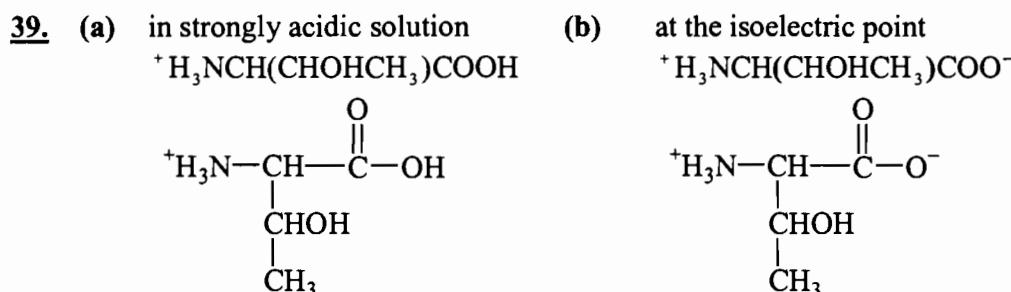
### Amino acids, Polypeptides, and Proteins

- 35.** (a) An  $\alpha$ -amino acid has an amine group ( $-\text{NH}_2$ ) bonded to the same carbon as the carboxyl group ( $-\text{COOH}$ ). For example: glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) is the simplest  $\alpha$ -amino acid.  
 (b) A zwitterion is a form of an amino acid where the amine group is protonated ( $-\text{NH}_3^+$ ) and the carboxyl group is deprotonated ( $-\text{COO}^-$ ). The zwitterion form of glycine is  $^+\text{H}_3\text{NCH}_2\text{COO}^-$ .

- (c) The pH at which the zwitterion form of an amino acid predominates in solution is known as the isoelectric point. The isoelectric point of glycine is  $pI = 6.03$ .
- (d) The peptide bond is the bond that forms between the carbonyl group of one amino acid and the amine group of another, with the elimination of a water molecule between them. The peptide bond between two glycine molecules is shown as an outlined bold dash (—) in the structure below.

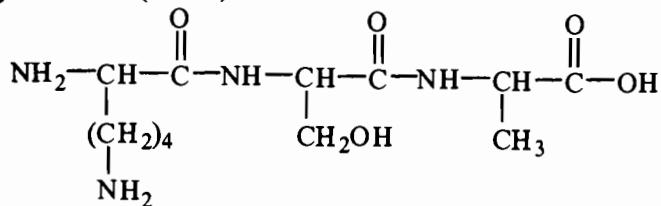


- (e) Tertiary structure describes how a coiled protein chain further interacts with itself to wrap into a cluster through a combination of salt linkages, hydrogen bonding and disulfide linkages, to name a few.
37.  $\text{pH} = 6.3$  is near the isoelectric point of proline (6.21). Thus proline will not migrate very effectively under these conditions. But  $\text{pH} = 6.3$  is considerably more acidic than the isoelectric point of lysine ( $pI = 9.74$ ). Thus, lysine is positively charged in this solution and will migrate toward the negatively charged cathode. And  $\text{pH} = 6.3$  is much less acidic than the isoelectric point of aspartic acid ( $pI = 2.96$ ). Aspartic acid, therefore, is negatively charged in this solution and will migrate toward the positively charged anode.

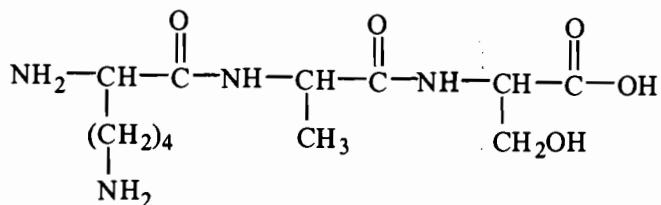


41. (a) The structures of the six tripeptides that contain one each of the amino acids alanine, serine, and lysine are drawn below (in no particular order).

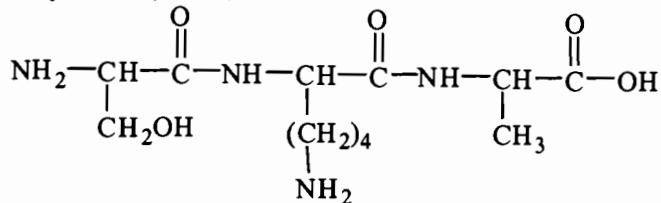
Lys-Ser-Ala (1 of 6)



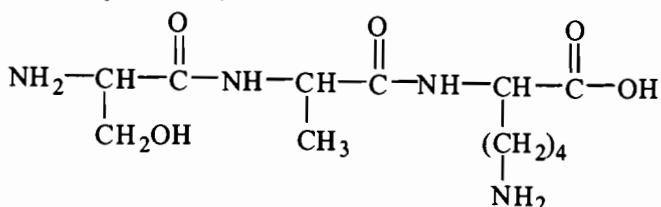
Lys-Ala-Ser (2 of 6)



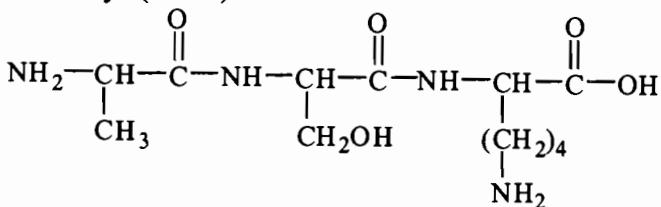
Ser-Lys-Ala (3 of 6)



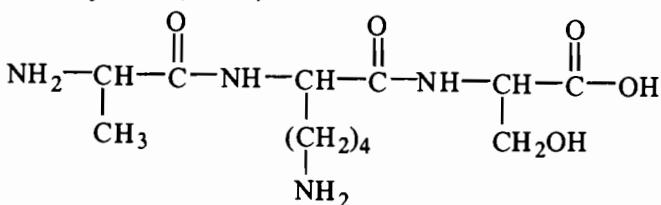
Ser-Ala-Lys (4 of 6)



Ala-Ser-Lys (5 of 6)

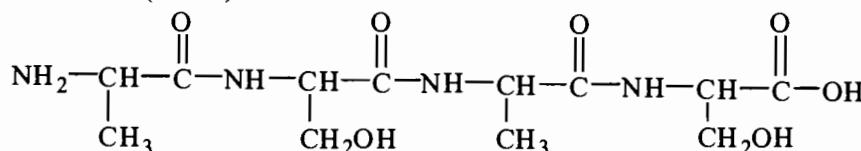


Ala-Lys-Ser (6 of 6)

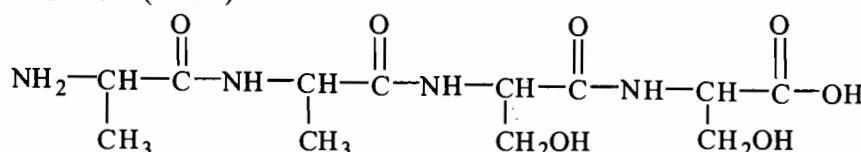


- (b) The structures of the six tetrapeptides that contain two serine and two alanine amino acids each follow (in no particular order).

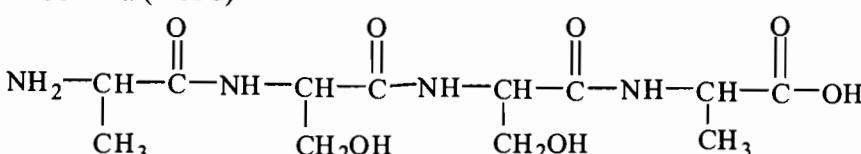
Ala-Ser-Ala-Ser (1 of 6)



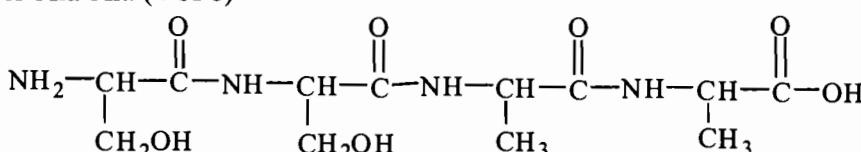
Ala-Ala-Ser-Ser (2 of 6)



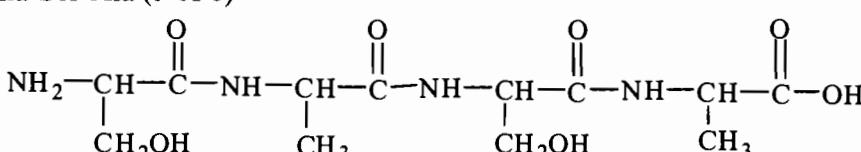
Ala-Ser-Ser-Ala (3 of 6)



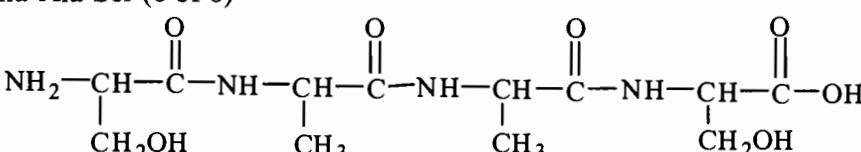
Ser-Ser-Ala-Ala (4 of 6)



Ser-Ala-Ser-Ala (5 of 6)



Ser-Ala-Ala-Ser (6 of 6)



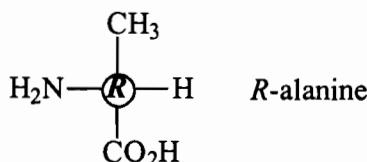
43. (a) We put the fragments together as follows, starting from the Ala end, simply placing them down in a matching pattern. We do not assume that the fragments are given with the N-terminal end first.

Fragments:	Ala	Ser				3rd fragment
	Ser	Gly	Val			1st fragment
		Gly	Val	Thr		5th fragment
			Val	Thr		2nd fragment, reversed
			Val	Thr	Leu	4th fragment, reversed
Result:	Ala	Ser	Gly	Val	Thr	Leu

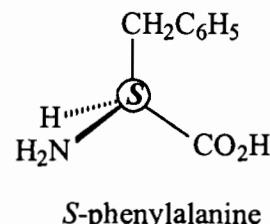
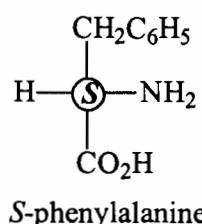
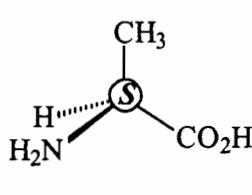
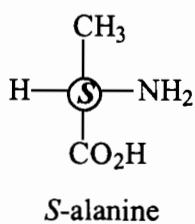
(b) alanyl-seryl-glycyl-valyl-threonyl-leucine, or alanylserylglycylvalylthreonylleucine

45. The *primary* structure of an amino acid is the sequence of amino acids in the chain of the polypeptide. The secondary structure describes how the protein chain is folded, coiled, or convoluted. Possible structures include  $\alpha$ -helices and  $\beta$ -pleated sheets. This secondary structure is held together principally by hydrogen bonds. The *tertiary* structure of a protein refers to how different parts of the molecules, often quite distant from each other, are held together into crudely spherical shapes. Although hydrogen bonding is involved here as well, disulfide linkages, hydrophobic interactions, and hydrophilic interactions (salt linkages) are responsible as well for tertiary structure. Finally, quaternary structure refers to how two or more protein molecules pack together into a larger protein complex. Not all proteins have a quaternary structure since many proteins have but one polypeptide chain.

47.

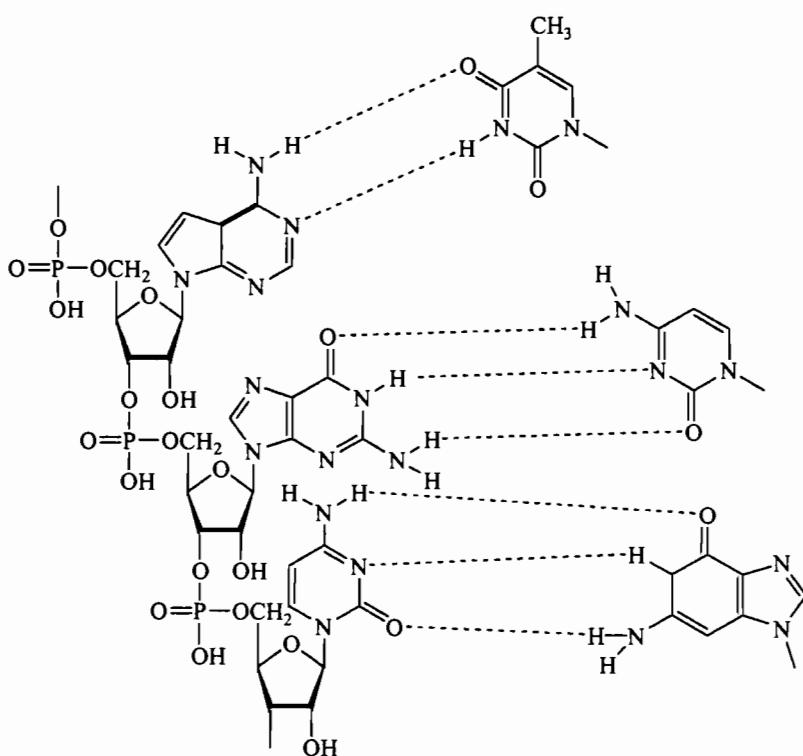


49.



## Nucleic Acids

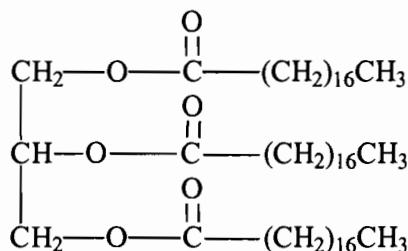
51. The two major types of nucleic acids are DNA, deoxyribonucleic acid, and RNA, ribonucleic acid. Both of them contain phosphate groups. These phosphate groups alternate with sugars to form the backbone of the molecule. These sugars are deoxyribose in the case of DNA and ribose in the case of RNA. Attached to each sugar is a purine or a pyrimidine base. The purine bases are adenine and guanine. One pyrimidine base is cytosine. In the case of RNA the other pyrimidine base is uracil, while in the case of DNA the other pyrimidine base is thymine.
53. The complementary sequence to AGC is TCG. The hydrogen bonding is shown in the drawing below. One polynucleotide chain is completely shown, as is the hydrogen bonding to the bases in the other polynucleotide chain. Because of the distortions that result from depicting a 3-D structure in two dimensions, the H- bonds themselves are distorted (they are all of approx. equal length) and the second sugar phosphate chain has been omitted.



## FEATURE PROBLEMS

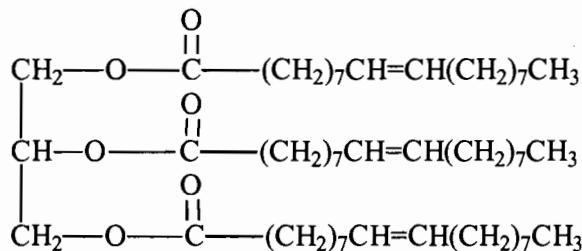
**70.**

**Glyceryl Tristearate**



Molar Mass = 891.5 g mol<sup>-1</sup>

**Glyceryl Trioleate**



Molar Mass = 885.45 g mol<sup>-1</sup>

(a) Saponification value of glyceryl tristearate: mass of KOH

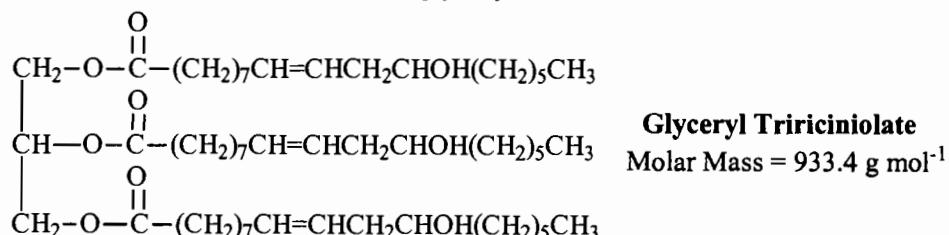
$$\begin{aligned}
 &= 1.00 \text{ g glyceryl tristearate} \times \frac{1 \text{ mol glyceryl tristearate}}{891.5 \text{ g glyceryl tristearate}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol glyceryl tristearate}} \\
 &\times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}} = 0.189 \text{ g KOH or } 189 \text{ mg KOH}
 \end{aligned}$$

Saponification value = 189

Iodine number for glyceryl trioleate: mass of I<sub>2</sub>

$$\begin{aligned}
 &= 100 \text{ g glyceryl trioleate} \times \frac{1 \text{ mol glyceryl trioleate}}{885.45 \text{ g glyceryl trioleate}} \times \frac{3 \text{ mol I}_2}{1 \text{ mol glyceryl trioleate}} \\
 &\times \frac{253.81 \text{ g I}_2}{1 \text{ mol I}_2} = 86.0 \text{ g I}_2 \quad \text{Iodine number} = 86.0
 \end{aligned}$$

(b) If we assume that castor oil is all glyceryl triricinolate



Iodine number for glyceryl triricinolate: mass of I<sub>2</sub>

$$\begin{aligned}
 &= 100 \text{ g glyceryl triricinolate} \\
 &\times \frac{1 \text{ mol glyceryl triricinolate}}{933.4 \text{ g glyceryl triricinolate}} \times \frac{3 \text{ mol I}_2}{1 \text{ mol glyceryl triricinolate}} \times \frac{253.81 \text{ g I}_2}{1 \text{ mol I}_2} \\
 &= 81.6 \text{ g I}_2 \quad \text{Iodine number} = 81.6
 \end{aligned}$$

Saponification value of glyceryl triricinolate: mass of KOH

= 1.00 g glyceryl triricinolate

$$\times \frac{1 \text{ mol glyceryl triricinolate}}{933.4 \text{ g glyceryl triricinolate}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol glyceryl triricinolate}} \times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}}$$

$$= 0.180 \text{ g KOH or } 180. \text{ mg KOH} \quad \text{Saponification value} = 180.$$

c) Safflower oil: Consider each component

**Palmitic acid:** Molar mass:  $C_3H_5(C_{15}H_{31}CO_2)_3 = 807.34 \text{ g mol}^{-1}$

Iodine number = 0 (saturated)

Saponification value of palmitic acid: mass of KOH

= 1.00 g palmitic acid

$$\times \frac{1 \text{ mol palmitic acid}}{807.33 \text{ g palmitic acid}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol palmitic acid}} \times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}}$$

$$= 0.208 \text{ g KOH or } 208 \text{ mg KOH} \quad \text{Saponification value} = 208$$

**Stearic acid:** Molar mass:  $C_3H_5(C_{17}H_{35}CO_2)_3 = 891.49 \text{ g mol}^{-1}$

Iodine number = 0 (saturated)

Saponification value of stearic acid: mass of KOH

$$= 1.00 \text{ g stearic acid} \times \frac{1 \text{ mol stearic acid}}{891.49 \text{ g stearic acid}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol stearic acid}} \times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}}$$

$$= 0.189 \text{ g KOH or } 189 \text{ mg KOH} \quad \text{Saponification value} = 189$$

**Oleic acid:** Molar mass:  $C_3H_5(C_{17}H_{33}CO_2)_3 = 885.45 \text{ g mol}^{-1}$

Iodine number for oleic acid: mass of  $I_2$

$$= 100 \text{ g oleic acid} \times \frac{1 \text{ mol oleic acid}}{885.45 \text{ g oleic acid}} \times \frac{3 \text{ mol } I_2}{1 \text{ mol oleic acid}} \times \frac{253.81 \text{ g } I_2}{1 \text{ mol } I_2} = 86.0 \text{ g } I_2$$

Iodine number = 86.0

Saponification value of oleic acid: mass of KOH

$$= 1.00 \text{ g oleic acid} \times \frac{1 \text{ mol oleic acid}}{885.45 \text{ g oleic acid}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol oleic acid}} \times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}}$$

$$= 0.190 \text{ g KOH or } 190. \text{ mg KOH} \quad \text{Saponification value} = 190.$$

**Linoleic acid:** Molar mass:  $C_3H_5(C_{17}H_{31}CO_2)_3 = 879.402 \text{ g mol}^{-1}$

Iodine number for linoleic acid: mass of  $I_2$

$$= 100 \text{ g linoleic acid} \times \frac{1 \text{ mol linoleic acid}}{879.402 \text{ g linoleic acid}} \times \frac{6 \text{ mol } I_2}{1 \text{ mol linoleic acid}} \times \frac{253.81 \text{ g } I_2}{1 \text{ mol } I_2}$$

$$= 173 \text{ g } I_2 \quad \text{Iodine number} = 173$$

Saponification value of linoleic acid: mass of KOH

$$= 1.00 \text{ g linoleic acid} \times \frac{1 \text{ mol linoleic acid}}{879.402 \text{ g linoleic acid}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol linoleic acid}} \times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}}$$

$$= 0.191 \text{ g KOH or } 191 \text{ mg KOH} \quad \text{Saponification value} = 191$$

**Linolenic acid:** Molar mass:  $C_3H_5(C_{17}H_{29}CO_2)_3 = 873.348 \text{ g mol}^{-1}$

Iodine number for linolenic acid: mass of  $I_2$

$$= 100 \text{ g linolenic acid} \times \frac{1 \text{ mol linolenic acid}}{873.354 \text{ g linolenic acid}} \times \frac{9 \text{ mol } I_2}{1 \text{ mol linolenic acid}} \times \frac{253.81 \text{ g } I_2}{1 \text{ mol } I_2}$$

$$= 261.6 \text{ g } I_2 \quad \text{Iodine number} = 261.6 \approx 262$$

Saponification value of linolenic acid: mass of KOH

$$= 1.00 \text{ g linolenic acid} \times \frac{1 \text{ mol linolenic acid}}{873.354 \text{ g linolenic acid}} \times \frac{3 \text{ mol KOH}}{1 \text{ mol linolenic acid}} \times \frac{56.1056 \text{ g KOH}}{1 \text{ mol KOH}}$$

$$= 0.193 \text{ g KOH or } 193 \text{ mg KOH} \quad \text{Saponification value} = 193$$

**Summary:**

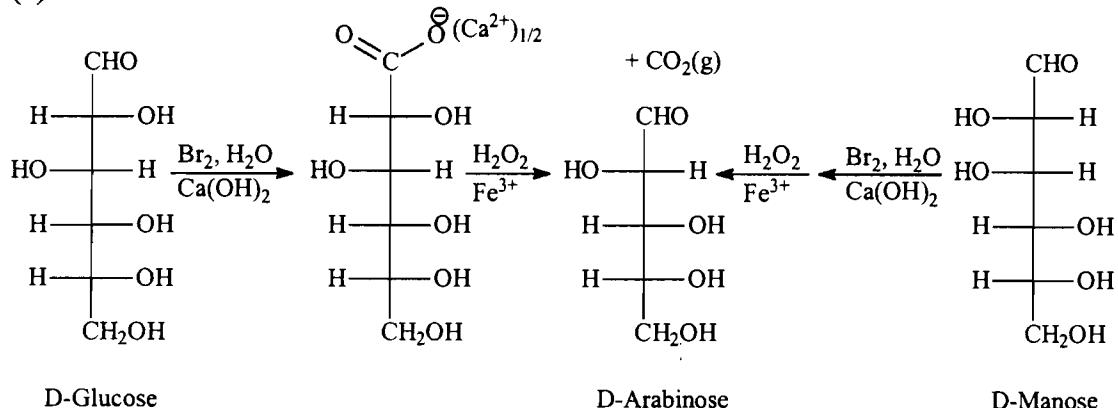
			High $I_2$ #	Low $I_2$ #	High Sap#	Low Sap#
Acid	$I_2$ #	Sap#	%	%	%	%
Palmitic	0	208	6-7	6	7	6
Stearic	0	189	2-3	2	3	3
Oleic	86	190	12-14	12	14	12
Linoleic	173	191	75-80	78.5	75.5	87.5
Linolenic	262	193	0.5-1.5	1.5	0.5	1.5
						0.5

Hence: The iodine number for safflower oil may range between 150 – 144

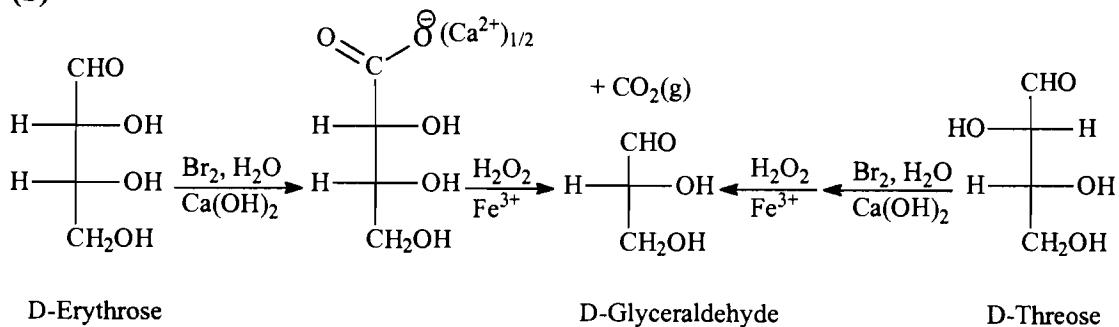
The saponification value for safflower oil may range between 211 – 179

(Note: the high iodine number contribution for each acid in the mixture is calculated by multiplying its percentage by its iodine number. The sum of all of the high iodine number contributions for all of the components in the mixture equals the high iodine number for safflower oil. Similar calculations were used to obtain the Low iodine number, along with the High/Low saponification numbers.)

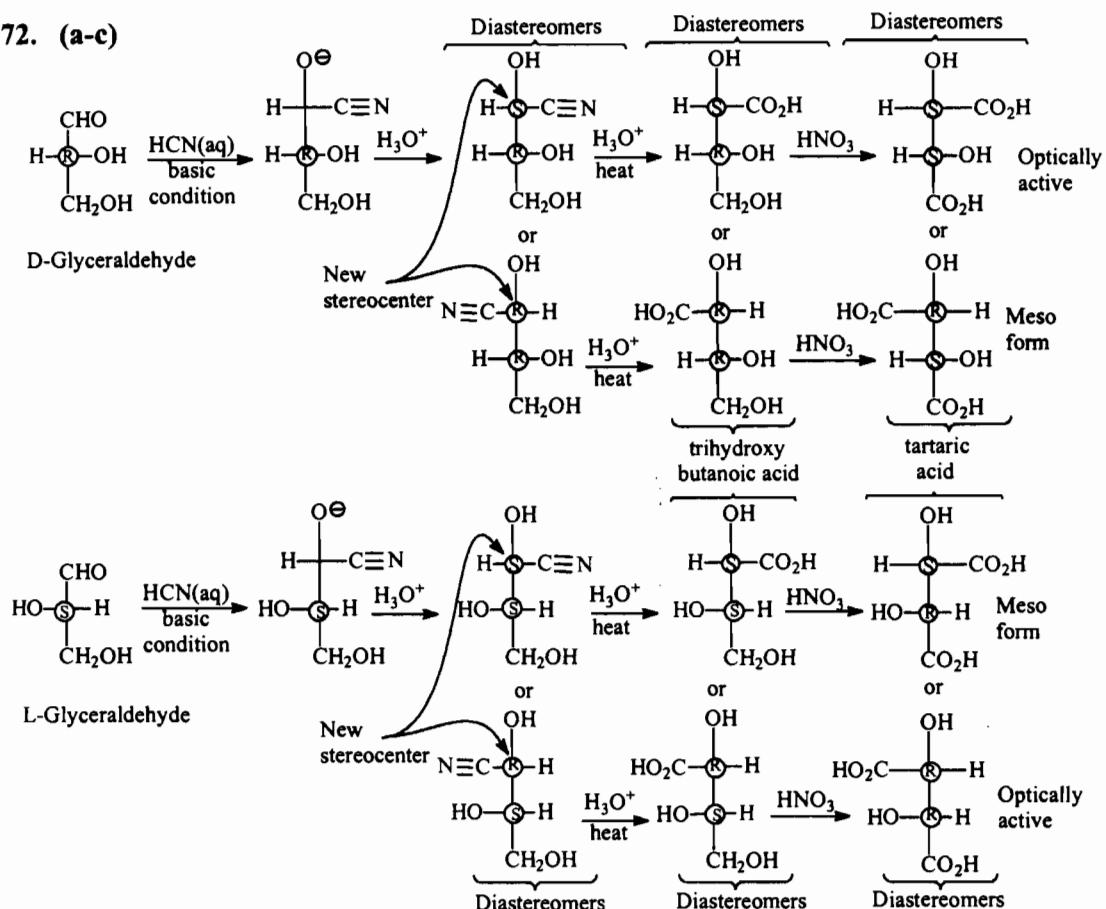
71. (a)



(b)

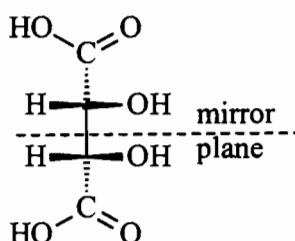


72. (a-c)



acid

(d) Meso form of Tartaric



Meso Form is not optically active because one end of the molecule rotates polarized light by  $+x$  degrees, the other end of the molecule rotates polarized light by  $-x$  degrees. The net result is that polarized light is unaffected by this type of compound, even though it has two chiral carbons. Meso forms must have a mirror image running through them, for every chiral carbon, there must exist its mirror image on the other side of the molecule.