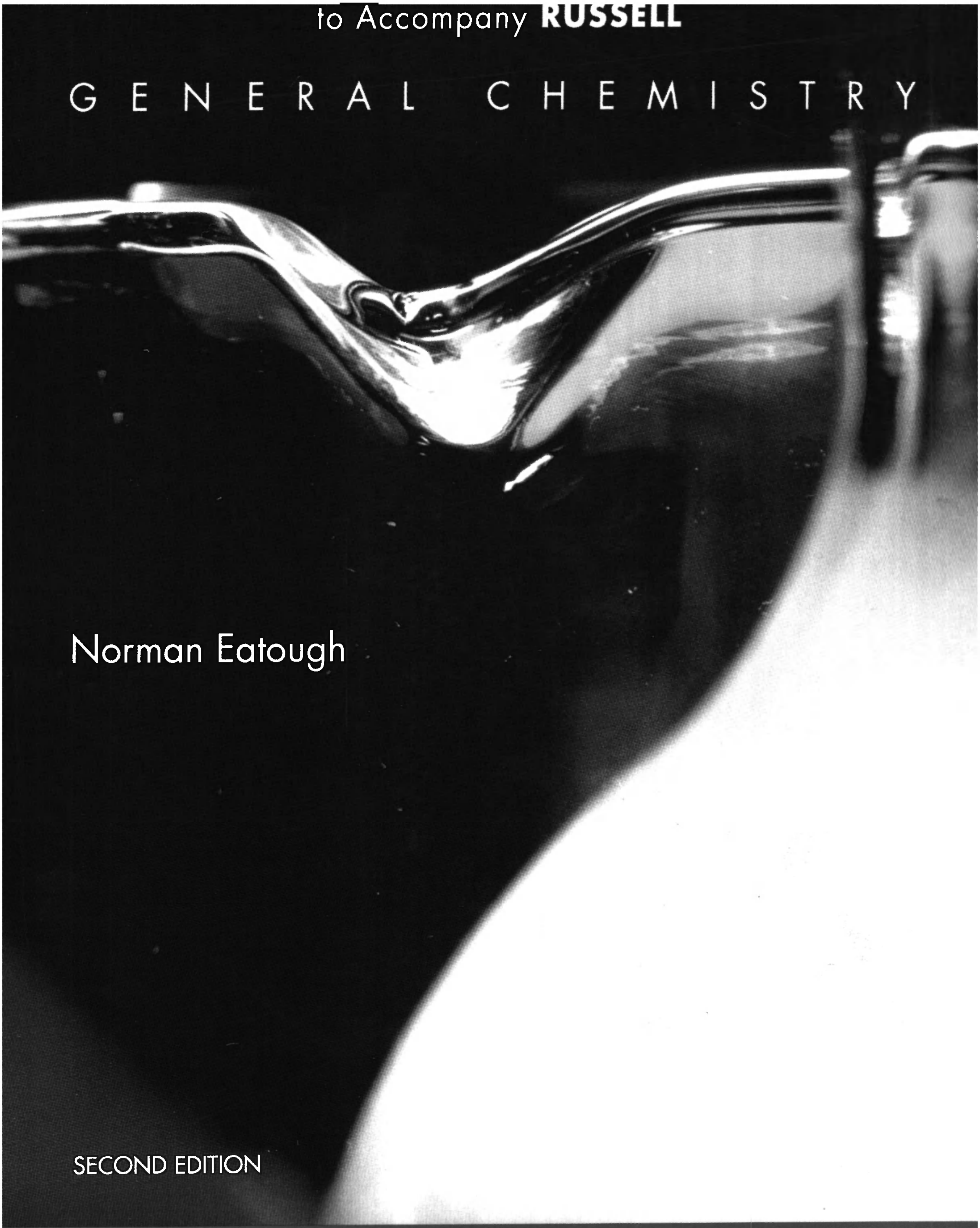
to Accompany **RUSSELL**
GENERAL CHEMISTRY



Norman Eatough

SECOND EDITION

THE PERIODIC TABLE OF THE ELEMENTS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
IUPAC groups → Traditional groups (USA) →	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0	
Periods 1									1 **H** 1.008									2 **He** 4.003	1
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18	2
3	11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95	3
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80	4
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** [98.91]	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3	5
6	55 **Cs** 132.9	56 **Ba** 137.3	71 **Lu** 175.0	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.1	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.7	83 **Bi** 209.0	84 **Po** [209.0]	85 **At** [210.0]	86 **Rn** [222.0]	6
7	87 **Fr** [223.0]	88 **Ra** [226.0]	103 **Lr** [260.1]	104 **Unq** [261.1]	105 **Unp** [262.1]	106 **Unh** [263.1]	107 **Uns** [262.1]	108 **Uno** [265.1]	109 **Une** [266.1]										7

57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** [144.9]	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0
89 **Ac** [227.0]	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** [237.0]	94 **Pu** [244.1]	95 **Am** [243.1]	96 **Cm** [247.1]	97 **Bk** [247.1]	98 **Cf** [251.1]	99 **Es** [252.1]	100 **Fm** [257.1]	101 **Md** [258.1]	102 **No** [259.1]

Key

Atomic number	27
Symbol	**Co**
Atomic mass	58.93

Values in brackets are masses of most stable isotopes.

THE ELEMENTS: NAMES, SYMBOLS, ATOMIC NUMBERS, AND ATOMIC MASSES

Element	**Symbol**	**Atomic number**	**Atomic mass***
Actinium	Ac	89	[227.02] (^{227}Ac)
Aluminum	Al	13	26.982
Americium	Am	95	[243.06] (^{243}Am)
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.922
Astatine	At	85	[209.99] (^{210}At)
Barium	Ba	56	137.33
Berkelium	Bk	97	[247.07] (^{247}Bk)
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.98
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.078
Californium	Cf	98	[251.08] (^{251}Cf)
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.933
Copper	Cu	29	63.546
Curium	Cm	96	[247.07] (^{247}Cm)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	[252.08] (^{252}Es)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	[257.10] (^{257}Fm)
Fluorine	F	9	18.998
Francium	Fr	87	[223.02] (^{223}Fr)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Helium	He	2	4.0026
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lw	103	[260.11] (^{260}Lw)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.938
Mendelevium	Md	101	[258.10] (^{258}Md)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94

Element	**Symbol**	**Atomic number**	**Atomic mass***
Neodymium	Nd	60	144.24
Neon	Ne	10	20.180
Neptunium	Np	93	[237.05] (^{237}Np)
Nickel	Ni	28	58.69
Niobium	Nb	41	92.906
Nitrogen	N	7	14.007
Nobelium	No	102	[259.10] (^{259}No)
Osmium	Os	76	190.2
Oxygen	O	8	15.999
Palladium	Pd	46	106.42
Phosphorus	P	15	30.974
Platinum	Pt	78	195.08
Plutonium	Pu	94	[244.06] (^{244}Pu)
Polonium	Po	84	[208.98] (^{209}Po)
Potassium	K	19	39.098
Praseodymium	Pr	59	140.91
Promethium	Pm	61	[144.91] (^{145}Pm)
Protactinium	Pa	91	231.04
Radium	Ra	88	[226.03] (^{226}Ra)
Radon	Rn	86	[222.02] (^{222}Rn)
Rhenium	Re	75	186.21
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.468
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.36
Scandium	Sc	21	44.956
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.87
Sodium	Na	11	22.990
Strontium	Sr	38	87.62
Sulfur	S	16	32.066
Tantalum	Ta	73	180.95
Technetium	Tc	43	[97.907] (^{98}Tc)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.93
Thallium	Tl	81	204.38
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.71
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Unnilennium	Une	109	[266.14] (^{266}Une)
Unnilhexium	Unh	106	[263.12] (^{263}Unh)
Unniloctium	Uno	108	[265.13] (^{265}Uno)
Unnilpentium	Unp	105	[262.11] (^{262}Unp)
Unnilquadium	Unq	104	[261.11] (^{261}Unq)
Unnilseptium	Uns	107	[262.12] (^{262}Uns)
Uranium	U	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.29
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.906
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.224

*Most of the values are the average masses of the atoms of the elements that occur naturally on earth. For an element that has no characteristic terrestrial distribution of natural isotopes, the atomic mass is enclosed in brackets and is the mass of the element's most stable isotope. All values are expressed relative to $^{12}\text{C} = 12$, exactly.

STUDY GUIDE

to accompany

Russell
GENERAL CHEMISTRY

STUDY GUIDE

to accompany

Russell
GENERAL CHEMISTRY
SECOND EDITION

Norman Eatough
California Polytechnic State University

McGraw-Hill, Inc.

New York St. Louis San Francisco Auckland Bogotá Caracas
Lisbon London Madrid Mexico Milan Montreal New Delhi
Paris San Juan Singapore Sydney Tokyo Toronto

To my Saturday Warriors:
Cory, Taylor, Kelci, Jordon, and Sharla

STUDY GUIDE to accompany

Russell: GENERAL CHEMISTRY

1 2 3 4 5 6 7 8 9 0 MAL MAL 9 0 9 8 7 6 5 4 3 2

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CONTENTS

TO THE STUDENT

This *Study Guide* is intended to help you understand the many principles, concepts, and calculations in general chemistry. It is written to accompany John B. Russell's *General Chemistry*, 2nd Ed. There is a section in the *Study Guide* corresponding to each section in the text. This makes it very easy to locate the examples and explanations in the *Study Guide* that correspond to specific areas in the text. The *Study Guide* is written to accompany the text, not to replace it. It should be used side by side with the text as you study. This *Study Guide* is designed to guide you through your study by helping organize concepts and correlate Learning Objectives with worked examples and homework problems in the text. Additional examples and explanations are given to illustrate all new mathematical operations and difficult concepts in the text. Each chapter in the *Study Guide* includes an overview of the text chapter, a summary of key equations when mathematical concepts are presented, an extensive list of learning objectives, an explanation of new skills including worked examples, a list of key terms and definitions, and a self test.

I Chapter Overview Chapter overviews are designed to give a brief introduction to the chapter and help you identify important concepts. Brief explanations of difficult areas and applications are given. It is intended that you read the chapter overviews before you read the corresponding text chapter or attend the lecture on that subject.

II Key Equations The most important equations are summarized and keyed to the text section. Brief explanations of the variables in the equations are included.

III Learning Objectives Learning objectives are a list of important concepts and operations presented in the chapter. They are correlated to text sections and homework problems and to the *Study Guide* New Skills section and Self Test problems. You can get maximum benefit from this section by using it to find examples and problems that apply to the specific learning objectives emphasized by your instructor.

IV New Skills Explanations and worked problems are presented to reinforce and supplement the examples and discussions in the text each time a new skill is introduced. The *Study Guide* often approaches a given concept in a manner somewhat different from the text presentation. Getting a slightly different view of a concept sometimes makes it easier to understand. Whenever a new skill is introduced, the first example is worked in step-by-step detailed procedure. When this skill is used in following examples, there will be a less detailed explanation and you will be expected to supply some steps yourself. When the explanations seem to leave out some steps, you should refer back to earlier examples involving the same skill for a more detailed presentation.

V Key Terms Significant key terms and definitions are listed with a reference to the section in the text where the term is used. It is very important that you become familiar with these terms as quickly as possible in each chapter you study. Being able to define and use scientific terms is basic to understanding the concepts and laws containing those terms. In many ways learning chemistry is much like learning a foreign language. You need to learn the vocabulary before you can learn to think in any language, including the language of chemistry. Each chapter builds on the previous work, and terms not learned will leave holes in your foundation chapters.

VI Self-Tests All chapters have true-false, completion, and multiple-choice questions. These questions are designed to test your mastery of the learning objectives. Make an honest effort to work all the problems before looking at the solutions. If you get an incorrect answer and do not understand where the error is, reread the text and *Study Guide* sections pertaining to that problem, rework the example problems, and then try the test problem again. If you are still unable to solve the problem, discuss your approach with your instructor.

Effective Study Habits No single approach to studying will work for all students. The text and *Study Guide* are designed to present concepts and problems in a logical manner, but they must be integrated into an effective total study pattern correlating text, *Study Guide*, classroom lectures, and problem sessions to give you a maximum benefit for time spent.

1 Your Effort Learning chemistry well enough to get an A is not impossible, but unless you are a gifted genius it will take considerable time and effort. You are the one who must decide to put forth the effort. This *Guide* is designed to give you the maximum benefit for your time. The key is learning to study *efficiently* so you do not waste time. A routine study schedule will help immensely, but this requires much self-discipline.

2 Preparation Before Lectures Use the *Study Guide* and text to prepare for lectures by rapidly reading the material the night before your lecture. Examine the tables, graphs, and figures so you know what will be covered in lecture. Do not expect to understand all the details and problems at this time. Even brief examination of the material *before* lecture will help you see why your instructor is covering a given topic and concentrate on how the concepts are approached and what points are emphasized. This will make the lectures more understandable. The text, the *Study Guide*, and your instructor should complement each other by presenting different views of the same material.

3 During Lecture Attend regularly and take concise notes, preferably in outline form. Your preparation before lecture will help you recognize the important points and examples as your instructor presents them.

4 After Lecture Spend some time, preferably the same day, reviewing your notes. If your notes seem sketchy, you should clarify points, add ideas, and correct errors while the lecture is still fresh on your mind. This serves the dual purpose of reinforcing concepts in your mind and providing meaningful review material to use in preparing for exams.

5 Homework Problems Often homework is not required or graded in college chemistry courses, but the types of problems assigned provide a valuable clue to what your instructor thinks is important. The more homework problems you do, the easier it will be to work similar problems on exams. Use the worked examples in the text and *Study Guide*. They are designed to help you work the problems at the end of the chapter, and they reinforce the concepts being studied.

6 Preparing for Exams The best preparation for an exam is regular and scheduled review of lecture materials every few days. Short periods of time spent in frequent reviews are much more effective than the same amount of time spent cramming the night before an exam. You learn effectively by repetition and identifying problem areas while there is still time to do something about them before exams.

7 Taking Exams If your grade depends entirely on one or two exams, they become very important. Start early to review your notes, homework problems, and examples. Try to anticipate the types of problems you are likely to encounter and work similar problems. The problems you work in class or discussion sections should be a clue to what to expect on exams. The presence of mind that comes from being well prepared can often help you over rough spots on the exam.

Problem Solving Some homework and exam problems will require mathematical operations. Usually the mathematics itself is not the major stumbling block. High-school algebra should provide sufficient background. The major challenge is transforming word problems into solutions. The best help in this area is practice. Learning by doing is the best way to develop the skills necessary to solve problems. A major purpose of the course, your text, and this *Study Guide* is to help you become proficient in solving problems.

1 Read the Problem Problems often do not explicitly state what is given and what is wanted. You will need to extract the data needed. It may help to write the data in a table when you start the problem. Determine what is wanted or expected for the solution. Look for the *find . . . how much . . .* and *what is . . .* phrases to determine what the problem is asking you to do. Be sure you understand all the terms used in the problem; use the text glossary whenever needed.

2 Plan Your Solution Only after you know what is given and what is wanted can you intelligently solve the problem. You can often use the unit-factor method to transform the data into an answer. This method is discussed in Section 1-8 of the text and *Study Guide*. You should not be worrying about plugging in numbers at this stage. Concentrate on the steps involved in arriving at an answer and try to see a pattern of steps that will take you all the way through the problem. Sometimes this may be a single equation from the text, but more often it will involve a series of equations or operations. There are usually several different methods that can be used for solving problems and no single one of these is the right way. Any method that uses sound chemical and mathematical principles is correct. The authors of the text and *Study Guide* favor the unit-factor or dimensional analysis approach whenever possible, and it will be emphasized throughout the course.

3 Solving the Problem Once you have a sound plan or equation, the problem is essentially "solved". All you have to do is substitute the given data into your plan and calculate an answer. Be sure to check to see if your answer seems reasonable. Take time to enjoy the sense of accomplishment when you arrive at this point.

4 When the Above Steps Do Not Work After applying the above approach, if an honest effort does not bear fruit and the solution evades you, seek help. Outline the best approach you have taken to the problem and show it to someone. Explaining your material to someone else is often an effective learning technique. If this still does not help, go to your instructor. Do not go with general questions or complaints such as "I don't understand this chapter." Your instructor will not be able to guess what your problems are and will not have time to give special instructions for the whole chapter. Prepare specific questions and show your approach and methods. You can expect meaningful help if you are prepared.

5 Electronic Calculators Many brands and models of fancy calculators are available on the market, but for this course an inexpensive calculator will do all you need. A hand calculator is an essential time-saving device. Choose one that has exponential or scientific display, a square root key, a log or ln key, and an inverse log or e^x key. Most instructors allow calculators on exams and students with them spend less time working the arithmetic part of problems and thus have a definite advantage over students who have not bothered to learn to use all of the function keys. Calculators are well worth the small investment. The owner's manual or instructions are the best source of information about any particular calculator. Keep them with you until you have memorized the essential operations.

Norman Eatough

Chapter 1

PRELIMINARIES AND PREMISES

CHAPTER OVERVIEW

In this introductory chapter we will be concerned with the basic methods and tools of chemistry. The first part of the chapter describes what chemistry is, why it is important, and how to study it. There is a list of key terms at the end of each chapter of the *Study Guide* along with a brief definition of each term and a notation of the section in the text where the term is discussed. It is imperative that you become familiar with these terms as quickly as possible in each chapter you study. Being able to define and use scientific terms is basic to understanding the concepts and laws containing those terms.

As you study, try to develop a better understanding of the different forms of matter, the types of energy, and how the nature of matter and energy is observed and measured. Much of this chapter is about changes in the nature and types of matter and energy and how they relate to each other.

We will see how mathematics is applied to problem solving in chemistry. There is no magic formula for working all chemistry problems, but you will see how a systematic approach to problems will solve the majority of challenges you will face.

1-1 Chemistry: what, why, and how?

Chemistry is the branch of science dealing with the nature, properties and composition of matter, its changes, and the laws describing those changes. If you have not yet read the "To the Student" section at the beginning of this *Study Guide*, do so now. Use the hints and suggestions there and in this section of the text and apply those that work for you personally.

1-2 Scientific methodology

Some scientific discoveries are made by accident or luck, but most come from an orderly and systematic approach to problems through the scientific method and the analysis of results of this method by a well-trained mind. A major objective of your chemistry course is to appreciate how the principles and laws of chemistry are uncovered and then used to predict the changes and reactions that can occur in a system. This is the scientific method in action.

1-3 Matter

Since chemistry is a study of matter and its changes, it is important to be aware of the structure of matter. Matter exists in three phases – solid, liquid, or gaseous – and can be either a pure substance or a heterogeneous or homogeneous mixture. Elements are the fundamental units of matter. There are 109 different elements, each represented by a unique chemical symbol. It would be worthwhile to learn the names and symbols of the first 30 elements. You are probably already familiar with most of them. Elements interact to form aggregates called compounds. The combination of elements in a compound is denoted by combining the chemical symbols into a chemical formula such as NaCl, H_2O, or H_2SO_4. Elements and compounds can be mixed in any proportions to form various types of mixtures. The differences between compounds and mixtures of elements are described in the text.

Chemistry is an exact science. It can be exact only if we take care to define, understand, and use words and terms in a precise manner. There are many new terms in this section. Learn them. If you have not yet found the glossary in the text, do so now and start using it.

1-4 Changes in matter

Throughout the course we will study the physical and chemical changes of matter. These changes are governed by several laws, two of which are introduced here. The law of conservation of mass states there is no gain or loss of mass during physical or chemical changes. The law of definite composition states that a given compound always has the same, definite, fixed ratio of elements.

1-5 Energy

Work is the movement of a mass against an opposing force such as gravity. Energy is the ability or capacity to do work. There are many types of energy, and energy can be transformed from one type into another. Mechanical energy can be energy of motion (kinetic energy) or energy of position (potential energy). Thermal energy and electrical energy are also commonly encountered in the study of chemistry. The law of conservation of energy states that energy can be transformed from one type to another, but cannot be created or destroyed. As the course progresses, we will see how the concepts of energy and matter are interrelated and will become aware of the energy changes that accompany changes in matter.

The differences between the terms *heat, energy,* and *temperature* should be clearly understood. Heat is energy in transit. Temperature is a measure of the average kinetic energy of the particles in an object. When heat is added to a substance the energy of the substance increases. This may result in an increase in temperature or a change in phase. This concept of adding heat to a substance during a phase change while the temperature remains constant should be clearly understood.

The unit for energy is joules. Temperature measurements throughout the text are expressed in degrees Celsius.

1-6 Numbers, their use and misuse

Many concepts in chemistry involve numbers that are almost incomprehensibly small or large. Expressing this wide range of numbers in exponential notation has several advantages. It is more compact, shows the number of significant figures explicitly, denotes the accuracy of the number, makes mathematical operations involving these large and small numbers easier, and is the only way many numbers you will use can be displayed or entered in electronic calculators.

We will review the use of exponential notation in basic mathematical operations and the use and abuse of significant figures in this section. Although these concepts will not be mentioned again, they will be used continually throughout the course. Note how significant figures are handled differently in addition and subtraction than in multiplication and division. Learn to round off answers to the number of significant figures justified by the accuracy of the number and not just copy the digits that appear on your calculator. Appendix D in the text will help if you are rusty on algebraic concepts such as the quadratic formula and logarithms.

1-7 Metric units

The SI system and the metric system of units are not identical. The SI system is much more specialized than the general metric system. The seven base units from the metric system used to form the SI system are given in Table 1-3 in the text. Combinations of two or more of the SI base units form the SI derived units shown in Table 1-4 in the text. Both SI base units and SI derived units are often used in combination with the metric prefixes in Table 1-5. Most of the units in these tables should already be familiar to you.

There are some non-SI units in common use. They are torr, millimeters of mercury (mmHg) and atmosphere (atm) for pressure, gram for mass, and liter (L) and milliliter (mL) for volume. The text uses SI units in most cases, but other units are sometimes more convenient and so will be used occasionally.

1-8 Solving numerical problems

If you are not familiar with the dimensional analysis or unit-factor method of problem solving, spend enough time on this section to see the advantages of this approach. Develop the habit of always including units on numbers you use in calculations. Observe how you can cancel units the same way you cancel algebraic quantities when multiplying or dividing. The strength in the unit factor method is its use of units as a guide in setting up problems. Proficiency in this only comes with practice. Work several problems by this method and you will soon see its power in setting up solutions to problems involving unit conversions.

The necessity of checking the units of your answer to be sure they are correct cannot be over-emphasized. It is surprising how many errors can be detected and eliminated by making sure your answer always has the correct units.

The concept of density is useful to describe the compactness of matter. It is a measure of the mass of a given volume of matter. In SI units the mass is in kilograms (kg) and the volume is in cubic meters (m^3), so the density is in kg m^{-3}. More commonly, the mass will be expressed in grams (g) and the volume in cubic centimeters (cm^3) or milliliters (mL), so the density is in g cm^{-3} or g mL^{-1}. Since a cubic centimeter is equal to a milliliter, g/cm^{-3} is equivalent to g mL^{-1}. The concept of density is simple, but note in the example problems and homework how the manner in which data are presented can make the simplicity hard to find. You will experience the chance to transform word problems into solutions and apply the techniques of problem solving discussed in the introduction to this *Study Guide* as you work density problems.

KEY EQUATION

1-5 Energy

$$^\circ C = \frac{5}{9}(^\circ F - 32)$$

LEARNING OBJECTIVES

As a result of studying Chapter 1 you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 18 of this *Study Guide*.

1-1 Chemistry: what, why, and how?

1. Define chemistry.
2. Understand why you are studying it.
3. Apply techniques to help you study efficiently.

1-2 Scientific methodology

1. Describe the acquisition of scientific knowledge in terms of observations, hypotheses, theories, and laws. (Text Prob. 1-1) (Self Test 1, 2)
2. Show how scientific theories are formulated from observations. (Text Prob. 1-3) (Self Test 1, 4, 16)
3. Tell the difference between hypothesis, theory, and law. (Text Probs. 1-2, 1-4) (Self Test 4, 16, 17)

1-3 Matter

1. Explain how mass and matter are related.
2. Explain how inertia and weight are related to mass.
3. List some differences between pure substances, mixtures, elements, and compounds. (Text Probs. 1-7, 1-9, 1-12, 1-13, 1-47, 1-48) (Self Test 20, 31).
4. Characterize each of the three states of matter.
5. Understand the meaning and use of chemical symbols and formulas. (Self Test 5).
6. Show the differences between phases, homogeneous mixtures, heterogeneous mixtures, and solutions. (Text Probs. 1-1, 1-6, 1-10, 1-47) (Self Test 9, 18, 19).
7. Reproduce the classification of matter in Fig. 1-4 of the text.

1-4 Changes in matter

1. List some differences between physical and chemical changes. (Self Test 32, 33).
2. State and understand the law of conservation of mass and use it in chemical calculations. (Text Example 1-1; Text Probs. 1-14, 1-50) (New Skills Example 1; Self Test 6, 45).
3. Calculate the percentage composition of a compound. (Text Example 1-2; Text Prob. 1-14) (New Skills Example 2; Self Test 42).
4. State and understand the law of definite composition and apply it to chemical compounds. (Text Probs. 1-13, 1-49, 1-51) (New Skills Example 3; Self Test 10, 43).

1-5 Energy

1. Write definitions of the terms *heat*, *energy*, and *work* and explain the relationship between them. (Text Prob. 1-15) (Self Test 7, 8, 21, 22).
2. Write definitions for kinetic energy and potential energy and discuss the relationship between these two types of energy. (Text Prob. 1-16, 1-17) Self Test 24, 25, 34).
3. Tell how the law of conservation of energy applies to the transformation of kinetic to potential energy. (Text Prob. 1-17).
4. Explain the difference between heat and temperature. (Text Prob. 1-15).
5. Relate temperature to kinetic energy.
6. Explain what happens when heat is added to a substance.
7. Make conversions between degrees Fahrenheit and degrees Celsius. (Text Probs. 1-19, 1-20) (New Skills Example 4; Self Test 44).

1-6 Numbers, their use and misuse

1. Express numbers in exponential notation. (Text Prob. 1-22) (New Skills Sec. 1-6; Self Test 26).
2. Explain the difference between exact numbers and measured numbers.
3. Define accuracy and precision of measured numbers and show how they are different. (Text Probs. 1-45, 1-53) (Self Test 35).

3. Define accuracy and precision of measured numbers and show how they are different. (Text Probs. 1-45, 1-53) (Self Test 35).
4. Give the number of significant figures in any number. (Text Probs. 1-21, 1-53) (New Skills Examples 9, 10; Self Test 15, 40).
5. Express answers to problems with the correct number of significant figures using the correct procedure for rounding off the answer. (Text Probs. 1-23, 1-44) (New Skills Examples 11, 12; Self Test 13, 35).
6. Use exponential notation in mathematical operations: addition, subtraction, multiplication, division, and taking roots. (Text Prob. 1-24) (New Skills Examples 5 to 8; Self Test 27).

1-7 Metric units

1. Recite the seven base units of the SI system. (Text Prob. 1-25) (Self Test 11, 23, 30).
2. Review the SI derived units in Table 1-4 in the text.
3. Know the values of the prefixes *kilo-*, *centi-*, and *milli-* used in the metric system. (Text Probs. 1-26, 1-27, 1-30, 1-31).
4. Cite the common non-SI units for pressure and volume.

1-8 Solving numerical problems

1. Use the dimensional analysis or unit-factor method in calculations. (Text Examples 1-3 to 1-6; Text Probs. 1-30 to 1-34, 1-55, 1-56) (New Skills Examples 13, 14; Self Test 14, 37 to 39).
2. Express any equality as a unit factor. (Text Probs. 1-28, 1-29) (Self Test 28, 29, 36).
3. Use units to check the correctness of answers in your calculations. (Self Test 12, 14).
4. Write a word definition for density. (Self Test 12).
5. Write a definition for density using a mathematical equation.
6. Use the concept of density in calculations of mass and volume of a substance. (Text Examples 1-7, 1-8; Text Probs. 1-35 to 1-43, 1-56) (New Skills Examples 15, 16, 17; Self Test 41).

NEW SKILLS

1-4 Changes in matter

1. Conservation of mass

The law of conservation of mass assures us that in a chemical reaction the mass of the products of the reaction must be equal to the mass of the reactants (starting materials). No mass is gained or lost in a chemical reaction. This concept allows us to make calculations involving the masses of products and starting materials in a reaction.

• EXAMPLE 1

Problem: Under certain conditions water can be decomposed into its elements, hydrogen and oxygen. When 18.0 g of water is decomposed, 16.0 g of oxygen is produced. How much hydrogen is produced?

Solution: The law of conservation of mass tells us

$$\text{Mass reactants} = \text{mass products}$$

In this decomposition water is the reactant and hydrogen and oxygen are the products, so the law of conservation of mass becomes:

$$\text{Mass water} = \text{mass hydrogen} + \text{mass oxygen}$$

Solving for mass of hydrogen

$$\text{Mass hydrogen} = \text{mass water} - \text{mass oxygen}$$

$$= 18.0\text{ g} - 16.0\text{ g} = 2.0\text{ g} \quad \bullet$$

Parallel Problem: Carbon dioxide gas is made of the elements carbon and oxygen. How many grams of carbon are in a 44.0-gram sample of carbon dioxide containing 32.0 grams of oxygen?
Ans. 12.0 g

Now do example 1-4 in the text.

2. *Law of definite composition: percentage composition of compounds*

The law of definite composition tells us that a given compound contains the same percentages of each element no matter how the compound was made. We can determine the percentage composition of the elements in a compound and know that it will always be the same.

• EXAMPLE 2

Problem: Using the data in the previous example find the percentage composition of water.

Solution: The percentage composition means the percent of the total mass that is hydrogen and the percent that is oxygen.

$$\%\text{ oxygen} = \frac{\text{mass of oxygen}}{\text{total mass of compound}} \times 100$$

$$= \frac{16.0\text{ g oxygen}}{18.0\text{ g water}} \times 100 = 88.9\%$$

$$\%\text{ hydrogen} = \frac{\text{mass of hydrogen}}{\text{total mass of compound}} \times 100$$

$$= \frac{2.0\text{ g hydrogen}}{18.0\text{ g water}} \times 100 = 11.1\%$$

CHECK: $\%\text{ hydrogen} + \%\text{ oxygen} = 100\%$

$$11.1\% + 88.9\% = 100\% \quad \bullet$$

Parallel Problem: Using the data in the previous parallel problem, find the percentage composition of carbon dioxide.
Ans. 27.3% carbon, 72.7% oxygen

3. *Law of definite composition: calculation of amounts of chemicals reacting*

The law of definite composition can also be used to calculate the mass of reactants needed to produce a given mass of products if the percentage composition is known.

• EXAMPLE 3

Problem: Teflon is a compound containing the elements carbon and fluorine. Its percentage composition is 38.7 percent carbon and 61.3 percent fluorine. How many grams of fluorine would be needed to react with carbon to produce 50.0 g of Teflon? How many grams of carbon would be used?

Solution: We can use the definition of percent fluorine to find the mass of fluorine needed to produce 50.0 g of Teflon.

$$\%\text{ fluorine} = \frac{\text{mass of fluorine}}{\text{mass of Teflon}} \times 100$$

Solving for the mass of fluorine gives

$$\text{Mass of fluorine} = \%\text{ fluorine} \times \text{mass of Teflon}$$

$$= \frac{61.3}{100} \times 50.0\text{ g} = 30.6\text{ g}$$

The mass of carbon required can be found from the law of conservation of mass

$$\text{Mass of Teflon} = \text{mass of carbon} + \text{mass of fluorine}$$

Solving for mass of carbon

$$\text{Mass of carbon} = \text{mass of Teflon} - \text{mass of fluorine}$$

$$= 50.0\text{ g} - 30.6\text{ g} = 19.4\text{ g}$$ •

Parallel Problem: Methane is a compound containing the elements carbon and hydrogen. Its percentage composition is 75.0 percent carbon and 25.0 percent hydrogen. How many grams of carbon would be needed to react with hydrogen to produce 20.0 gram of methane? *Ans.* 5.00 g

Now work example 1-5 in the text.

1-5 Energy

It will often be necessary to convert from one system of units of temperature to another. We can illustrate this process with the temperature units introduced in Section 1-5.

• EXAMPLE 4

Problem: Europeans use the Celsius temperature scale exclusively. If a weather report gives the temperature in Berlin as 18.5°C, what temperature is this on the Fahrenheit scale?

Solution: The equation relating the Celsius and Fahrenheit temperature scales is

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

This can be rearranged to find °F in the form

$$^{\circ}F = \frac{9}{5}\,^{\circ}C + 32$$

Substituting the value given in the problem statement for °C into the equation and solving for °F gives

$$^{\circ}F = \frac{9}{5}(18.5) + 32 = 65.3^{\circ}F \bullet$$

Parallel Problem: Normal body temperature is 98.6°F. What is this in °C?
Ans. 37.0°C

1-6 Numbers, their use and misuse

1. Exponential notation

Often in solving chemical problems you will use numbers that are very large or very small. Most calculators will not accept these numbers unless they are entered in exponential notation. Some calculators automatically convert numbers to exponential notation after all the digits are used. Learning to convert large or small numbers to exponential notation will help you perform calculations easily and confidently on your calculator.

Multiplication and division are actually easier in exponential notation.

The general form of a number in exponential notation is

$$A \times 10^{n}$$

where A represents a number between 1 and 10 and n is the exponent. The number A (the coefficient) is multiplied by some power or multiple of 10. Thus

$$2 \times 10^{6} \quad \text{is} \quad 2 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \quad \text{or} \quad 2{,}000{,}000$$

If the exponent is negative, we divide by 10 that number of times. Thus

$$3 \times 10^{-4} \quad \text{is} \quad 3 \times \frac{1}{10} \times \frac{1}{10} \times \frac{1}{10} \times \frac{1}{10} \quad \text{or} \quad 0.0003$$

To convert a number to exponential notation move the decimal point so the coefficient is between 1 and 10. Count the number of places the decimal point was moved. This is the value of the exponent, n. If the decimal point was moved to the left, the exponent is positive; if it was moved to the right, the exponent is negative. Thus

3,860,000	is	3.86×10^{6}
0.000475	is	4.75×10^{-4}

Negative numbers can be converted to exponential notation in the same manner

−10,400	is	-1.04×10^{4}
-0.000055	is	-5.5×10^{-5}

2. Mathematical calculations using exponential notation

(a) MULTIPLICATION USING EXPONENTIAL NOTATION. Multiplication of two numbers in exponential notation is performed by multiplying coefficients and adding exponents.

• EXAMPLE 5

Problem: Multiply 20,000 by 3,000,000 using exponential notation.

Solution: First express the numbers in exponential notation.

20,000	is	2×10^4
3,000,000	is	3×10^6

Now multiply coefficients and add exponents.

$$(2 \times 10^4)(3 \times 10^6) = 6 \times 10^{6+4} = 6 \times 10^{10} \bullet$$

Parallel Problem: Multiply 1500 by 35,000 using exponential notation.
Ans. 5.2×10^7

• EXAMPLE 6

Problem: Multiply 0.008 by 800,000 using exponential notation.

Solution: Negative exponents are added algebraically in multiplication.

$$(8 \times 10^{-3})(8 \times 10^5) = 64 \times 10^{-3+5} = 64 \times 10^2 = 6.4 \times 10^3$$

Note that in all mathematical operations the coefficient part of exponential notation is treated in a common, ordinary manner. •

Parallel Problem: Multiply 0.0055 by 0.377 using exponential notation.
Ans. 2.1×10^{-3}

(b) DIVISION USING EXPONENTIAL NOTATION. Division is performed by dividing coefficients and subtracting exponents.

• EXAMPLE 7

Problem: Divide 0.009 by 3,000,000 using exponential notation.

Solution:

$$\frac{9 \times 10^{-3}}{3 \times 10^6} = 3 \times 10^{-3-6} = 3 \times 10^{-9} \bullet$$

Parallel Problem: Divide 0.0043 by 9,500,000 using exponential notation.
Ans. 4.5×10^{-10}

(c) ADDITION AND SUBTRACTION USING EXPONENTIAL NOTATION. Addition and subtraction can be performed only if all numbers involved have the same exponent. If the exponents are different they must be adjusted by moving the decimal point in the coefficient the same number of places to the left as the exponent is increased, or the same number of places to the right as the exponent is decreased. When the exponents are equal, the coefficients can be added and the exponent remains unchanged. Hand calculators make this adjustment automatically.

• EXAMPLE 8

Problem: Add $(2.0 \times 10^3) + (4.0 \times 10^4) + (5.00 \times 10^5)$

Solution:

2.0×10^3	is	0.020×10^5
4.0×10^4	is	0.40×10^5
5.00×10^5	is	5.00×10^5

$$0.020 \times 10^5 + 0.40 \times 10^5 + 5.00 \times 10^5 = 5.42 \times 10^5$$ •

Subtraction is done in the same manner. The exponents are made equal and then the coefficients are subtracted.

Parallel Problem: Subtract 2.3×10^2 from 4.7×10^3
Ans. 4.5×10^3

3. Significant figures

Significant figures are an indication of the reliability of an experimental measurement. Often the last significant figure in a measurement is estimated in the experiment and its precision or accuracy may be in doubt.

For example, suppose you weighed yourself on a pair of scales and observe the pointer to be one-fifth of the way between the 55- and 56-kg marks. You would report your weight as 55.2 kg. This indicates you read the scales with a precision of ±0.1 kg. Even though there is some doubt in the reliability of the last digit, the measured value is considered to be precise to three significant figures.

There are four simple rules to determine the number of significant figures in a measured number.

1 All digits other than zero are significant.
2 All zeros between nonzero digits are significant.
3 Zeros following a nonzero digit in a number with a decimal point are always significant.
4 Zeros that are not preceded by a nonzero digit simply locate the decimal point and are not significant figures.

NOTE: This does not mean to imply that locating the decimal point is an insignificant act; in fact, in some ways the choice of term *significant figures* is unfortunate. Significant figures tell us the significance of the error in measurement compared to the size of the number, not the location of the decimal point.

• EXAMPLE 9

Problem: How many significant figures are in each of the following: 4.073, 0.0072, 10, 0.0360?

Solution:

4.073	4 significant figures
0.0072	2 significant figures
10	1 significant figure
0.0360	3 significant figures •

Parallel Problem: How many significant figures are in each of the following: 20.050; 0.0070; 200; 200.0?
Ans. 5 sig fig; 4 sig fig; 1 sig fig; 4 sig fig

• EXAMPLE 10

Problem: Write the number four hundred too illustrate different measurements with one, two, three, and four significant figures.

Solution:

1 significant figure	400	or	4×10^2
2 significant figures	?		4.0×10^2
3 significant figures	400.	or	4.00×10^2
4 significant figures	400.0	or	4.000×10^2

The best way to show two significant figures is using exponential notation. •

An answer cannot be more precise than the least precise data used. Care should be taken to preserve the correct number of significant figures in mathematical operations to show the correct precision for your answers.

When numbers are added or subtracted, the measurement with the lowest precision determines the number of significant figures in the answer.

Parallel Problem: Write the number one-tenth to indicate measurements with one, two, three, and four significant figures.
Ans. 1 sig fig = 0.1; 2 sig figs = 0.10; 3 sig figs = 0.100; 4 sig figs = 0.1000

• EXAMPLE 11

Problem: The masses of four objects are found to be 473.1, 7.33, 0.14, and 0.0037 kg. What is the total mass of the four objects?

Solution: The least accurate measurement has an accuracy of ± 0.1 kg and the sum cannot be more accurate than this. One might be tempted to add the masses as follows:

$$\begin{array}{rl} 473.1 & \text{kg} \\ 7.33 & \text{kg} \\ 0.14 & \text{kg} \\ \underline{0.0037} & \underline{\text{kg}} \\ 481.5737 & \text{kg} \end{array}$$

Even though 473.1 has the most significant figures, it is accurate to only ± 0.1 kg; the sum cannot be more accurate than this, and we must round off the answer to the nearest 0.1 kg.
The correct answer is 481.6 kg. Note that there are four significant figures in the answer even though some measurements have only two significant figures. •

Parallel Problem: The volumes of four objects are found to be 2.071, 0.031, 20.62, and 0.27 liters. What is the total volume of the four objects?
Ans. 22.9 L

When numbers are multiplied or divided, the answer will have the same number of significant figures as the number in the data with the fewest significant figures. In multiplication and division it is the fewest number of significant figures in the data, not the location of the decimal point, that tells how to round off the answer to the correct number of significant figures. An example will show how exponential notation takes the guesswork out of determining significant figures.

• EXAMPLE 12

Problem: Divide 4.739×10^6 by 3.71×10^4.

Solution:

$$\frac{4.739 \times 10^6}{3.71 \times 10^4} = 1.28 \times 10^2 \quad \bullet$$

Parallel Problem: Divide 2.6×10^{-3} by 7.034×10^{-2}.
Ans. 3.7×10^{-2}

The concept of significant figures is easy to understand, but students often forget to apply it in calculations. Problems usually will not specifically ask for the correct number of significant figures, but you should always be aware of the precision your answer deserves in each problem in the text or *Study Guide*.

4. *Rounding off numbers*

A number is rounded off by dropping digits to the right of the last significant figure. The following rules can be used to round off answers to the correct number of significant figures.

a When the digit to the right of the last significant figure is less than 5, the last significant figure remains unchanged. For example, 9.7346 becomes 9.73 to three significant figures.

b When the digit to the right of the last significant figure is greater than 5, the last significant figure is increased by 1. For example, 83.478 becomes 83.5 to three significant figures.

c When the digit to the right of the last significant figure is 5, the last significant figure is increased by 1 if it is odd but remains unchanged if it is even. For example, 57.55 and 57.65 both give 57.6 when rounded off to three significant figures.

1-8 Solving numerical problems

Most instructors will assume you have a basic understanding of algebra and handling algebraic equations. If you are rusty in this area, consult your bookstore for a paperback book on basic mathematics for chemistry. There are several good ones available.

We will proceed directly to the dimensional analysis or unit-factor approach to problem solving. Many students who say they are having trouble with chemistry actually understand the chemistry but are stumbling over the mathematics. We have already seen how exponential notation simplifies the arithmetic. If you are still unconvinced, work Prob. 1-24 in the text. The general approach of the unit-factor method will simplify calculations in a wide field of problems in chemistry. You will use the method extensively in later chapters, so now is the time to learn it well. It will take practice to get used to the method. It is simply a method of analyzing the units (dimensions) of numbers and using these units to set up factors to convert from the quantity given in a problem to the answer desired. Let the units guide you through the problem. It is important to recognize the information given in a problem and separate it from the question asked. This takes practice and persistence.

In dimensional analysis units are treated just like numbers in algebraic operations: they may be cancelled or multiplied just like numbers.

Let us analyze the reverse of Example 1-3 in the text.

• EXAMPLE 13

Problem: If you are 147 cm tall, what is your height in inches?

Solution: First: What is given and what is desired in the problem? 147 cm is given. The number of inches equal to 147 cm is the desired value. The problem could be rewritten to read "How many inches are equal to 147 cm?"

To solve the problem we need a unit factor that relates the given units to the desired units, in this case a conversion equation for centimeters and inches. Several conversion equations are given in Table 1-3 in the text. There are two that relate centimeters to inches. They are

$$1\text{ cm} = 0.394\text{ in}$$
$$1\text{ in} = 2.54\text{ cm}$$

Let us divide both sides of the first conversion equation by 0.394 in

$$\frac{1\text{ cm}}{0.394} = \frac{0.394\text{ in}}{0.394\text{in}} = 1$$

We have formed a unit factor for changing inches to centimeters

$$\frac{1\text{ cm}}{0.394\text{ in}} - 1$$

Let us go back and divide both sides of the first conversion equation by 1 cm

$$\frac{1\text{ cm}}{1\text{ cm}} = 1 = \frac{0.394\text{ in}}{1\text{ cm}}$$

We have found a second unit factor from the conversion equation

$$\frac{0.394\text{ in}}{1\text{ cm}} = 1$$

Similarly, we can form two unit factors from the second conversion equation: one by dividing both sides by 2.54 cm

$$\frac{1\text{ in}}{2.54\text{ cm}} = \frac{2.54\text{ cm}}{2.54\text{ cm}} = 1$$

and another by dividing by 1 in

$$\frac{1\text{ in}}{1\text{ in}} = 1 = \frac{2.54\text{ cm}}{1\text{ in}}$$

We have formed four unit factors from the two conversion equations. Indeed, each conversion equation in Table 1-3 in the text can be used to form two unit factors.
The four unit factors are

$$\frac{1\text{ cm}}{0.394\text{ in}} = 1 \qquad \frac{0.394\text{ in}}{1\text{ cm}} = 1$$

$$\frac{1\ \text{in}}{2.54\ \text{cm}} = 1 \qquad \frac{2.54\ \text{cm}}{1\ \text{in}} = 1$$

These are all fractions, or unit factors, equal to unity.

To solve the problem you must multiply the given quantity, 147 cm, by the unit factor that will make the answer appear in the correct units. To do this you must plan ahead from the given data to the answer. Given units are centimeters; desired units are inches.

$$\cancel{\text{cm}} \times \frac{\text{in}}{\cancel{\text{cm}}} = \text{in}$$

If centimeters are multiplied by in/cm, centimeters can be canceled to leave the desired inches.

The problem is essentially solved; all we need to do is add the correct numbers to the unit factors. We have a choice of two unit factors for in/cm. Either will work.

$$147\ \cancel{\text{cm}} \times \frac{0.394\ \text{in}}{1\ \cancel{\text{cm}}} = 57.9\ \text{in}$$

or

$$147\ \cancel{\text{cm}} \times \frac{1\ \text{in}}{2.54\ \cancel{\text{cm}}} = 57.9\ \text{in}$$

Choosing one of the other unit factors leads to an incorrect answer:

$$147\ \text{cm} \times \frac{2.54\ \text{cm}}{1\ \text{in}} = 373\ \text{cm}^2/\text{in} \quad \bullet$$

You may not recognize that the number 373 is incorrect, but the units cm^2/in tell you the answer is not correct. Always look at the numerical answer *and* the units to help tell if the answer is correct.

The same reasoning and principles can be applied to the unit-factor method for problems in which more than one unit factor is needed to get the answer.

Parallel Problem: A person weighs 115 lbs. What is her weight in kilograms?
Ans. 52.3 kg

• EXAMPLE 14

Problem: An imported car has a fuel economy rating of 15.0 km/liter. How many miles per gallon is this?

Solution: The problem asks us to convert from units of km/liter to miles per gallon. The "per" in miles per gallon can be read as "divided by", or mi/gal.

We need to convert

$$\frac{\text{km}}{\text{liter}} \quad \text{to} \quad \frac{\text{mi}}{\text{gal}}$$

Two conversions are required here: kilometers to miles and liters to gallons. Examine Table 1-6 in the text for equations that can be used to give the necessary unit factors.

$$1\ \text{km} = 0.621\ \text{mi}$$

from which we can build the unit factor:

$$\frac{0.621\ \text{mi}}{1\ \text{km}} = 1$$

The conversion of liters to gallons does not appear in Table 1-6, but we can accomplish the desired conversion by first converting liters to quarts and then use a familiar relation to convert quarts to gallons.

$$1\ \text{liter} = 1.06\ \text{qt} \qquad \text{or} \qquad \frac{1\ \text{liter}}{1.06\ \text{qt}} = 1$$

and

$$4\ \text{qt} = 1\ \text{gal} \qquad \text{or} \qquad \frac{4\ \text{qt}}{1\ \text{gal}} = 1$$

Now we can use these unit factors in a systematic fashion to obtain the desired units.

$$\frac{\cancel{\text{km}}}{\cancel{\text{liter}}} \times \frac{\text{mi}}{\cancel{\text{km}}} \times \frac{\cancel{\text{liter}}}{\cancel{\text{qt}}} \times \frac{\cancel{\text{qt}}}{\text{gal}} = \frac{\text{mi}}{\text{gal}}$$

The unit factors are assembled to cancel the given units and introduce the desired units. If the units are not right in the answer, go back and see if a unit factor has been inverted. Now we add the numbers to the unit factors to get the answer.

$$\frac{15.0\ \text{km}}{\text{liter}} \times \frac{0.621\ \text{mi}}{1\ \text{km}} \times \frac{1\ \text{liter}}{1.06\ \text{qt}} \times \frac{4\ \text{qt}}{1\ \text{gal}} = 35.2\ \text{mi/gal}$$

Check the significant figures also. Since 1 km, 1 liter, 4 qt, and 1 gal are all *defined* quantities, they have very high precision compared to the other numbers. They do not determine the number of significant figures in the answer. •

Parallel Problem: A speed limit is posted as 90 kilometers/hr. How many feet per second is this?
Ans. 82 ft/sec

Now work through Examples 1-4 to 1-6 and the parallel problems in the text.

1. Calculation of density

Density is an important physical property of matter defined as the mass of substance per unit volume. Recalling that "per" means to divide:

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

Mass is usually expressed in grams and volume in cubic centimeters

$$\text{Density} = \frac{\text{g}}{\text{cm}^3} = \text{g cm}^{-3}$$

The volume of a substance changes with temperature since most substances expand on heating. This means that density decreases as temperature increases. Density values are usually given at 25°C, and unless a different temperature is specified we will assume the densities in the text are for 25°C.

• EXAMPLE 15

Problem: An empty container has a mass of 87.63 g. When 10.00 mL of a certain liquid is placed in the container, the total mass is 95.71 g. What is the density of the liquid?

Solution: The volume of the liquid is 10.00 mL or 10.00 cm^3 since 1 mL is the same as 1 cm^3. The mass of liquid is found by subtracting the mass of the empty container from the total mass.

$$\text{Total mass} = \text{mass empty container} + \text{mass liquid}$$

$$\text{Mass liquid} = \text{total mass} - \text{mass empty container}$$

$$= 95.71\text{ g} - 87.63\text{ g} = 8.08\text{ g}$$

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{8.08\text{ g}}{10.00\text{ cm}^3} = 0.808\text{ g cm}^{-3}$$ •

Parallel Problem: What is the mass of an object which displaces 9.60 mL of water when immersed and has a density of 3.70 g cm^{-3}?
Ans. 35.5 g

Now go through Example 1-7 in the text.

The units of density are g cm^{-3}. This means that density can be used as a unit factor between mass and volume. In fact, the importance of density in calculations is its use in converting mass to an equivalent volume or vice versa.

Let us examine this use. First we will find the volume equivalent to a given mass.

• EXAMPLE 16

Problem: Mercury (Hg) is sold commercially in flasks containing 70 lb of mercury. What is the volume (in liters) of 70.0 lb of mercury? The density of mercury is 13.54 g cm^{-3}.

Solution: The given quantity in the problem is 70.0 lb of mercury. The desired quantity is the volume in liters. We need a unit factor to convert pounds to liters. Since we do not have the density expressed in units of lb $liter^{-1}$ (is this a consistent set of units for density?) we must convert pounds to grams with the unit factor

$$\frac{454\text{ g}}{1\text{ lb}} = 1$$

and cm^{-3} to $liter^{-1}$ with the unit factor

$$\frac{1 \times 10^3\text{ cm}^3}{1\text{ L}} = 1$$

The density of Hg is given as 13.54 g cm^{-3}. This means 1 cm^3 of Hg has a mass of 13.54 g or, in equation form

$$1\text{ cm}^3 \sim 13.54\text{ g Hg}$$

where ~ is read "is equivalent to"
The unit factors

$$\frac{1\ \text{cm}^3}{13.54\ \text{g}} = 1 \qquad \text{and} \qquad \frac{13.54\text{g}}{1\ \text{cm}^3} = 1$$

can be assembled from the given density.
To convert from a given mass to a volume we select the unit factor

$$\frac{1\ \text{cm}^3}{13.54\ \text{g}} = 1$$

Assemble the unit factors to give the desired units, liters of Hg, as follows

$$\text{lb Hg} \times \frac{\text{g Hg}}{\text{lb Hg}} \times \frac{\text{cm}^3\ \text{Hg}}{\text{g Hg}} \times \frac{\text{liter Hg}}{\text{cm}^3\ \text{Hg}} = \text{liters Hg}$$

If the wrong unit factor had been chosen $\left(\frac{13.54\ \text{g}}{1\ \text{cm}^3}\right)$, what would be the units in the answer?

The above equation shows how the unit factor method is used to solve density problems. Now we insert the appropriate numbers into the unit factors and find the numerical answer.

$$70.0\ \text{lb Hg} \times \frac{454\ \text{g Hg}}{1\ \text{lb Hg}} \times \frac{1\ \text{cm}^3\ \text{Hg}}{13.54\ \text{g Hg}} \times \frac{1\ \text{liter Hg}}{10^3\ \text{cm}^3\ \text{Hg}} = 2.35\ \text{liters Hg} \bullet$$

Parallel Problem: Calculate the weight in lbs of 15.0 gallons of gasoline. The density of gasoline is 0.800 g/cm^3.
Ans. 99.7 lbs

Now try Example 1-8 in the text.

2. *Use of density in calculations*
   Another use of density is to find the mass of a volume of substance.

• EXAMPLE 17

Problem: What is the mass of 1.00 ft^3 of air? The density of air at 25°C is 1.18 g L^{-1}.

Solution: We will do this problem in parts. First we will find the mass of 1.00 liter of air and then convert this to the mass of 1.00 ft^3. The density tells us that 1 liter of air has a mass of 1.18 g.

$$\text{Density} = \frac{1.18\ \text{g}}{1\ \text{L}}$$

We can convert the volume from liters to cubic feet with unit factors from Table 1.3 in the text.

$$\frac{1.18\ \text{g}}{1\ \text{L}} \times \frac{1\ \text{L}}{10^3\ \text{mL}} \times \frac{1\ \text{mL}}{6.10 \times 10^{-2}\ \text{in}^3} \times \frac{12^3\ \text{in}^3}{1\ \text{ft}^3} = 33.4\ \text{g ft}^{-3}$$

Thus 1 ft^3 of air has a mass of 33.4 g. •

Parallel Problem: What is the volume in liters of 10.0 lbs of carbon dioxide gas having a density of 1.80 g/L?
Ans. 2.52×10^3 L

KEY TERMS

1-1 Chemistry: what, why, and how?

Chemistry: The study of the nature, properties, and composition of matter, and the changes which matter can undergo.

1-2 Scientific methodology

Data: Records of observations.

Hypothesis: A new and untested explanation of observed data.

Law: A general statement about some aspect of the behavior of nature.

Qualitative: Having to do with the nature or essence of something without regard to quantity.

Quantitative: Having to do with the amount of something.

Scientific method: A logical process of acquiring knowledge.

Theory: An acceptable statement which explains observed data in terms of a model.

1-3 Matter

Compound: A pure substance composed of two or more elements chemically combined in a fixed ratio.

Element: A simple, fundamental, elementary substance composed of atoms with the same atomic number which cannot be broken down into a simpler substance by chemical means.

Fluid: The ability of gases and liquids to flow.

Gas: Matter for which the volume and shape are variable. Gases expand to fill the container uniformly.

Heterogeneous mixture: A nonuniform combination of two or more substances in which the components have distinct boundaries.

Homogeneous mixture: Substance consisting of a single phase with uniform composition.

Inertia: The resistance of an object to change in its motion.

Liquid: Matter characterized by constant volume which adapts to the shape of the container.

Mass: A measure of the quantity of matter.

Matter: Anything that has mass and occupies space.

Mixture: Two or more substances physically combined.

Phase: The state of matter (solid, liquid, or gas) characterized by uniform properties.

Pure substance: Matter consisting of a single component with fixed composition and properties.

Solid: A state of matter characterized by constant volume and shape independent of the container.

Solution: A homogeneous mixture

1-4 Changes in matter

Chemical change: Transformation of a substance into a different chemical substance.

Chemical reaction: The process by which a chemical change occurs.

Law of conservation of mass: Matter is neither created nor destroyed in chemical reactions.

Law of definite composition: A pure compound is always composed of a fixed, characteristic ratio of elements.

Physical change: Alteration in the measurable properties of a substance but not its composition.

Product: The substance produced in a chemical reaction.

Reactant: The substance consumed in a chemical reaction.

1-5 Energy

Celsius: Temperature scale on which the freezing point of water is 0°C and the normal boiling point is 100°C.

Energy: The ability or capacity to do work.

Fahrenheit: Temperature scale on which the freezing point of water is 32°F and the normal boiling point is 212°F.

Heat: Energy in transit from a hotter object to a colder one.

Kinetic energy: Energy of motion.

Law of conservation of energy: Energy may be converted from one form to another without changing the total energy.

Mechanical energy: Energy possessed by an object because of its position or motion.

Mechanical work: Movement of an object against an opposing force.

Potential energy: Energy of an object that depends on its position.

Temperature: A measure of the average kinetic energy of the particles of a substance.

1-6 Numbers, their use and misuse

Accuracy: A measure of the closeness of data to the real value.

Exact number: A number known with perfect certainty.

Exponential notation: A method of writing numbers as a product of a coefficient and a multiplier. The coefficient is written with one digit to the left of the decimal. The multiplier is ten raised to an integral power.

Measured number: A number with some degree of uncertainty.

Precision: A measure of the agreement among a series of measurements.

Scientific notation: Same as exponential notation.

Significant figures: Digits that show the precision of a number.

1-7 Metric units

SI base units: A metric system of units used in scientific measurements.

SI derived units: Combinations of two or more SI base units.

1-8 Solving numerical problems

Density: Mass per unit volume.

Dimensional analysis: A method of calculation in which the dimensions (units) of a number are treated as if they were algebraic quantities.

Unit factor: An algebraic expression that equates a measurement in two different systems of units.

SELF TEST

(Answers to Self Tests may be found at the back of this *Study Guide*.)

True or False

____ 1. Science begins with observations.

____ 2. Science vocabulary is relatively easy to master because each term has a precise meaning.

____ 3. An understanding of mathematics is necessary for an understanding of chemistry.

____ 4. A scientific theory is a tested and widely accepted scientific hypothesis.

____ 5. NaCl is a chemical symbol.

____ 6. The mass of products produced in a chemical reaction is always equal to the mass of reactants consumed.

____ 7. Heat is the same as energy.

____ 8. Energy is the capacity to do work.

____ 9. Solutions can be gaseous, liquid, or solid.

____ 10. The percent composition of any given compound always remains constant.

____ 11. The SI unit for volume is the liter.

____ 12. A possible unit of density could be kg ft^{-3}.

____ 13. The number 48.507 rounded off to two significant figures is 48.

____ 14. If you can select the right unit factor you can convert a mass measurement to a density (mass per volume) measurement.

____ 15. The number 45.70 has three significant figures.

Completion

16. A tentative answer or explanation of scientific observation is called a ____________________.

17. A ________________________ is a well-tested statement based on observations of the behavior of nature which is used to predict what might happen under different circumstances.

18. All solutions are ____________________ mixtures.

19. A ________________________ mixture consists of a single phase.

20. A ________________________ consists of two or more elements bonded together.

21. ________________________ is the movement of a mass against an opposing force.

22. ________________________ is energy moving from one object to another.

23. The SI unit of energy is the ____________________.

24. Energy of position is called ____________________.

25. Energy of motion is called ____________________.

26. The number 0.000370 can be expressed as __________________ in exponential notation.

27. 8.00×10^{-4} divided by 2.0×10^{6} is __________________.

28. The unit factor for converting milliliters to liters is ______________.

29. The unit factor for converting kilograms to grams is __________________.

30. The SI base unit for mass is the ________________.

Multiple Choice

31. A pure substance that can be decomposed into two or more elements by ordinary chemical means is called
(a) an element (b) an atom (c) a compound (d) a mixture

32. Which of the following represents a chemical change?
(a) boiling water
(b) forming of frost in a refrigerator
(c) turning on an electric stove
(d) turning on a gas stove

33. Which of the following represents a physical change?
(a) rusting of a car door
(b) cooking an egg
(c) dissolving sugar in water
(d) tarnishing of silverware

34. Which of the following is the best example of kinetic energy?
(a) a book on a table
(b) an automobile waiting at a street light
(c) pulling against a spring
(d) a moving golf ball

35. The individual masses of four different objects are measured as 75.0, 6.72, 4.0, and 0.671 grams. The total mass of the four objects is
(a) 86.391 g (b) 86.3 g (c) 86.4 g (d) 86 g

36. The correct unit factor to convert centimeters to meters is
(a) $\frac{100\text{ cm}}{1\text{ m}}$ (b) $\frac{100\text{ m}}{1\text{ cm}}$
(c) $\frac{1\text{ cm}}{100\text{ m}}$ (d) $\frac{1\text{ m}}{100\text{ cm}}$

37. Given 1 lb = 454 g, the mass in kilograms of a person weighing 145 lbs is
(a) 0.319 kg (b) 65,830 kg (c) 65.830 kg (d) 65.8 kg

38. How many kilometers are in 1 mile? (1 in = 2.54 cm, 1 ft = 12 in, 1 mi = 5280 ft)
(a) 1.61 km (b) 0.58 km (c) 0.621 km (d) 173 km

39. How many kilometers per hour is the 55 mph speed limit? See Prob. 38 for conversion equations.
(a) 34 (b) 55 (c) 88 (d) 225

40. The correct number of significant figures in a mass measurement of 11.020 g is
(a) 2 (b) 3 (c) 4 (d) 5

41. The density of iron is 7.86 g cm^{-3}. What is the volume of a piece of iron that has a mass of 55.0 g?
(a) 432 cm^3 (b) 62.9 cm^3 (c) 7.00 cm^3 (d) 0.143 cm^3

42. The elements sodium and chlorine combine to form common table salt, NaCl. If 23.0 g sodium combines with 35.7 g chlorine, what is the percentage of sodium in the table salt formed?
(a) 65.0% (b) 58.4% (c) 39.4% (d) 12.4%

43. The percentage composition of the compound sulfur dioxide, is 40.0% sulfur and 60.0% oxygen. How many grams of oxygen would be required to react with 50.0 grams of sulfur to form sulfur dioxide?
(a) 75.0 g (b) 33.3 g (c) 30.0 g (d) 20.0 g

44. A comfortable room temperature is 72°F. What temperature is this on the Celsius scale?
(a) 58°C (b) 39°C (c) 22°C (d) 295°C

45. Water is 11.1% hydrogen and 88.9% oxygen. If 4.70 g hydrogen reacts with oxygen to form water, how much oxygen is used?
(a) 0.587 g (b) 4.18 g (c) 5.59 g (d) 37.6 g

Chapter 2

FORMULAS, EQUATIONS, AND STOICHIOMETRY

CHAPTER OVERVIEW

We saw in Chapter 1 how chemical symbols are used as a shorthand notation to describe chemical changes. Chapter 2 expands this concept by introducing several different kinds of chemical formulas, showing how to name them and applying them quantitatively to chemical changes. You should become familiar with uses and limitations of each type of chemical formula. You will also be introduced to the mathematical calculations important to chemical reactions. These mathematical operations are called "stoichiometry."

2-1 The microstructure of matter

It is easy to measure the properties of bulk matter such as temperature, pressure, volume, and mass, but much more challenging to make measurements on atoms, the fundamental building blocks of the elements. No one has ever seen an atom, yet we have a large amount of information about atomic behavior. We will have much more to say about atoms in Chapters 5 and 6.

2-2 Chemical formulas

Chemical formulas are a shorthand method of conveying information about the composition of a compound. Sometimes we may want to convey different types of information about a compound and this can be done by using the appropriate kind of formula. There are three types: molecular, empirical, and structural. Notice how each type has definite limitations to its ability to present a complete picture of a compound and its structure.

2-3 Atomic and other masses

The atomic mass of an element is much more than just a number. It represents the relative mass of atoms of different elements on the microscale (world of atoms), but it has another meaning on the macroscale (observable scale on which we can make convenient measurements). It is the mass in grams of Avogadro's number of atoms. Molecular mass is simply the extension of the atomic mass concepts from atoms into molecules: the mass in grams of Avogadro's number of molecules. *Formula* is a more general term and applies to any chemical formula.

2-4 The mole

The word *mole* was coined as an abbreviation of the term *molecule* or *molecular mass*. The molecular mass is the mass of one mole of any given compound. Avogadro's number of particles is called a mole. The term *mole* means two things: (1) Avogadro's number of particles of the substance; (2) the mass of substance contained in that number of particles. The numerical value of a mole, in grams, depends on the formula mass of the substance. You will see as you study this chapter that a mole of substance is the basic measuring quantity or unit used in chemical calculations.

2-5 Compound stoichiometry

Stoichiometry is a large word that means the arithmetic of chemical formulas and equations. The dual meaning of atomic mass is seen again in the interpretation of chemical formulas. Formulas represent the atomic composition of a compound on the microscale but also have another meaning relating to macroscale. On a macroscopic scale the formula represents one mole of the compound. A molecular formula tells the number of atoms in a molecule and also the number of moles of atoms in a mole of molecules of a compound. It is essential that you understand each of these meanings and how they are different yet intimately related.

Calculating empirical formulas and molecular formulas from experimental data will help you develop an understanding of formula stoichiometry.

2-6 Chemical equations

The dual microscale and macroscale meaning of atomic mass and chemical formulas extends into chemical equations. Both meanings must be clearly understood. It may help you understand chemical equations if you treat them like algebraic equations. Reactants are written on the left-hand side of the equation and products on the right. The arrow separating reactants and products signifies "yields," "forms," or "reacts to form." The equation becomes a shorthand method of describing a chemical change in which reactants form products.

Chemical reactions obey the law of conservation of mass so the total mass of reactants always equals the total mass of products. Atoms are conserved during chemical reactions so each element must have the same number of atoms on the reactant side of the equation as on the product side, and the total number of atoms must be the same in the reactants as in the products. The total number of moles is not necessarily conserved and may change. It is often troublesome to students to call an equation balanced that does not have the same total number of moles of reactants and products, but it is only the atoms that must be balanced on both sides of the equation, not the total number of moles of compounds.

2-7 Reaction stoichiometry

In this section you will see the quantitative aspects of chemical formulas applied directly to chemical changes. You will work several problems showing the application of stoichiometry and limiting reagent to chemical reactions. In these applications the adage "learn by doing" takes on a very significant meaning. It will take much effort and practice to become proficient at these calculations.

2-8 Solution stoichiometry

This section is a brief introduction to solutions with emphasis on the concentration unit, molarity. Molarity is a common method of expressing concentrations of solutions in chemical laboratories. You will see how to relate the number of moles of solute to the volume and molarity of solutions. You will calculate changes in concentration when solutions are diluted. One of the main reasons for presenting the material in Section 2-8 is to help you prepare for a laboratory experiment in titration. Study this section carefully as you prepare for the laboratory exercise.

2-9 The mole: additional comments

It is important that you feel confident about your understanding of the meaning and use of *mole*. The mole concept will be used throughout the course, so get a firm understanding of it now. Calculating molecular mass should become second nature to you before you finish this chapter.

2-10 Chemical nomenclature: a first look

In this section you are introduced to information and rules to help understand the naming of chemical compounds. Note that each systematic name is related to the formula of the compound in a definite way. The simple rules of nomenclature in this section give the names of nearly 1000 binary compounds. Different classes of names are presented.

(1) binary metal-nonmetal compounds (Text Table 2-2)
(2) binary nonmetal-nonmetal compounds (Text Table 2-3)
(3) ternary compounds containing oxygen (Text Table 2-4)
(4) acids and bases (Text Table 2-5)

KEY EQUATION

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{No. of liters of solution}}$$

LEARNING OBJECTIVES

As a result of studying Chapter 2 you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 44 of this *Study Guide*.

2-1 The microstructure of matter

1. Define and use the terms *atom* and *molecule* (Self Test 5).
2. Understand that not all substances are molecular in nature.

2-2 Chemical formulas

1. Relate the elemental composition of a compound to its chemical formula (Self Test 1, 3, 7, 9, 42)
2. List the differences in information conveyed by molecular, empirical, and structural formulas (Self Test 8)

2-3 Atomic and other masses

1. Given an example illustrating the dual meaning of atomic mass on the microscopic (or molecular) scale and the macroscopic (or observable) scale.
2. Explain how amu and atomic mass are related and how they differ. (Text Probs. 2-2, 2-11, 2-12)
3. Calculate molecular mass from atomic masses given the molecular formula. (Text Examples 2-1) (New Skills Example 1; Self Test 6, 18, 24).
4. Give an example showing how molecular mass and formula mass are related. (Text Example 2-2)

2-4 The mole

1. Use Avogadro's number as a unit factor in calculations. (Text Example 2-3; Text Probs. 2-4, 2-5, 2-7) (Self Test 14, 16).
2. Define *mole* (Self Test 2).
3. Calculate the number of moles in a given number of molecules or atoms of a substance and the number of molecules or atoms in a given number of moles. (Text Example 2-3) (New Skills Examples 2, 3; Self Test 14, 31, 37).
4. Calculate the number of grams in a given number of moles or molecules of a substance and the number of moles or molecules in a given number of grams. (Text Examples 2-4 to 2-8; Text Probs. 2-3 to 2-11, 2-63, 2-64) (New Skills Examples 4 to 10; Self Test 16, 17, 19 to 22, 32, 36).

2-5 Compound stoichiometry

1. Define *empirical formula* and give an example illustrating its relation to molecular formula. (Text Prob. 2-13) (Self Test 33, 38, 42).
2. Calculate the number of moles of each kind of atom in a given number of moles of a substance. (Text Examples 2-9 to 2-11; Text Probs. 2-18, 2-19) (Self Test 1, 7, 9).
3. Calculate the percentage composition from the molecular formula of a compound. (Text Example 2-12; Text Probs. 2-25, 2-26) (New Skills Example 11; Self Test 23, 34).
4. Calculate the empirical formula of a substance from its composition. (Text Examples 2-13, 2-20; Text Probs. 2-14 to 2-17, 2-27 to 2-30, 2-65) (New Skills Example 12; Self Test 44).
5. Determine the molecular formula from the empirical formula and molecular mass of a compound (Text Example 2-14; Text Probs. 2-16, 2-30, 2-66, 2-68) (New Skills Example 13).
6. Calculate the amounts of chemicals reacting or produced in the formation or decomposition of simple compounds. (Text Probs. 2-20 to 2-24, 2-67, 2-70 to 2-72) (Self Test 23).

2-6 Chemical equations

1. Write and balance simple chemical equations. (Text Examples 2-15, 2-16; Text Probs. 2-31 to 2-33) (New Skills Example 14; Self Test 4, 43).

2-7 Reaction stoichiometry

1. Calculate the amount of a substance reacting with or produced from a given amount of another substance using a balanced chemical equation. (Text Examples 2-17 to 2-20; Text Probs. 2-34 to 2-38) (New Skills Examples 15, 16, 17).
2. Calculate the amount of products formed when reactants are not present in stoichiometric amounts and determine which reactant is the limiting reagent. (Text Example 2-21; Text Probs. 2-39 to 2-41, 2-76) (New Skills Example 17; Self Test 25).

2-8 Solution stoichiometry

1. Define the terms *aqueous solution*, *solvent*, and *solute*. (Self Test 26).
2. Define *molarity* in words and with an equation. (Self Test 15).
3. Use the equation for molarity to calculate any one of the variables: number of moles of solute, volume of solution, or molarity, given the other two. (Text Examples 2-22, 2-24; Text Probs. 2-45 to 2-50) (New Skills Examples 18, 19, 20; Self Test 39).
4. Calculate the grams of solute necessary to prepare a solution if the molarity and volume of solution are given. (Text Example 2-23) (New Skills Example 21; Self Test 40, 41, 45).
5. Calculate the molarity of a solution after it is diluted. (Text Example 2-25; Text Probs. 2-51, 2-52) (New Skills Example 22; Self Test 41).
6. Define *acid* and *base*.
7. Write equations for neutralization reactions between acids and bases. (Text Probs. 2-57 to 2-62) (Self Test 27).
8. Describe how an acid-base titration could be carried out.
9. Calculate the molarity of an acid or base given the molarity of one of them and the volume of each necessary to reach the equivalence point in a titration. (Text Example 2-26; Text Probs. 2-57 to 2-62, 2-73, 2-78) (New Skills Example 23; Self Test 35).

2-9 The mole: additional comments

1. Gain an appreciation for the size of a mole.

2-10 Chemical nomenclature: a first look

1. Write names for binary metal-nonmetal compounds. (Text Table 2-2, Text Prob. 2-42) (Self Test 10 to 12, 28).
2. Write names for binary nonmetal-nonmetal compounds. (Text Table 2-3; Text Prob. 2-44) (Self Test 30).
3. Write formulas of binary compounds using Greek prefixes when given the name and combining ratio of the atoms. (Text Probs. 2-43, 2-44).
4. Write names and formulas for ternary compounds containing oxygen. (Text Table 2-4) (Self Test 13, 29).
5. Name and give formulas for simple binary acids and bases and the ternary acids in Text Table 2-5. (Text Probs. 2-54 to 2-56).

NEW SKILLS

As you have no doubt observed, this chapter contains many worked example problems. There are several areas of application of mathematics to chemistry (stoichiometry) that need to be mastered. Let us get started.

2-3 Atomic and other masses

1. Determination of molecular mass from atomic masses

For substances composed of molecules, the mass of 6.02×10^{23} molecules is the molecular mass in grams. The molecular mass in atomic mass units (amu's) is the sum of the atomic masses of all the atoms contained in the molecule.

• EXAMPLE 1

Problem: What is the molecular mass of carbon dioxide, CO_2?

Solution: A molecule of CO_2 is composed of one atom of carbon and two atoms of oxygen. The atomic mass of carbon and oxygen are found in the periodic table inside the front cover of the main text.

The molecular mass of carbon dioxide is found as follows:

	Masses on Microscale 1 molecule of CO_2	Masses on Macroscale 6.02×10^{23} molecules of CO_2
1 atom of carbon/ molecule CO_2	12 amu C/molecule CO_2	12 g C/mol CO_2
2 atoms of oxygen/ molecule CO_2	2 x 16 amu O/molecule CO_2	32 g O/mol CO_2
Molecular mass	44 amu/molecule CO_2	44 g/mol CO_2

Thus the molecular mass has the same numerical value in the microscale and macroscale, but the units are different. •

Parallel Problem: What is the molecular mass of aluminum oxide, Al_2O_3?
Ans: 102

2-4 The mole

1. The concept of a mole

It is important to be able to express a quantity of matter in units of moles, number of atoms, or grams. Let us investigate the concept of a mole further to see how to convert from one of these units to another.

A mole is a quantity like a dozen. It is a fixed number of particles but not a fixed mass. You will not find a balance or scale in the laboratory with units of "mole." The following illustration shows how a mole is like a dozen. There are 12 things in a dozen, so the unit factor is:

$$\frac{12\ \text{things}}{\text{dozen}}$$

You can calculate the number of dozens in a given number of things:

$$\text{Number of dozens} = \frac{\text{number of things}}{\text{12 things/dozen}}$$

• EXAMPLE 2

Problem: There are 6.0 x 10^9 people in the world. How many dozens of people are there?

Solution: The number of dozens $= \dfrac{6.0 \times 10^9 \text{ people}}{\text{12 people/dozen}}$

$$= 5.0 \times 10^8 \text{ dozens} \bullet$$

Parallel Problem: One gross is 12 dozen. How many gross people are there in the world?
Ans: 4.2 x 10^7 gross

The number of moles is calculated in the same way as the number of dozens. There are 6.02 x 10^{23} things in a mole, so the unit factor is:

$$\frac{6.02 \times 10^{23} \text{ things}}{\text{mol}}$$

$$\text{Number of moles} = \frac{\text{number of things}}{60.2 \times 10^{23} \text{ things/mol}}$$

• EXAMPLE 3

Problem: There are 4.0 x 10^9 people in the world. How many moles of people are there?

Solution: Number of moles $= \dfrac{6.0 \times 10^9 \text{ people}}{6.02 \times 10^{23} \text{ people/mol}}$

$$= 1.0 \times 10^{-14} \text{ mol} \bullet$$

Parallel Problem: A stack of dollar bills reaching from the earth to the sun would contain about 3 x 10^{15} dollars. How many moles of dollar bills would this be?
Ans: 5 x 10^{-9}

Things can have mass; therefore, moles and dozens may be related to mass.

• EXAMPLE 4

Problem: If an average person has a mass of 70 kg, what would be the mass of one dozen people?

Solution: Use the unit-factor approach:

$$\frac{70 \text{ kg}}{\text{person}} \left(\frac{12 \text{ people}}{\text{dozen}} \right) = 840 \text{ kg dozen}^{-1} \bullet$$

Parallel Problem: A penny has a mass of 3.0 grams. What would be the mass of one dozen pennies?
Ans: 36 g doz^{-1}

• EXAMPLE 5

Problem: Using the data from Example 4, what would be the mass of one mole of people?

Solution: The unit factor method used in Example 4 applies here also. One mole of people would have a mass of:

$$\frac{70 \text{ kg}}{\text{person}}\left(\frac{6.02 \times 10^{23} \text{ people}}{\text{mol}}\right) = 4.2 \times 10^{25} \text{ kg mol}^{-1} \bullet$$

Parallel Problem: Using the data from Parallel Problem 4, what would be the mass of one mole of pennies?
Ans: 1.8×10^{24} g mol^{-1}

When the things are atoms, the mass of 1 mol, or 6.02×10^{23} atoms, is the atomic mass. The mass of a carbon atom is 12.0 amu.

$$\frac{12 \text{ amu}}{\text{C atom}}\left(6.02 \times 10^{23} \frac{\text{C atoms}}{\text{mol C}}\right) = 7.2 \times 10^{24} \text{ amu/mol C}$$

To convert this large number to the unit of mass common to macroscale applications

$$\frac{7.2 \times 10^{24} \text{ amu}}{\text{mol C}}\left(\frac{1 \text{ g}}{6.02 \times 10^{23} \text{ amu}}\right) = 12 \text{ g/mol C}$$

Did you notice the versatility of Avogadro's number in the last step? When things are molecules, the mass of 1 mol or 6.02×10^{23} molecules is the molecular mass.

2. *Calculations involving moles and grams of a substance*

If you are given the number of grams of a compound you can calculate the number of moles provided you know the molecular or formula mass.

$$\text{Number of moles} = \frac{\text{grams}}{\text{grams mole}^{-1}} - \frac{\text{grams}}{\text{molecular mass}}$$

• EXAMPLE 6

Problem: The air in an average dormitory room contains about 20.0 kg of O_2. How many moles of O_2 are in the room?

Solution: The molecular mass of O_2 is 32.0 g mol^{-1}.

$$\text{Number of moles of } O_2 = \frac{20000 \text{ g } O_2}{32.0 \text{ g mol}^{-1}} = 625 \text{ mol } O_2 \bullet$$

Parallel Problem: A toy helium balloon contains 7.00 grams of helium. How many moles of helium are in the balloon?
Ans: 1.75 moles

• EXAMPLE 7

Problem: There are 250 g of H_2O in a beaker. How many moles of H_2O are in the beaker?

Solution: The molecular mass of H_2O is

$$\begin{array}{rl} \text{2 atoms of H} & 2.0 \\ \text{1 atom of O} & 16.0 \\ \text{Molecular mass of } H_2O = & 18.0 \text{ g mol}^{-1} \end{array}$$

$$\text{Number of moles of } H_2O = \frac{250 \text{ g}}{18.0 \text{ g mol}^{-1}} = 13.9 \text{ mol } H_2O \quad \bullet$$

Parallel Problem: One cup of sugar has a mass of 200 grams. The molecular mass of sugar is 342 g mol^{-1}. How many moles are there in a cup of sugar?
Ans: 0.585 mol

Text Examples 2-4, 2-7, and 2-8 give additional examples of calculations involving moles and grams of substance.

3. Calculations involving moles and number of particles of a substance

The number of particles can be calculated from the number of moles by using Avogadro's number as a unit factor.

$$\text{Number of particles} = \text{number of moles} \left(\frac{6.02 \times 10^{23} \text{ particles}}{1 \text{ mol}}\right)$$

• EXAMPLE 8

Problem: How many molecules of O_2 are there in the average dormitory room of Example 6?

Solution: $\text{Number of molecules} = 625 \text{ mol } O_2 \left(\frac{6.02 \times 10^{23} \text{ molecules } O_2}{\text{mol } O_2}\right)$

$$= 3.76 \times 10^{26} \text{ molecules } O_2 \quad \bullet$$

Parallel Problem: How many atoms of helium are in the toy helium balloon of Parallel Problem 6?
Ans: 1.05 x 10^{24} molecules

• EXAMPLE 9

Problem: How many molecules of H_2O are there in the beaker of water in Example 7?

Solution: Number of molecules = 13.9 mol H_2O $\left(\frac{6.02 \times 10^{23} \text{ molecules } H_2O}{\text{mol } H_2O}\right)$

$$= 8.37 \times 10^{24} \text{ molecules } H_2O \bullet$$

Parallel Problem: How many molecules of sugar are in the cup of sugar in Parallel Problem 7?
Ans: 3.52×10^{23} molecules

Examples 2-3, 2-5, and 2-6 in the text give additional examples of calculations involving moles and number of particles in a substance.

4. *Calculations relating mass to the number of particles in a substance*

Now let us tie all these concepts together in one typical examples in which you are asked to calculate the number of atoms of an element in a given mass of substance.

• EXAMPLE 10

Problem: How many atoms of sodium could be obtained from a salt shaker that contains 20.0 g of salt?

Solution: First calculate the number of moles of salt (NaCl) in the salt shaker. The formula mass of NaCl is

1 atom of Na	23.0
1 atom of Cl	35.5
Formula mass of NaCl =	58.5 g mol^{-1}

$$\text{Number of moles of NaCl} = \frac{20.0 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.342 \text{ mol NaCl}$$

The number of molecules of NaCl is found as follows:

$$\text{Number of molecules of NaCl} = 0.342 \text{ mol NaCl} \left(\frac{6.02 \times 10^{23} \text{ molecules NaCl}}{1 \text{ mol NaCl}}\right)$$

$$= 2.06 \times 10^{23} \text{ molecules NaCl}$$

We could obtain one atom of Na from each molecule of NaCl, so

$$\text{Atoms of Na} = \text{molecules of NaCl} = 2.06 \times 10^{23} \text{ atoms Na}$$

This calculation can be performed in a single step if the appropriate unit factors are chosen and assembled correctly.

$$\begin{matrix}\text{Molecule}\\ \text{of Na}\end{matrix} = 20.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}} \times \frac{6.02 \times 10^{23} \text{ molecules NaCl}}{1 \text{ mol NaCl}} \times \frac{1 \text{ atom Na}}{1 \text{ molecule NaCl}}$$

$$= 2.06 \times 10^{23} \text{ atoms Na} \bullet$$

Parallel Problem: How many hydrogen atoms are in the beaker of water in Example 7?
Ans: 1.67×10^{25} atoms of hydrogen

2-5 Compound stoichiometry

1. Calculation of percentage composition (elemental composition) of a compound when the chemical formula is given

• EXAMPLE 11

Problem: Calculate the percentage composition of NaCl.

Solution: This problem asks us to find the percent by mass of Na and Cl in a sample of NaCl. We need a basis for calculation, so for convenience let us base our calculations on 1 mol of NaCl. One mole of NaCl contains 1 mol of Na atoms and 1 mol of Cl atoms.

$$\begin{aligned} \text{1 mol Cl atoms} &= 35.5\text{ g} \\ \text{1 mol Na atoms} &= \underline{23.0\text{ g}} \\ \text{1 mol NaCl molecules} &= 58.5\text{ g} \end{aligned}$$

The percent of an element is the mass of that element divided by the total mass (mass fraction) times 100.

$$\%\text{ Na} = \frac{23.0\text{ g Na}}{58.5\text{ g NaCl}} \times 100 = 39.3\%$$

$$\%\text{ Cl} = \frac{35.5\text{ g Cl}}{58.5\text{ g NaCl}} \times 100 = 60.7\% \quad \bullet$$

Parallel Problem: Calculate the percentage composition of $MgBr_2$.
Ans: 13.2% Mg, 86.8% Br

Now go through Example 2-12 of the text.

2. Determination of empirical formula of a compound when the percentage composition (elemental composition) is given

When a new compound is synthesized or the identification of an unknown compound is sought, a standard procedure for determining the chemical formula of the compound is by experimentally determining its percentage or elemental composition.

• EXAMPLE 12

Problem: It was experimentally determined that a compound containing only phosphorus and oxygen contained 43.7 percent phosphorus. What is the empirical formula of the compound?

Solution: We need to establish a basis for calculation. A convenient basis is usually 100 g of the compound under consideration. Since 100 g of the compound is 43.7 percent P, the mass of P and O are found by

$$\text{g P in 100 g compound} = 100(0.437) = 43.7\text{ g P}$$

$$\text{g O} = 100\text{ g} - 43.7\text{ g} = 56.3\text{ g O}$$

Since the empirical formula is a ratio of moles of atoms in the compound rather than a mass ratio, we need to convert the mass to number of moles for each type of atom.

$$\text{mol P} = 43.7\text{ g P} \times \frac{1\text{ mol P}}{31.0\text{ g P}} = 1.41$$

$$\text{mol O} = 56.3\text{ g O} \times \frac{1\text{ mol O}}{16.0\text{ g O}} = 3.52$$

We have determined the ratio of phosphorus to oxygen is 1.41 mol of P to 3.52 mol of O. The formula of our compound could be written as $P_{1.41}O_{3.52}$; strictly speaking this is an accurate indication of the mole ratio, but conventionally we express the subscripts in chemical formulas as small whole numbers. To do this we normalize the numbers by dividing both by the smaller number

$$\text{mol P} = \frac{1.41}{1.41} = 1.00$$

$$\text{mol O} = \frac{3.52}{1.41} = 2.50$$

The formula could now be written as $PO_{2.5}$, but the subscripts are still not both whole numbers. If we multiply the normalized ratios by small integers, we get integers that represent the moles of each component and preserve the original ratio.

$$\text{mol P} = 1.00 \times 2 = 2.00$$

$$\text{mol O} = 2.50 \times 2 = 5.00$$

P_2O_5 is the simplest formula with whole numbers for subscripts and is called the empirical formula. •

Parallel Problem: A compound containing only carbon and hydrogen has 82.65% carbon and 17.34% hydrogen. What is the empirical formula of the compound?
Ans: C_2H_5

Example 2-13 in the text illustrates the determination of the empirical formula of a compound containing four different kinds of atoms. The procedure is no different.

3. Determination of molecular formulas from empirical formulas

The molecular formula can be obtained from the empirical formula if the molecular mass is known.

• EXAMPLE 13

Problem: The molecular mass of the compound of phosphorus and oxygen in the previous example was found to be 284 g mol^{-1}. What is the molecular formula of the compound?

Solution: First we determine the empirical mass for the empirical formula, P_2O_5.

2 mol of P	2 x 31 =	62 g
5 mol of O	5 x 16 =	80 g
Empirical mass of P_2O_5		142 g mol $^{-1}$

The molecular formula must be some integral multiple of the empirical formula. This means the molecular formula is composed of some integral number of empirical formulas.

It might be written as $(P_2O_5)_x$, where x is a whole number. It follows that the molecular mass must be x times the empirical mass, or:

$$x = \frac{\text{molecular mass}}{\text{empirical mass}}$$

For our compound

$$x = \frac{284\ \text{g mol}^{-1}}{142\ \text{g mol}^{-1}} = 2$$

and the molecular formula consists of two empirical formulas. We could write it as $(P_2O_5)_2$ or better and more conventionally as P_4O_{10}. •

Parallel Problem: The molecular mass of the compound in the previous Parallel Problem is 58 g mol^{-1}. What is the molecular formula of the compound?
Ans: C_4H_{10}

Now work through Experiments 2-13 and 2-14 in the text.

2-6 Chemical equations

1. *Interpreting chemical equations*

Let us analyze the chemical equation

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O$$

The equation can be read "two molecules of hydrogen react with one molecule of oxygen to produce two molecules of water." An equally valid interpretation is "2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O." We need to analyze the microscopic and macroscopic interpretations further.

	$2\ H_2(g)$	+	$O_2(g)$	→	$2\ H_2O(l)$
Microscale interpretation	2 molecules of H_2	react with	1 molecule of O_2	to produce	2 molecules of water
Macroscale interpretation (mole basis)	2 mol of H_2	react with	1 mol of O_2	to produce	2 mol of water
Macroscale interpretation (gram basis)	4 g of hydrogen	react with	32 g of oxygen	to produce	36 g of water

The microscopic interpretation of a chemical reaction is relatively straightforward. It tells the number of molecules of each reacting substance and of the products. The equation is said to be balanced when the same number of atoms of each different element appears on each side of the equation. The macroscopic interpretation (gram basis) illustrates the mass information conveyed by a chemical equation. This information is not as readily apparent from the equation itself, but can you see how a combination of the equation and the molecular mass gives the mass of each compound? If not, come back to this concept after you have worked some of the example problems and it should become clear. The conservation of mass requirement for a chemical reaction should be quite apparent. The total mass of reactants (4 + 32 = 36 g) is the same as the total mass of products; thus mass is conserved (or, in other words, remains constant).

Now let us look at the macroscopic interpretation (mole basis). If you think of a mole as being an abbreviation of molecular mass, you see that the equation seems to say "2 molecular masses (mol) of H_2 react with 1 molecular mass (mol) of O_2 to produce two molecular masses (mol) of water." Notice that while mass is conserved, the total number of moles of substance is not. We start with 2 mol of hydrogen plus 1 mol of oxygen, or 3 mol total, and we end with 2 mol of water. There was a decrease in total number of moles as the reaction proceeded. If this is troublesome, go back to the microscopic interpretation and observe that the total number of molecules also changes from three molecules of reactants to two molecules of product. A balanced chemical equation does *not* require the same total number of moles on each side of the equation; only the individual atoms need be balanced.

2. *Balancing chemical equations*

Chemical equations are balanced when the law of conservation of mass is obeyed and the chemical formulas are correct. The same number of atoms of each element must appear in the reactants and in the products. Care must be taken to represent the reacting substances by their correct chemical formulas when balancing an equation.

• EXAMPLE 14

Problem: Methane is the main component of natural gas. Write a balanced chemical equation for the combustion of methane gas, CH_4, in oxygen to form carbon dioxide and water.

Solution: A balanced chemical equation shows the ratio of compounds involved in the reaction. We need to know the formulas of reactants and products of the reaction. You will be given these formulas at first, but you should gradually become able to predict the products of a reaction if you know the reactants. For the complete combustion (reaction with oxygen) of a compound containing carbon and hydrogen the products are CO_2 and H_2O. The unbalanced equation for the reaction is

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

We need to balance the equation. You could balance it by selecting coefficients (the number in front of the formula) at random until you hit on a set giving the same number of atoms of C, H, and O on each side of the arrow, but usually it is best to start by balancing carbon first, then hydrogen, and finally oxygen. Since there is one atom of carbon on each side of the equation, carbon is already balanced. (When the coefficient of a compound is unity, it is not indicated in the equation.) There are four atoms of H in CH_4 and only two in H_2O. We certainly do not want to put four atom of H on the right-hand side of the equation by changing the subscript from H_2O to H_4O because it would no longer represent water. We can, however, indicate more than one molecule (mole?) of water by putting a coefficient of 2 in front of the H_2O, which gives four atoms of H on each side of the equation.

$$CH_4 + O_2 \rightarrow CO_2 + 2\,H_2O$$

Now we can balance the O atoms. The coefficients of CH_4, CO_2, and H_2O have been determined and we do not wish to change them because it will disrupt the balancing we have done so far. There are four atoms of O on the right-hand side of the equation. We can indicate four atoms of O on the left-hand side by placing a coefficient of 2 in front of the O_2 formula. The balanced equation is

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \quad \bullet$$

Parallel Problem: Write a balanced chemical equation for the combustion of propane, C_3H_8, in oxygen to form carbon dioxide and water.
Ans: $C_3H_8 + 5\ O_2 = 3\ CO_2 + 4\ H_2O$

2-7 Reaction stoichiometry

1. Stoichiometric calculations using balanced chemical equations

If you have developed a sound understanding of the mole, chemical formulas, unit factors, and chemical equations, stoichiometric calculations will be straightforward. You will need to practice to become confident about your approach to the problems, but you should soon see that the same fundamental technique and approach is used for all problems of stoichiometry.

Let us work through a problem using a balanced chemical equation to calculate amounts of substances undergoing reaction.

• EXAMPLE 15

Problem: How many moles of oxygen are needed for complete combustion of 10 mol of methane?

Solution: We can use the balanced chemical equation from Example 14 to work this problem.

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

The balanced equation tells us 2 mol of O_2 are required for each mole of CH_4. The number of moles of O_2 required for combustion of 10 mol of CH_4 is

$$\text{mol } O_2 = 10 \text{ mol } CH_4 \left(\frac{2 \text{ mol } O_2}{1 \text{ mol } CH_4}\right)$$

$$= 20 \text{ mol } O_2$$

Note how the unit factor needed to convert the given moles of CH_4 to the required moles of O_2 was constructed from the coefficients in the balanced equation. •

Parallel Problem: How many moles of oxygen are needed for complete combustion of 10 mol of propane? (See the previous Parallel Problem)
Ans: 50 mol O_2

Now work carefully through Examples 2-15, 2-16, and 2-17 in the text.

• EXAMPLE 16

Problem: How many grams of CO_2 are produced when 100 g of CH_4 undergo complete combustion?

Solution: From the previous example the balanced reaction is

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

The reaction gives the ratio of compounds on a mole basis. The problem asks us to find the mass of substance produced. We need to change the quantity of CH_4 to number of moles before using the coefficients to give a ratio of substances reacting.

$$\text{mol } CH_4 = 100 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.0 \text{ g } CH_4} = 6.25 \text{ mol } CH_4$$

A unit factor can be constructed from the coefficients in the balanced reaction to give the moles of CO_2 produced from the given amount of CH_4.

$$\text{mol } CO_2 = 6.25 \text{ mol } CH_4 \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4} = 6.25 \text{ mol } CO_2$$

Now we can determine the grams of CO_2

$$\text{g } CO_2 = 6.25 \text{ mol } CO_2 \times \frac{44 \text{ g } CO_2}{1 \text{ mol } CO_2} = 275 \text{ g } CO_2$$

We can combine these steps in one equation by compiling the unit factors in a systematic manner to proceed from the given quantity to the desired quantity.

$$\text{g } CO_2 = 100 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.0 \text{ g } CH_4} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4} \times \frac{44.0 \text{ g } CO_2}{1 \text{ mol } CO_2} = 275 \text{ g } CO_2$$

Notice how this chain of unit factors proceeds in a systematic manner. Grams of given substances are converted to moles by using the molecular mass as a unit factor; then the stoichiometric coefficients from the chemical equation are used to convert to moles of the desired substance; and finally the molecular mass of the desired substance is used as a unit factor to convert the moles of grams. •

Parallel Problem: How many grams of water are produced when 50 grams of CH_4 undergo complete combustion to carbon dioxide and water?
Ans: 7.0 g H_2O

Now work through Example 2-18 in the text.

2. *Concept of limiting reagent*

Often the reactants in a process are not present in stoichiometric amounts (the mole ratio indicated by the ratio of coefficients in the balanced equation). When this is true, one of the reactants will be consumed first and the excess of the other will remain unreacted. The reactant consumed first in a chemical reaction is the limiting reagent because it limits or determines the amount of product that can form.

• EXAMPLE 17

Problem: How many moles of water can be produced when 100 g of CH_4 is placed in a container with 100 g of O_2 and combustion is allowed to go to completion?

Solution: Again, the balanced chemical equation is

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

At this point we do not know whether the CH_4 or the O_2 will be consumed first as the reaction proceeds. It is not apparent from the masses of reacting substances. We need to change the given masses to number of moles.

$$\text{mol of } CH_4 \text{ available} = 100 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.0 \text{ g } CH_4} = 6.25 \text{ mol } CH_4$$

$$\text{mol of } O_2 \text{ available} = 100 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.0 \text{ g } O_2} = 3.12 \text{ mol } O_2$$

Since 2 mol of O_2 are used for each mole of CH_4, the number of moles of CH_4 used for 3.12 mol of O_2 is

$$\text{mol } CH_4 \text{ used} = 3.12 \text{ mol } O_2 \times \frac{1 \text{ mol } CH_4}{2 \text{ mol } O_2} = 1.56 \text{ mol } CH_4 \text{ used}$$

So there are 6.25 – 1.56 = 4.69 mol of CH_4 in excess; O_2 is the limiting reagent and limits the amount of H_2O that can be produced.

$$\text{mol } H_2O = 3.12 \text{ mol } O_2 \times \frac{2 \text{ mol } H_2O}{2 \text{ mol } O_2} = 3.12 \text{ mol } H_2O \quad \bullet$$

Parallel Problem: How many moles of CO_2 are produced when 50.0 g of CH_4 is placed in a container with 30.0 g of O_2 and combustion is allowed to go to completion?
Ans: 6.25 mol H_2O

Now work through Example 2-21 in the text.

2-8 Solution stoichiometry

1. *Molar concentration*

Molarity is defined as moles of solute per liter of solution. The mathematical definition is

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

This definition is an important equation for solving problems on molarity. It allows us to find any one of the variables – molarity, amount of solute, or volume of solution – if the other two are known. The following examples show how this is done.

• EXAMPLE 18

Problem: What is the molarity of 250 mL of a solution that contains 0.330 moles of NaCl?

Solution: The definition of molarity solves this problem directly.

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

Substituting the given information we get

$$M = \frac{0.330 \text{ mol NaCl}}{0.250 \text{ L solution}} = 1.32 \text{ Molar} \quad \bullet$$

Parallel Problem: What is the molarity of 1500 mL of a solution that contains 2.30 moles of solute?
Ans: 1.53 M

• EXAMPLE 19

Problem: How many moles of KBr are in 300 mL of an 0.113 M solution?

Solution: The definition of molarity will solve this problem. Express the definition in terms of the number of moles of solute:

$$\text{moles KBr} = 0.113 \text{ M } (0.300 \text{ L}) = 0.339 \text{ mol} \quad \bullet$$

Parallel Problem: How many moles of solute are in 1800 mL of an 0.670 M solution?
Ans: 1.21 moles of solute

• EXAMPLE 20

Problem: What volume of 0.875 molar solution of KCl would be required to give 2.30 moles of KCl?

Solution: Use the definition of molarity expressed in terms of volume of solution:

$$\text{Volume} = \frac{2.30 \text{ mol KCl}}{0.875 \text{ M}} = 2.63 \text{ liters} \quad \bullet$$

Parallel Problem: What volume of 1.33 M solution is required to give 0.500 moles of solute?
Ans: 0.376 L

• EXAMPLE 21

Problem: How many grams of NaCl are required to make 1.00 L of 0.250 M solution?

Solution: The definition of molarity can be used to solve this problem if we remember that grams of solute is related to the number of moles and molecular mass.

$$\text{grams solute} = (\text{moles solute}) \ (\text{mol mass solute})$$

First we will find the number of moles of solute needed to make the solution.

$$\begin{aligned} \text{moles solute} &= (\text{M})(\text{liters of solution}) \\ &= (0.250 \text{ M})(1.00 \text{ L}) \\ &= 0.250 \text{ moles NaCl} \end{aligned}$$

The number of grams to give 0.250 moles of NaCl is:

$$\text{grams NaCl} = (0.250\ \text{mol})(58.4\ \text{g mol}^{-1})$$

$$= 14.6\ \text{g NaCl} \quad \bullet$$

Parallel Problem: How many grams of KBr are required to make 500 mL of 0.750 M solution?
Ans: 44.6 g KBr

2. Dilution

Solutions used in chemical laboratories are often made by diluting a concentrated stock solution. The molarity of the dilute solution can be determined from the molarity of the concentrated solution and the volume of water added.

• EXAMPLE 22

Problem: A dilute solution of NaCl is made by adding 500 mL of water to 100 mL of 2.00 M stock solution. What is the molarity of the dilute solution?

Solution: The number of moles of NaCl is not changed when the stock solution is diluted with water. Let us solve the definition of molarity for moles of solute.

$$\text{moles solute} = (\text{M})(\text{volume solution})$$

Since the moles of solute remains constant we can say:

$$\text{moles solute} = [(\text{M})(\text{volume})]_{\text{stock}} = [(\text{M})(\text{volume})]_{\text{dilute}}$$

$$\text{or: } \text{M}_{\text{dilute}} = \text{M}_{\text{stock}} \frac{\text{volume stock solution}}{\text{volume dilute solution}}$$

In our problem:

volume stock solution = 100 mL, and
volume dilute solution = 100 mL + 500 mL = 600 mL

Therefore:

$$\text{M}_{\text{dilute}} = 2.00\ \text{M} \frac{100\ \text{mL}}{600\ \text{mL}} = 0.333\ \text{M} \quad \bullet$$

Notice that the molarity of the dilute solution is obtained from multiplying the molarity of the concentrated solution by the ratio of volumes of the two solutions.

Parallel Problem: What is the molarity of the solution made by adding 200 mL of water to 700 mL of 1.50 M stock solution?
Ans: 0.428 M

3. Titration

Titration is a technique for determining the concentration of a solution by reacting a known volume of one solution with a carefully measured volume of a second solution whose concentration is known. The procedure for doing this is described in the text. You will probably perform a titration experiment in the laboratory portion of your course. The following problem illustrates a typical titration problem.

- **EXAMPLE 23**

Problem: 25.00 mL of KOH solution is titrated exactly to the equivalence point with 15.0 mL of 0.450 M H_2SO_4 solution. What is the molarity of the KOH solution?

Solution: The neutralization reaction gives the moles of acid and base reacting in the titration.

$$2\,KOH + H_2SO_4 = K_2SO_4 + 2\,H_2O$$

The moles of H_2SO_4 reacting is:

$$\text{moles } H_2SO_4 = (M_{H_2SO_4})(\text{volume}) = 0.450\text{ M }(0.015\text{ L}) = 0.00675\text{ mol}$$

The moles of KOH reacting with this amount of H_2SO_4 is:

$$\text{moles KOH} = 0.00675\text{ mol } H_2SO_4\ \frac{2\text{ mol KOH}}{1\text{ mol } H_2SO_4} = 0.0135\text{ mol KOH}$$

The resulting molarity of KOH is:

$$M = \frac{0.0135\text{ mol KOH}}{0.025\text{ L}} = 0.540\text{ M} \bullet$$

Parallel Problem: 20.00 mL of $Ca(OH)_2$ solution is titrated exactly with 15.00 mL of 0.0250 M HCl solution. What is the molarity of the $Ca(OH)_2$ solution?
Ans: 0.00938 M

Now work through Example 2-26 in the text.

KEY TERMS

2-1 The microstructure of matter

Atom: The smallest particle of an element which shows the properties of the element.

Chemical bond: The force that holds atoms together in molecules.

Molecule: The smallest aggregate of atoms exhibiting the chemical properties of a pure substance. A combination of two or more atoms.

2-2 Chemical formulas

Chemical formula: A representation of a chemical compound.

Diatomic molecule: Molecules consisting of two atoms.

Empirical formula: A formula expressing the simplest whole-number ratio of atoms of each element in a compound. Same as simplest formula.

Molecular formula: A formula giving the actual number of atoms of each element in a molecule.

Simplest formula: Same as empirical formula.

Structural formula: A sketch showing the arrangement of atoms in a molecule or polyatomic ion.

2-3 Atomic and other masses

Atomic mass: The weighted average (taking into account abundance) of the masses of isotopes of an element.

Atomic mass unit: A unit of mass equal to $\frac{1}{12}$ the mass of a ${}^{12}_{6}C$ atom, abbreviated amu.

Formula mass: The sum of the atomic masses of the atoms in a chemical formula.

Molecular mass: The sum of the atomic masses of the atoms in a molecule.

2-4 The mole

Avogadro's number: The number of atoms in 12 grams of ${}^{12}_{6}C$. 6.02×10^{23} particles mole^{-1}.

Mole: Avogadro's number of particles of any substance. Also the amount of substance in one molar mass.

2-5 Compound stoichiometry

Elemental analysis: The relative amounts of each kind of atom in a molecule expressed as percent by mass. Same as percent composition.

Percent composition: Same as elemental analysis.

Stoichiometry: A study of the mass relationships in chemistry.

2-6 Chemical equations

Balanced equation: A chemical equation with the same number of each type of atom in the reactants and in the products.

Chemical equation: A symbolic representation of a chemical reaction.

2-7 Reaction stoichiometry

Combustion analysis: Determination of elemental composition from data obtained by combustion of a compound.

Limiting reagent: The reactant consumed first in a chemical reaction.

Stoichiometric ratio: A fixed ratio of compounds in a chemical reaction given by the coefficients of the balanced chemical equation.

2-8 Solution stoichiometry

Acid: A substance which produces hydrogen ions in solution (Arrhenius definition).

Aqueous solution: A solution in which water is the solvent.

Base: A substance that produces hydroxide ion in solution (Arrhenius definition).

Buret: A measuring tube used to dispense a measured amount of solution.

Concentrated solution: A solution with a high concentration of solute.

Dilute solution: A solution with a low concentration of solute.

Dilution: Making a solution more dilute by adding more solvent.

Equivalence point: The point in a titration where the actual moles of acid and base which have been combined are equal to the stoichiometric ratio.

Hydrogen ion: H^+

Hydroxide ion: OH^-

Molar concentration: The number of moles of solute per liter of solution. Same as molarity.

Molarity: Same as molar concentration.

Neutralization: Reaction between hydrogen ions and hydroxide ions to form water.

Pipet: A device for dispensing a known volume of liquid.

Solute: The substance dissolved in a solution.

Solvent: The dissolving media of a solution.

Titration: Addition of one reactant to another reactant until an equivalnce point is reached.

Volumetric flask: A container holding a precise amount of liquid.

2-10 Chemical nomenclature: a first look

Binary compound: A compound consisting of two different elements.

IUPAC: International Union of Pure and Applied Chemistry.

Nomenclature: The systematic naming of chemical compounds.

Periodic table: A systematic arrangement of the elements by atomic number.

Systematic name: A chemical name conforming to the IUPAC rules of nomenclature.

Ternary compound: A compound consisting of three different elements.

Trivial name: A chemical name in common use which does not conform to systematic rules of nomenclature.

SELF TEST

True or False

_____ 1. The formula $AlCl_3$ indicates one mole of aluminum chloride contains one mole of aluminum atoms and three moles of chlorine atoms.

_____ 2. A mole signifies a number of particles.

_____ 3. One mole of H_2O contains three moles of atoms.

_____ 4. In balancing a chemical reaction you always make the total moles of product equal the total moles of reactant.

_____ 5. A molecule of oxygen is the same as an atom of oxygen.

_____ 6. The molecular mass of a compound is the sum of the atomic masses of the elements of which the compound is formed.

_____ 7. There are four moles of oxygen atoms in one mole of $Ba_3(PO_4)_2$.

_____ 8. Structural formulas depict the spatial geometry of atoms in molecules.

_____ 9. There are six moles of oxygen atoms in two moles of $Ba(NO_3)_2$.

_____ 10. The correct name for Na_2S is disodium sulfide.

_____ 11. The correct name for KI is potassium iodide.

_____ 12. A compound that contains one atom of magnesium and two atoms of chlorine is named magnesium chlorine.

_____ 13. The correct name for KNO_3 is potassium nitrogen trioxide.

_____ 14. One mole of hydrogen (H_2) contains 6.02×10^{23} hydrogen atoms.

_____ 15. Molarity times liters equals moles.

Completion

16. There are __________________ atoms of nitrogen in 28 g of NH_3.

17. There are __________________ moles of N_2 in 14 g of N_2.

18. The formula mass of $Al_2(SO_4)_3$ is __________________.

19. 3.01×10^{23} molecules of CO_2 have a mass of __________________ grams.

20. The number of grams in 3.00 moles of KCl is __________________.

21. The number of grams in 3.0×10^{22} molecules of KCl is __________________.

22. The number of moles of $Al_2(SO_4)_3$ that could be prepared from 8.34 g of sulfur is __________________.

23. The percent by mass of sulfur in K_2S is __________________.

24. One mole of sulfuric acid, H_2SO_4, has a mass of __________________ grams.

25. When reactants are not present in stoichiometric amounts one of them must be the __________________.

26. The major component of a solution is called the __________________; each of the other components is called a __________________.

27. The reaction between an acid and base is called a __________________ reaction.

28. The name of Li_3P is __________________.

29. The name of $Ca_2(PO_4)_3$ is __________________.

30. The chemical formula for chlorine trifluoride is __________________.

31. In a mole of H_2O, there are Avogadro's number of

(a) hydrogen atoms
(b) hydrogen molecules
(c) oxygen atoms
(d) oxygen molecules

32. Avogadro's number of hydrogen atoms have a mass of

(a) 6.02×10^{23} g
(b) $\frac{1}{6.02} \times 10^{23}$ g
(c) 1 g
(d) 2 g

33. The empirical formula of the compound $C_{12}H_8O_4$ is

(a) CHO
(b) $C_6H_4O_2$
(c) C_3H_2O
(d) $C_4H_2O_2$

34. Sulfur dioxide, SO_2, is a troublesome pollutant generated from sulfur in coal during combustion in coal-fired power plants. The percent by mass of sulfur in SO_2 is

(a) 50 percent
(b) 67 percent
(c) 25 percent
(d) 10 percent

35. How many milliliters of 0.100 M $Ca(OH)_2$ are required to neutralize 30.0 mL of 0.250 M HNO_3?

(a) 12.0
(b) 24.0
(c) 37.5
(d) 75.0

36. The number of atoms of oxygen in 10 g of CO_2 is

(a) 2.7×10^{23}
(b) 1.4×10^{23}
(c) 2.0
(d) 0.45

37. In a mole of NH_3 there are Avogadro's number of

(a) hydrogen atoms
(b) hydrogen molecules
(c) nitrogen atoms
(d) nitrogen molecules

38. A compound is composed only of elements X and Y. An analysis shows the elemental composition is 50 % X and 50 % Y. Which of the following is true about the compound?

(a) The molecular formula is XY.
(b) The empirical formula is XY.
(c) The formula weight is 100 g.
(d) The empirical formula cannot be determined without more information.

39. If 1.00 mol of a compound is dissolved in enough water to make 100 mL of solution, what is the molarity of the resulting solution?

(a) 1.0 M
(b) 0.1 M
(c) 10.0 M
(d) 0.010 M

40. If 24 grams of NaOH are dissolved to make 400 mL of solution, what is the molar concentration of the solution?

(a) 3.0
(b) 2.5
(c) 2.0
(d) 1.5

41. A sodium hydroxide, NaOH, solution is made by dissolving 20.0 g of NaOH in enough water to give 500 mL of solution A. Water is added to 100 mL of solution A to make 200 mL of solution B. What is the molarity of solution B?

(a) 0.250 M
(b) 0.500 M
(c) 1.00 M
(d) 2.00 M
(e) 3.00 M

42. All of the following are true about the information conveyed by the chemical formula, N_2O_4, for the compound dinitrogen tetroxide except:
(a) The mass of one molecule of N_2O_4 is 92 amu.
(b) The mass of one mole of N_2O_4 is 92 grams.
(c) There are six atoms in a molecule of N_2O_4.
(d) NO_2 would be a better way to write the molecular formula.

43. Gasoline is a complex mixture of compounds containing carbon and hydrogen. It is often represented by a single compound, octane, C_8H_{16}. When the chemical reaction for the combustion of octane

$$C_8H_{16} + O_2 \rightarrow CO_2 + H_2O$$

is balanced the coefficients are (from left to right)
(a) 1, 1, 1, 1
(b) 1, 12, 8, 16
(c) 1, 12, 8, 8
(d) 1, 6, 8, 16

44. A compound has an elemental analysis of 49.08 percent Mn and 50.92 percent F. What is the empirical formula of the compound?
(a) MnF
(b) Mn_2F
(c) MnF_2
(d) MnF_3

45. The molarity of a solution containing 3.54 grams of NaCl in 500 mL of solution is
(a) 0.0303
(b) 0.0606
(c) 0.121
(d) 1.77

Chapter 3

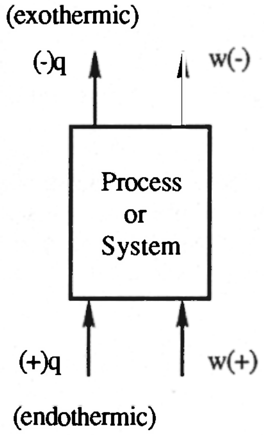
THERMOCHEMISTRY

CHAPTER OVERVIEW

In Chapter 2 you studied the mass and mole relationships of chemical substances in reactions. In Chapter 3 we see that energy is also an important part of chemical changes. In fact, sometimes the most important product in a chemical reaction is heat. You should be able to think of at least two common reactions where the products of a reaction are of no value or even harmful, but the reaction is carried out on a large industrial scale for the energy produced. In thermochemistry, we include energy changes along with chemical changes.

3-1 The first law of thermodynamics

The sign convention for heat flow must be memorized and understood. Remember that for exothermic processes, heat is transferred from the chemical reaction to the surroundings and is given a negative sign. For endothermic processes heat flows from the surroundings to the chemical reaction and is given a positive sign. Work done on the system by the surroundings is positive, work done on the surroundings by the system is negative. Heat and work flowing into the system are positive quantities. Heat and work flowing out of the system are negative.



The first law of thermodynamics, also called the law of conservation of energy, shows there are only two ways to change the energy of a system: either by transfer of heat in or out of the system or through work done on or by the system.

$$\Delta E = q + w$$

Heat is equal to the change in energy for a process taking place at constant volume.

$$q(\text{const. vol.}) = \Delta E$$

3-2 Heat and enthalpy

Heat is equal to the change in enthalpy for a process taking place at constant pressure.

$$q(\text{const. press.}) = \Delta H$$

For processes involving work of expansion or compression of gases, the difference between ΔH and ΔE is equal to the work of expansion or compression. For a phase change involving a gas, such as the boiling of water to make steam, the difference between ΔH and ΔE can be significant. For changes that do not involve significant changes in volume, or other types of work, ΔH = ΔE. This commonly occurs when all components are either liquid or solid.

3-3 Calorimetry

The bomb calorimeter described in the text is a common device for measuring energies of chemical reactions. These measurements are one source of the thermochemical data given in Text Tables 3-2 and 3-3. The energy released in a bomb calorimeter is determined from the rise in temperature of the water and bomb using the relation:

$$q_{\text{reaction}} = -\left[(75.3\ \text{J}\ ^\circ\text{C}^{-1}\ \text{mol}^{-1})\ (n_{H_2O}) + C_{\text{cal}}\right]\ \Delta t$$

where n_{H_2O} is the moles of water in the calorimeter, C is the heat capacity of the calorimeter without any water, and Δt is the temperature rise of the bomb and water.

3-4 Thermochemical equations

Thermochemical equations allow us to relate the heat change in chemical reactions to the moles or grams of chemicals reacting. The enthalpy of reaction is a direct function of the amount of material reacting. For instance, if all the coefficients of a chemical equation are doubled, the ΔH for the reaction is also doubled. This means you must be sure to match the ΔH of reaction with its appropriate balanced equation. The ΔH for any reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.

It would be very inconvenient to measure ΔH in a bomb calorimeter every time you needed a thermochemical value. You have undoubtedly learned through your laboratory experience that it is easier and therefore usually preferable to obtain answers with your head than with your hands. Hess's law in combination with enthalpies of formation allows us to calculate enthalpies of reaction for all kinds of reactions, even including some that cannot be measured experimentally.

3-5 The combustion of coal: a thermochemical illustration

The thermochemical equations for the combustion of several fossil fuels and the generation of synthetic fuels are presented along with a brief introduction to some problems associated with combustion processes.

KEY EQUATIONS

3-1 The first law of thermodynamics

First law of thermodynamics (also called the law of conservation energy):

$$\Delta E = q + w$$

where: ΔE = energy change of a system
q = heat gained (or lost) by a system from its surroundings
w = work done on (or by) a system by its surroundings

Heat for a process at constant volume:

$$q_{\text{(const. vol.)}} = \Delta E$$

3-2 Heat and enthalpy

Heat for a process at constant pressure:

$$q_{\text{(const. press.)}} = \Delta H$$

3-3 Calorimetry

Heat capacity: The amount of heat necessary to raise the temperature of a substance 1°C.

$$C_{H_2O} = 75.3 \text{ joules mol}^{-1}\ {}^{\circ}\text{C}^{-1}$$

Heat associated with a temperature change of a given amount of matter:

$$q = nC\Delta t$$

where: q = heat change in the substance
n = moles of substance
C = heat capacity of the substance in J mol^{-1} °C^{-1}
Δt = $t_{\text{final}} - t_{\text{initial}}$

Heat change of a calorimeter:

$$q = [(75.3 \text{ J } {}^{\circ}\text{C}^{-1} \text{ mol}^{-1})(n_{H_2O}) + C_{\text{cal}}]\Delta t$$

where: q = heat transferred from a chemical reaction to the calorimeter
C_{cal} = heat capacity of the calorimeter without any water
Δt = temperature change of the calorimeter = $(t_f - t_i)$

3-4 Thermochemical equations

$$\Delta H^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{f(\text{products})} - \sum \Delta H^{\circ}_{f(\text{reactants})}$$

LEARNING OBJECTIVES

As a result of studying Chapter 3, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 59 of this *Study Guide.*

3-1 The first law of thermodynamics

1. Clearly distinguish between heat absorbed and released by a system and between work done on or done by a system. (Self Test 1)
2. Clearly distinguish between exothermic and endothermic reactions and give examples of each. (Self Test 6, 31, 38, 39)
3. Write a word statement and a mathematical definition of the first law of thermodynamics and use them to relate heat transfer and work to the energy change in a process. (Text Example 3-1; Text Probs. 3-1, 3-2) (New Skills Example 3; Self Test 2, 5, 8, 9, 16, 20, 21, 22, 32, 40)

3-2 Heat and enthalpy

1. Relate the heat transfer to the enthalpy change in a process. (Text Example 3-2; Text Prob. 3-2) (New Skills Example 1; Self Test 5, 7, 18, 20, 21)
2. Predict when ΔE and ΔH will be similar in magnitude and when they will be different. (Text Probs. 3-4 to 3-6, 3-22) (New Skills Example 2; Self Test 17)

3-3 Calorimetry

1. Describe a bomb calorimeter and tell how it is used to measure heats of chemical reactions. (Self Test 24, 28)
2. Define heat capacity and use it to calculate the heat change when a given amount of material goes through a given temperature range. (Text Example 3-3; Text Probs. 3-7 to 3-12, 3-24) (New Skills Example 4; Self Test 3, 10, 23, 33, 35, 45)
3. Calculate the heat released by a reaction in a bomb calorimeter. (Text Example 3-4; Text Probs. 3-13 to 3-15, 3-25, 3-30) (New Skills Example 5; Self Test 34)

3-4 Thermochemical equations

1. Be able to write thermochemical equations. (Self Test 25)
2. Relate the sign of ΔH to the endothermic or exothermic nature of a reaction. (Self Test 19)
3. Cite the conditions for the standard state of a substance. (Self Test 11)
4. Define standard enthalpy of formation of a compound and recognize that the standard heat of formation of elements is always zero. (Self Test 11, 26, 27)
5. Use Hess's law to calculate ΔH° of reaction from tabulated values of ΔH°_f or by combining appropriate thermochemical reactions. (Text Examples 3-5, 3-6; Text Probs. 3-16 to 3-21, 3-23, 3-26, 3-27, 3-31, 3-32) (New Skills Example 6; Self Test 29, 30, 36, 37, 41, 42)

3-5 The combustion of coal: a thermochemical illustration

1. Write thermochemical equations for the complete combustion of hydrocarbons. (Self Test 4)
2. Predict some products resulting form the incomplete combustion of hydrocarbons. (Self Test 13, 44)

3. Compare the heat energies potentially available from different fuels. (Text Probs. 3-28, 3-29) (Self Test 14)
4. Tell how water gas is produced form coal. Write the chemical reactions for this process. (Text Prob. 3-29) (Self Test 15)

NEW SKILLS

3-1 The first law of thermodynamics

The heat transferred in a chemical reaction is equal to ΔE or ΔH depending on the conditions under which the reaction is carried out. The heat transferred, q, is equal to ΔE for constant volume processes or to ΔH for constant pressure processes. The relation between q and ΔE for a general process is given by the first law, $q = \Delta E - w$. Note that $w = 0$ for all constant volume processes.

• EXAMPLE 1

Problem: Tell whether the heat transferred in each of the following systems is a measure of ΔE or of ΔH.

(a) a combustion reaction in a bomb calorimeter in which the moles of gas remain constant
(b) a chemical reaction taking place in solution in an open beaker with no gas evolved
(c) a chemical reaction taking place in solution in an open beaker with a gaseous product being released from the solution
(d) a chemical reaction taking place that consumes oxygen from the atmosphere but does not produce any gaseous products

Solution: (a) Bomb calorimeter reactions are constant volume processes, so $q = \Delta E$. In this system the process is also at constant pressure, so $q = \Delta E = \Delta H$; (b), (c), and (d) are all constant pressure processes, so $q = \Delta H$ in each case. •

Parallel Problem: Tell whether the heat transferred in each of the following is a measure of ΔE or of ΔH.

(a) burning of carbon monoxide gas to carbon dioxide in an open flame
(b) the reaction between hydrochloric acid and magnesium to produce hydrogen gas and magnesium chloride
(c) the combustion of methane to all gaseous products inside a strong, fixed volume container

Ans: (a) ΔH (b) ΔH (c) ΔE

• EXAMPLE 2

Problem: For each of the reactions in Example 1 tell whether ΔE and ΔH are approximately equal or significantly different from each other in magnitude. If they are significantly different, tell which is greater, ΔE or ΔH.

Solution: In general $q = \Delta E - w$, so for a constant pressure process $\Delta H = \Delta E - w$; therefore w is a measure of the difference between ΔH and ΔE for a constant pressure process.

(a) the process is constant pressure and constant volume; therefore $\Delta E = \Delta H$
(b) same as (a)
(c) significantly different because w is large. w is negative; therefore $\Delta H > \Delta E$
(d) significantly different because w is large. w is positive; therefore $\Delta H < \Delta E$ •

Parallel Problem: For each of the reactions in the previous Parallel Problem, tell whether ΔE and ΔH are approximately equal or significantly different. If they are different, tell which is greater.
Ans:
(a) w is positive; therefore $\Delta H < \Delta E$
(b) w is negative; therefore $\Delta H > \Delta E$
(c) $\Delta H = \Delta E$

3-2 Heat and enthalpy

The first law of thermodynamics can be used to calculate ΔE, q, or w if any two of these quantities are known.

• EXAMPLE 3

Problem: A reaction takes place at constant pressure. If 2.0 kJ of heat is evolved by the reaction and 0.50 kJ of work is done on the reaction by the surroundings, what is:
(a) q (b) w (c) ΔE (d) ΔH?

Solution: (a) heat is evolved; therefore $q = -2.0$ kJ
(b) work is done on the system, so $w = +\ 0.50$ kJ
(c) $\Delta E = q + w = -\ 2.0 \text{ kJ} + 0.50 \text{ kJ} = -\ 1.5 \text{ kJ}$
(d) $\Delta H = q = -\ 2.0$ kJ •

Parallel Problem: A reaction takes place at constant volume and constant pressure. If 2.0 kJ of heat is absorbed by the reaction from the surroundings, what are the values for
(a) q (b) w (c) ΔE (d) ΔH?
Ans:
(a) $q = 2.0$ kJ
(b) $w = 0$ since the process is at constant volume
(c) $\Delta E = 2.0$ kJ
(d) $\Delta H = 2.0$ kJ

3-3 Calorimetry

1. Heat capacity

Heat capacity relates the heat absorbed or released by a given amount of substance to temperature change.

• EXAMPLE 4

Problem: 100 grams of silver absorbed 0.446 kJ of heat and its temperature increased from 20.0°C to 39.0°C. What is the molar heat capacity of silver?

Solution: This problem can be solved easily using the relation $q = nC\Delta t$. First we will solve this equation for C.

$$C = \frac{q}{n\Delta t}$$

where:

$$q = +0.446 \text{ kJ}$$

$$n = \frac{100 \text{ g}}{108 \text{ g mol}^{-1}} = 0.926 \text{ mol}$$

$$\Delta t = t_f - t_i = 39.0 - 20.0 = 19^\circ\text{C}$$

$$C = \frac{q}{n\Delta t} = \frac{446\text{J}}{(0.926 \text{ mol})(19.0^\circ\text{C})} = 25.3 \text{ J mol}^{-1}\ {}^\circ\text{C}^{-1}$$ •

Parallel Problem: 150 grams of silver absorbed 0.330 kJ of energy. What is the temperature change of the silver?
Ans: 9.4°C

2. *Calorimeters*

The heat given off by a reaction in a calorimeter is absorbed by the calorimeter and the water surrounding the bomb. We can calculate the heat absorbed by the calorimeter and water and relate it to the heat of reaction of the substance combusted. Many of the heat of combustion and heat of formation values in tables such as 3-2 and 3-3 in the text were determined in this manner.

• EXAMPLE 5

Problem: A sample of aluminum weighing 1.00 g is placed in a bomb calorimeter with enough oxygen to ensure complete combustion. The calorimeter contains 1150 g of water and has a heat capacity (without the water) of 1256 J $^\circ\text{C}^{-1}$. Combustion of the aluminum causes the temperature of the bomb and water to rise from 20.00°C to 25.11°C. Calculate the enthalpy of combustion of aluminum in kJ mol^{-1}.

Solution: The heat released from the combustion of aluminum is absorbed by the bomb and water. The heat of the combustion reaction is related to the heat absorbed as follows:

$$q_{\text{reaction}} = -(q_{\text{water}} + q_{\text{cal}})$$

The negative sign in the above equation is a result of the sign convention that heat evolved is negative and heat absorbed is positive.

We can make use of the heat capacity relation for the q terms as follows:

$$q_{\text{water}} = (nC\Delta t)_{\text{water}}$$

$$q_{\text{cal}} = (C\Delta t)_{\text{cal}}$$

Our equation becomes:

$$q_{\text{reaction}} = -[(nC\Delta t)_{\text{water}} + (C\Delta t)_{\text{cal}}]$$

Since Δt is always the same for the water and calorimeter:

$$q_{\text{reaction}} = -[(nC)_{\text{water}} + C_{\text{cal}}]\Delta t = -[(75.3 \text{ J mol}^{-1}\ {}^\circ\text{C}^{-1})n_{\text{water}} + C_{\text{cal}}]\Delta t$$

In our problem:

$$n_{\text{water}} = \frac{1150\ \text{g}}{18.0\ \text{g mol}^{-1}} = 63.9\ \text{mol}$$

$$C_{\text{cal}} = 1256\ \text{J °C}$$

$$\Delta t = t_f - t_i = 25.11 - 20.00 = 5.11\ \text{°C}$$

Substituting these values in our equation gives:

$$q_{\text{reaction}} = -[(75.3\ \text{J mol}^{-1}\ \text{°C}^{-1})(63.9\ \text{mol}) + 1256\ \text{J °C}^{-1}](5.11\ \text{°C})$$

$$= -31{,}000\ \text{J or } -31.0\ \text{kJ}$$

This is the heat of reaction for 1.00 g of aluminum. We can find the molar heat of reaction by multiplying by the molar mass of aluminum:

$$q_{\text{reaction}} = -31.0\ \text{kJ g}^{-1}\ (27.0\ \text{g mol}^{-1}) = -837\ \text{kJ mol}^{-1}$$ •

Parallel Problem: It is desired to know the heating value of a sample of coal. 0.500 g of the coal is placed in the calorimeter described above with the same amount of water. On combustion a temperature rise of 2.22°C is observed. What is the heat of combustion of the coal sample in kJ g^{-1}?
Ans: 26.9 kJ g^{-1}

3-4 Thermochemical equations

Enthalpy changes accompanying chemical changes are often measured experimentally, but they are also calculated from tabulated values of ΔH°_f and ΔH°_{Rxn} using Hess's law. There are many chemical reactions for which the enthalpy change cannot be measured directly, so calculated ΔH values are used.

• EXAMPLE 6

Problem: When carbon is burned with just enough oxygen to form carbon monoxide, the actual products are a mixture of carbon dioxide and unburned carbon, so the $\Delta H^o f$ of carbon monoxide cannot be determined experimentally. It can be determined from readily available experimental data by application of Hess's law. Use Hess's law to calculate $\Delta H^o f$ of CO given the heats of combustion of C and CO. The heats of combustion of carbon and carbon monoxide can be determined experimentally.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -390.5\ \text{kJ}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -283.0\ \text{kJ}$$

Solution: The chemical reaction for the formation of CO from its elements can be obtained from the given reactions by reversing the reaction of combustion of CO and adding it to the combustion reaction for carbon.

$$\begin{array}{ll} CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) & \Delta H = +283.0\ kJ \\ C(s) + O_2(g) \rightarrow CO_2(g) & \Delta H = -393.5\ kJ \\ \hline CO_2(g) + C(s) + O_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) + CO_2(g) & \Delta H = -110.5\ kJ \end{array}$$

If 1 CO_2 and 1/2 O_2 are subtracted from both sides of this equation, the desired equation for the heat of formation of CO is obtained.

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H^o{}_f = -110.5\ kJ$$

The ΔH for the overall reaction is found by treating the ΔH values for the given reactions in the same manner. Simply add the ΔH values of the elementary reactions to get ΔH of the overall reaction.

$$(\Delta H^o{}_f)_{CO} = 283.0 - 393.5 = -110.5\ kJ$$

Thus $\Delta H^o{}_f$ for CO has been determined from available experimental data by application of Hess's law. •

Parallel Problem: The heat of combustion of sulfur to sulfur dioxide cannot be measured calorimetrically because a mixture of sulfur dioxide and sulfur trioxide always results when the reaction is carried out. Use Hess's law to calculate the heat of combustion of sulfur to sulfur dioxide.
Ans: $-296.8\ kJ\ mol^{-1}$

Example 3-5 in the text is a similar problem. In general, the application of Hess's law leads to:

$$\Delta H^o{}_{reaction} = \Sigma(\Delta H^o{}_f)_{products} - \Sigma(\Delta H^o{}_f)_{reactants}$$

from which the ΔH^o of any reaction may be calculated from tabulated values of the standard enthalpy of formation. Example 3-6 in the text shows the application of this equation to calculate the heat of combustion of methyl alcohol.

KEY TERMS

3-1 The first law of thermodynamics

Endothermic: A process in which the system absorbs heat from the surroundings.

Exothermic: A process in which the system transfers heat to the surroundings.

First law of thermodynamics: The law of conservation of energy expressed as $\Delta E = q + w$.

Surroundings: The universe outside of the system.

System: That portion of the universe under study.

Thermochemistry: The heat changes associated with chemical or physical changes.

3-2 Heat and enthalpy

Enthalpy: The heat change of a system at constant pressure.

3-3 Calorimetry

Calorimeter: A device for measuring heat changes associated with chemical or physical changes.

Heat capacity: The quantity of heat necessary to raise the temperature of a system by 1°C.

Molar heat capacity: The quantity of heat necessary to raise the temperature of one mole of a substance by 1°C.

3-4 Thermochemical equations

Enthalpy of reaction: The quantity of heat released or absorbed by a reaction.

Formation reaction: A reaction in which one mole of a single product is formed from its uncombined elements.

Hess's law: The change in enthalpy for any process depends only on the nature of the reactants and products and is independent of the path of reaction.

Standard enthalpy of formation: The enthalpy of reaction for a formation reaction when all reactants and products are in their standard state.

Standard state: The form of a substance that is most stable at a pressure of one atmosphere.

Thermochemical equation: The combination of a balanced chemical equation and the corresponding value of ΔH for the reaction.

3-5 The combustion of coal: a thermochemical illustration

Water gas: A mixture of hydrogen and carbon monoxide gases used as an industrial fuel.

SELF TEST

True or False

_____ 1. Work done on the system by the surroundings is positive.

_____ 2. The change in energy of a system is equal to the heat absorbed by the system plus the work done on the system.

_____ 3. Specific heat and heat capacity are different names for the same quantity.

_____ 4. The thermochemical equation for the combustion of methane gas, CH_4, is $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + H_2O(\ell) \quad \Delta H = -802\ \text{kJ}$

_____ 5. The amount of heat absorbed or released by a system during a change depends upon how the change occurs.

_____ 6. A reaction that occurs with evolution of heat is exothermic and has a negative value for q.

_____ 7. The change in heat and the change in enthalpy are exactly the same for a constant pressure process.

_____ 8. When a system does work without any heat input its energy decreases.

_____ 9. A system evolves 2.00 J of energy and does 1.7 J of work. Its change in energy is 0.3 J.

_____ 10. Molar heat capacity is the amount of heat necessary to raise the temperature of one mole of a substance 1°C.

_____ 11. The standard state of a substance is the form which is stable at one atmosphere at some unspecified temperature.

_____ 12. Fossil fuels will continue to be a major source of supply for our energy needs for many years to come.

_____ 13. Carbon monoxide, methyl alcohol, and formaldehyde can all result from the incomplete combustion of natural gas.

_____ 14. Molar heats of combustion give a good means of comparing different hydrocarbon fuels.

_____ 15. Water gas is a combustible fuel made from coal and water.

Completion

16. If a system absorbs heat from its surroundings and has work done on it by the surroundings, the sign of ΔE is ________________________.

17. ΔE and ΔH have similar values when there is no significant change in ____________ for a reaction.

18. $\Delta H = q$ under the condition of ________________________.

19. The sign of ΔH is ________________________ for an exothermic reaction.

20. A chemical reaction takes place in an open beaker and evolves a gas. Is the heat evolved equal to ΔE, ΔH or both? __________________________

21. Ice melts in an open beaker. Is the heat evolved equal to ΔE, ΔH, or both? ________________________.

22. Give a mathematical equation for the first law of thermodynamics. ________________________

23. The units of molar heat capacity are usually ______________________.

24. The evolution or absorption of heat during a chemical reaction can be measured by using a device called a ______________________.

25. The combination of a balanced chemical equation and its enthalpy of reaction is called a (an) ________________________.

26. The standard enthalpy of formation of a compound is the ΔH for the reaction in which one mole of the compound is formed from ______________________.

27. The standard enthalpy of formation of an element has a value of _________________.

28. In a bomb calorimeter experiment the heat evolved is equal to what thermodynamic variable? __________________________.

29. State Hess's law in words ____.

30. Give a mathematical equation for calculating enthalpies of reaction using enthalpies of formation and Hess's law. ______________________________

Multiple Choice

31. Water evaporates from an open beaker. The sign of the heat flow
(a) is negative
(b) is positive
(c) depends on the temperature
(d) cannot be determined because there is no heat flow in the process

32. If a system absorbs heat from its surroundings and its energy remains constant, it must
(a) do work on the surroundings
(b) have work done on it by the surroundings
(c) expand in to a vacuum
(d) violate the first law of thermodynamics since energy cannot be conserved if heat is absorbed

33. If 50 g of water is heated from 20°C to 30°C, the heat absorbed by the water is
(a) 116 J
(b) 500 J
(c) 2090 J
(d) 9000 J

34. A 0.500-gram sample of methane, CH_4, is placed with enough oxygen to ensure complete combustion into a bomb calorimeter. The bomb was immersed in 1020 g of water and the methane ignited. The bomb and water temperature changed from 20.00°C to 25.32°C. The bomb has a heat capacity of 1.163 kJ $°C^{-1}$. What is the heat of combustion of one mole of methane?
(a) 28.9 kJ
(b) –28.9 kJ
(c) 925 kJ
(d) –925 kJ

35. If 20 g of water originally at 25°C is heated to 35°C, the value of q for the water is
(a) +200 J
(b) +46.4 J
(c) +836 J
(d) –836 J

36. Calculate ΔH for the reaction $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$
$P_4(s) + 6\,Cl_2(g) \rightarrow 4\,PCl_3(g)$ $\Delta H = -1084$ kJ
$P_4(s) + 10\,Cl_2(g) \rightarrow 4\,PCl_5(g)$ $\Delta H = -1528$ kJ
(a) 444 kJ
(b) –444 kJ
(c) 111 kJ
(d) –111 kJ

37. Using the data below, calculate the heat of reaction for a coal gasification process: $2\,C(s) + 2\,H_2O(g) \rightarrow CH_4(g) + CO_2(g)$.
$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ $\Delta H° = +131.3$ kJ
$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ $\Delta H° = -41.2$ kJ
$CO(g) + 3\,H_2(g) \rightarrow CH_4(g) + H_2O(g)$ $\Delta H° = -206.1$ kJ
(a) +15.3 kJ
(b) 378.6 kJ
(c) –116.0 kJ
(d) –378.6 kJ
(e) –157.2 kJ

38. $H_2(g)$ and $Cl_2(g)$ react according to the following equation, forming $HCl(g)$
$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ $\Delta H° = -92.0$ kJ
If $H_2(g)$ and $Cl_2(g)$ are mixed in an insulated vessel, the reaction that occurred would be
(a) endothermic, and the temperature of the reaction system would rise
(b) exothermic, and the temperature of the reaction system would rise
(c) endothermic, and the temperature of the reaction system would fall
(d) exothermic, and the temperature of the reaction system would fall

39. When a process results in a transfer of energy from the system to the surroundings
    (a) the process is exothermic
    (b) q for the process is negative
    (c) q for the process is positive
    (d) none of these is correct

40. What is ΔE for the evaporation of 1 mol of water at its normal boiling point? The molar heat of vaporization is 40.7 kJ mol^{-1}.
    (a) 40.7 kJ (b) –40.7 kJ
    (c) 37.6 kJ (d) 0

41. Given the enthalpy of the following reactions at 25°C and 1 atm pressure:
    $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H^\circ = -296.8$ kJ mol^{-1}
    $SO_2 + 1/2\ O_2 \rightarrow SO_3(g)$ $\Delta H^\circ = -98.9$ kJ mol^{-1}
    What is the standard enthalpy of formation of SO_3?
    (a) –395.7 kJ (b) –197.9 kJ
    (c) +197.9 kJ (d) cannot be determined from the data given

42. What is the standard enthalpy of reaction for the combustion of ethylene
    $C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(\ell)$
    given these standard enthalpies of formation? (see Table 3-2 of the text):
    $(\Delta H^o{}_f)C_2H_4(g) = +52.3$ kJ, $(\Delta H^o{}_f)CO_2(g) = -393.5$ kJ, and $(\Delta H^o{}_f)H_2O(\ell) = -285.8$ kJ
    (a) –1411 kJ (b) +1411 kJ
    (c) –627 kJ (d) –731.6 kJ

43. Of the energy sources mentioned in the text, which one is most likely to decrease in importance during your lifetime?
    (a) coal (b) alternative sources
    (c) water power (d) oil and natural gas

44. Which of the following compounds result from the combustion of fossil fuels and add to air pollution problems?
    (a) NO (b) formaldehyde
    (c) carbon monoxide (d) all of these

45. What is the molar heat capacity of mercury if 1.400 J of heat is required to raise the temperature of 2.00 g of mercury from 24.00°C to 26.00°C?
    (a) 0.35 J $mol^{-1}\ {}^\circ C^{-1}$ (b) 1.12 J $mol^{-1}\ {}^\circ C^{-1}$
    (c) 5.60 J $mol^{-1}\ {}^\circ C^{-1}$ (d) 70.2 J $mol^{-1}\ {}^\circ C^{-1}$

Chapter 4

GASES

CHAPTER OVERVIEW

4-1 Variables used for describing gas behavior

Matter exists in three states: solid, liquid, or gas. Depending on the temperature and pressure, most substances can exist in any one of these states. We are familiar with water in each state: solid (ice), liquid (water), and gas (steam or water vapor). Chapter 4 introduces us to the gaseous state. It is the best understood and probably the simplest state to study. We will learn the ABC's of gas behavior (Avogadro's principle, Boyle's law, Charles' law, Dalton's law) and see how they are used to predict gas behavior.

The gas laws use four variables to describe gas behavior.

1. Pressure, P, defined as force per unit area and usually measured in units of atmospheres, kilo pascals, or millimeters of mercury (torr).
2. Volume, V, usually measured in liters.
3. Absolute temperature, T, measured in kelvins.
4. Number of moles, n.

The gas laws allow us to calculate the effect of changes in these variables.

4-2 Pressure-volume relationship: Boyle's law

It is very important to keep track of which variables are changing and which remain constant as you use the gas laws. In Boyle's law the temperature and number of moles of gas remain constant and we determine the changes in pressure and volume. We know from experience that a large volume of air escapes from a tire when the pressure is released. That is, as the pressure decreases, the volume increases. This is an inverse proportion. If we decrease the volume by half, the pressure doubles. We can say, therefore, that at constant temperature the volume of a given number of moles of gas is inversely proportional to the pressure. Suppose we have a sample of gas a pressure P_1 and volume V_1. If the pressure is decreased to P_2 while the temperature is held constant, the volume will increase to V_2 and the change can be depicted as

$$\begin{array}{cc} & V_2 \\ & \uparrow \\ P_1 & V_1 \\ \downarrow & \\ P_2 & \end{array}$$

Since this is an inverse proportion, the volume increases as the pressure decreases. Mathematically this becomes

$$P_1V_1 = P_2V_2$$

This equation is Boyle's law. It allows calculation of changes in pressure and volume when the amount of gas and the temperature remain constant.

4-3 Temperature effects: Charles' law

1. Charles' law

A gas expands as it is heated at constant pressure. That is, when the temperature increases, the volume increases. The temperature is directly proportional to the volume. If one increases, the other must increase also. This means that at constant pressure the volume of a given number of moles of gas is directly proportional to the absolute temperature. This is Charles' law. Mathematically, it is stated as

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

2. The combined law

We could develop a law between the pressure and temperature changes that would look very much like Charles' law if we desired, but instead let us examine the equation resulting from combining Boyle's and Charles' laws to give the combined law.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

For a given quantity of gas this law allows calculations of pressure, volume, and temperature changes. Note that if the temperature is held constant ($T_1 = T_2$), the combined law reduces to Boyle's law. If the pressure is held constant so that $P_1 = P_2$, the combined law reduces to Charles' law. This is especially significant because if you recognize which variables are constant and which are changing, the combined law can be used to calculate all problems in the Boyle's law, Charles' law, and combined law sections of the text. Try this and see.

The text describes two methods for using the gas laws. Method 1 simply plugs the given values into the appropriate formula and calculates the answer. Method 2 tries to get you to visualize the effect of changing the pressure, volume, or temperature and set up ratios that change the desired variable in the right direction (increase or decrease). If you take a few minutes to think about what is happening in the problem and have an understanding of how these variables affect each other, the quantitative calculations should not be too difficult. If you rely on memorized formulas to solve the problem, you will get less out of this chapter.

4-4 The ideal-gas law

1. Avogadro's principle

Avogadro's principle, molar volume, and combining volumes of gases are closely related principles. Avogadro's principle states: At a given temperature and pressure, equal volumes of all gases contain equal numbers of molecules or moles. Consequently, 1 liter of all gases contains the same number of moles and 1 mol of all gases must occupy the same volume. At standard conditions of 0°C and 1 atm, 1 mol of any gas occupies 22.4 liters. This is the standard molar volume. Since chemical reactions involve fixed numbers of moles of chemicals, gaseous chemical reactions involve fixed volumes of the gases. This allows a new interpretation of chemical reactions for gases

$2\ H_2(g)$	$+$	$O_2(g)$	$\rightarrow$	$2\ H_2O(g)$
2 liters of hydrogen	react with	1 liter of oxygen	to produce	2 liters of water

Thus, we see that volume relations are the same as mole relations. This is Gay-Lussac's law of combining volumes. It will be used in calculations of stoichiometry of gases.

2. The ideal-gas law

Boyle's law, Charles' law, and Avogadro's principle may be combined into one equation, the ideal gas law:

$$PV = nRT$$

R is called the ideal gas constant and has a value of 0.0821 liter atm $\text{mol}^{-1}\ \text{K}^{-1}$, when P is in atmospheres, V is in liters, n is in moles, and T is in kelvins.

Most gas problems, even those involving Boyle's, Charles', and the combined laws, can be solved with the ideal-gas law. You must pay particularly close attention to the units on each variable when using this equation. Make sure your units are consistent. Problems involving molecular weight and density of gases are simply applications of the ideal-gas law.

4-5 Other properties of the ideal gas

1. Dalton's law

In a mixture of gases that do not react chemically, each gas acts independently, as if it were alone in the container, unaffected by the presence of other gases. Thus, each gas exerts its own, independent pressure called a partial pressure, and the sum of partial pressures of all gases in the container gives the total pressure. This is Dalton's law. Stated mathematically it becomes:

$$P_{\text{total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}}$$

where P_{total} is the pressure that would be measured by a barometer or pressure gauge and P_{A}, P_{B}, and P_{C} are partial pressures of gases A, B, and C. Dalton's law can be used to find the total number of moles of gas in a mixture. The total number of moles of gas is the sum of the moles of each individual gas in a mixture:

$$n_{\text{total}} = n_{\text{A}} + n_{\text{B}} + n_{\text{C}}$$

where n_{A}, n_{B}, and n_{C} are the moles of gases A, B, and C present in the mixture. Notice that Dalton's law is simply saying: "The total (pressure) is the sum of the parts (partial pressures)," and the same reasoning applies to total moles. Dalton's law is frequently used to find the partial pressure of a gas collected over water in a laboratory experiment (Text Example 4-12).

2. Graham's law

Diffusion and *effusion* are terms used to describe the same gas behavior under different situations, the relative rate of movement or mixing of gases. Graham's law says the rate of movement of a gas (diffusion or effusion) is inversely proportional to its molecular mass. Mathematically this is stated:

$$\frac{\text{Rate}_{\text{A}}}{\text{Rate}_{\text{B}}} = \frac{\sqrt{\text{M}_{\text{B}}}}{\sqrt{\text{M}_{\text{A}}}}$$

Usually the rates of movement are determined experimentally to find the molecular mass of an unknown gas in calculations involving Graham's law.

4-6 Kinetic-molecular theory

The kinetic-molecular theory is a physical model of the behavior of gases based on a few very basic assumptions which correlate very well with experimental measurements. Developed in full, it provides convincing evidence that molecules exist and beautifully joins a simple but efficient theory or model to experimental observations. The assumptions of the kinetic-molecular theory are:

1. A gas is composed of a large number of tiny particles (molecules).
2. The molecules of a gas are in violent motion and collide frequently. The total energy remains constant on collision. Energy may be transferred from one molecule to another, but there is no loss of total energy.
3. There are no forces of attraction or repulsion between molecules.
4. The average kinetic energy of the gas molecules is proportional to the absolute temperature.

A successful theory should adequately describe experimental observations. Note that the observed behavior of gases described below can be correlated with the assumptions of the kinetic-molecular theory listed above:

1. Gases are compressible.
2. Gases expand to fill the container and diffuse rapidly. This accounts for the observed brownian motion in gases. Since gases do not lose energy, the gaseous state is permanent.
3. The gaseous state is permanent even at high pressures. Real gases may have significant forces of attraction or repulsion which cause deviation from ideal behavior at high pressures.
4. Assumption 4 above leads to Graham's law of diffusion.

4-7 Gas stoichiometry

We will see how the coefficients in a balanced chemical equation can be used to determine the amounts of gases involved in chemical changes.

4-8 Real gases

The equations we have discussed so far apply only to "ideal gases." Actually there is no such thing as an ideal gas. It is a simplified model or representation of gas behavior that allows fairly accurate calculations to be carried out in a simple manner. The imaginary ideal or perfect gas is one in which there are no interacting forces between molecules and the volume of the atoms is negligible compared to the total volume. If such a gas existed, it would obey the gas laws exactly. Its pressure would be exactly reduced by half when the volume is doubled. Atoms of real or actual gases attract or repel each other and occupy some space, so they do not follow the ideal gas equations exactly. Fortunately, most gases exhibit very close to ideal behavior at normal conditions of temperature and pressure, so the ideal gas equations are a very good approximation to real gas behavior under normal conditions.

Although real gases do not follow the ideal-gas law exactly, the ideal-gas law is useful because it gives quite accurate results unless the pressure becomes very large or the temperature is very low. Figures 4-16 and 4-18 in the text show how the actual pressure-volume behavior of N_2 and CO_2 deviates from PV behavior predicted by the ideal-gas law. Over what range of temperature and pressure would you say the ideal-gas law holds for these gases?

The van der Waals equation attempts to account for the two main reasons for nonideal behavior in gases: (1) molecules occupy space and (2) they attract or repel each other. It is easy to calculate pressure with the van der Waals equation but difficult to solve for volume. The values of a and b are different for different gases, so each real gas has its own van der Waals constants. The van der Waals equation predicts real gas behavior better than the ideal-gas law but is still not exact. More complicated equations and calculations are used to get more accurate results. Industrial firms often buy and sell gases at very high pressures and low temperatures where there is considerable deviation from ideal-gas or van der Waals behavior; thus, more complex equations are required to determine the amounts of gas bought or sold. The ideal-gas law predicts no temperature change as an ideal gas expands in to a vacuum. Most real gases cool during expansion. Carbon dioxide from a CO_2 fire extinguisher cools enough to form dry ice as it expands because forces of attraction between CO_2 molecules must be overcome as the gas expands. The energy to overcome these forces comes from the CO_2 molecules and they cool as they give up their kinetic energy.

Hydrogen and helium have repelling forces between molecules at room temperature and pressure, so they become warmer during expansion. This makes hydrogen a hazardous gas to handle under pressure because enough heat can be generated as H_2 expands to cause combustion or explosion.

KEY EQUATIONS

4-2 Pressure-volume relationship: Boyle's law

$$PV = k \quad \text{or} \quad P_1V_1 = P_2V_2$$

4-3 Temperature effects: Charles' law

Charles' law $V = aT$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Combined law $\frac{PV}{T} = c$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

4-4 The ideal-gas law

Ideal-gas law $PV = nRT$

4-5 Other properties of the ideal gas

Dalton's law $P_{\text{total}} = P_A + P_B + P_C$

Graham's law of diffusion

$$\frac{\text{Rate}_A}{\text{Rate}_B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

4-8 Real gases

van der Waal's equation $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$

LEARNING OBJECTIVES

As a result of studying Chapter 4, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 78 in this *Study Guide*.

4-1 Variables used for describing gas behavior

1. Define pressure and make a sketch showing how barometers and manometers measure it. (Text Prob. 4-1) (Self Test 17)
2. Give the common units for pressure, volume, and temperature. (Self Test 17)

4-2 Pressure-volume relationship: Boyle's law

1. Write a mathematical statement of Boyle's law and use it to calculate pressure-volume relations in gases at constant temperature. (Text Examples 4-1, 4-2; Text Probs. 4-3, 4-4) (Self Test 1, 2, 12, 20, 31)
2. Make a sketch showing the PV behavior of an ideal gas at constant temperature. (Text Fig. 4-5)

4-3 Temperature effects: Charles' law

1. Describe a method of determining absolute zero and explain why the Kelvin temperature scale is used in Charles' law. (Self Test 3)
2. Write a mathematical statement of Charles' law and use it to calculate temperature-volume changes at constant pressure for gases. (Text Examples 4-3, 4-4; Text Probs. 4-5 to 4-7) (New Skills Example 1; Self Test 11, 19, 30, 32)
3. Use pressure ratios, volume ratios, and temperataure ratios in combined gas law calculations. (Text Examples 4-5, 4-6; Text Probs. 4-14 to 4-18, 4-27, 4-37) (New Skills Example 2; Self Test 21, 33, 34, 35)

4-4 The ideal-gas law

1. Give an example illustrating Gay-Lussac's law of combining volumes. (Self Test 7)
2. State Avogadro's principle and give an example showing how it relates volume to moles of a gas. (Self Test 4)
3. Write the ideal-gas law and use it to calculate pressure-volume-temperature-mass relationships in gases. (Text Examples 4-7, 4-8; Text Probs. 4-19 to 4-21, 4-50) (New Skills Example 3; Self Test 5, 16)
4. Memorize the numerical value and units of the ideal-gas constant. (Text Prob. 4-59) (Self Test 24)
5. Cite the value of temperature and pressure at STP.
6. Cite the value of the molar volume of a gas at STP, and calculate molar volumes at any value of temperature and pressure. (Text Probs. 4-12, 4-13) (New Skills Example 3; Self Test 5)
7. Calculate the molecular mass of a gas from its measured density. (Text Examples 4-9, 4-11; Text Probs. 4-28 to 4-30, 4-34, 4-35) (Self Test 25, 43)

4-5 Other properties of the ideal gas

1. Use an example to show what is meant by the partial pressure of a gas. (Self Test 6, 22)
2. Write Dalton's law and use it to calcualte the total pressure when partial pressures are known and to find the partial pressure of a gas collected over water. (Text Examples 4-10, 4-11; Text Probs. 4-22 to 4-24, 4-54) (New Skills Example 4; Self Test 10)
3. Calculate the density of a gas from its molecular mass. (Text Prob. 4-25)(Self Test 13, 36, 39)
4. Explain the difference between diffusion and effusion and use measured values to calculate molecular mass of gases. (Text Prob. 4-8) (Self Test 23, 28, 29)

5. Use Graham's law to calculate (a) the molecular mass of a gas from measured effusion rates and (b) the relative rates of diffusion of gases. (Text Examples 4-12, 4-13; Text Probs. 4-10, 4-11) (Self Test 8, 27, 44)

4-6 Kinetic-molecular theory

1. List the assumptions of the kinetic-molecular theory.
2. Use examples to illustrate how observed properties of gases are explained by the theory. (Text Probs. 4-9, 4-31 to 4-33, 4-42, 4-52) (Self Test 9, 38)
3. Explain how Boyle's law, Charles' law, Graham's law, and Avogadro's principle relate to kinetic theory.

4-7 Gas stoichiometry

1. Calculate the amounts of gases used or produced in chemical reactions. (Text Examples 4-14 to 4-16; Text Probs. 4-36, 4-38 to 4-40, 4-55 to 4-58, 4-60) (New Skills Examples 5 to 7; Self Test 37, 45)

4-8 Real gases

1. Explain how the volume of molecules and intermolecular forces cause departure from ideal-gas behavior for real gases. (Text Probs. 4-41, 4-48, 4-49, 4-62) (Self Test 38)
2. Explain why departure from ideal behavior is most pronounced at high pressures and low temperatures. (Self Test 14, 40, 41)
3. Calculate the pressure or temperature of a gas using the van der Waals equation. (Text Example 4-17; Text Probs. 4-47, 4-61) (New Skills Examples 1; Self Test 42)
4. Explain the physical significance of the constants *a* and *b* in the van der Waals equation. (Text Probs. 4-44 to 4-46)
5. Compare the free expansion of an ideal gas and a real gas and explain the difference in temperature changes for the two gases. (Text Probs. 4-42, 4-43) (Self Test 15, 26)

NEW SKILLS

4-2 Pressure-volume relationship: Boyle's law

Boyle's law states that the product of the pressure and volume of a gas at constant temperature is equal to a constant number.

$$PV = k$$

If the pressure or volume of a gas changes while the temperature remains the same, Boyle's law says the product of pressure and volume does not change.

The mathematical equation for the constant PV relation is

$$P_1V_1 = P_2V_2$$

Subcript 1 refers to an initial state and subscript 2 refers to a final state after the change in pressure or volume.

Solving for V_2

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

Note that the final volume is found by multiplying the initial volume by a ratio of pressures. We can use this reasoning to assemble a pressure ratio without referring to the equation. When pressure is reduced, the volume increases, so the pressure ratio must have a value greater than 1. On the other hand, if the pressure is increased, the volume will decrease. For V_2 to be less than V_1, the pressure ratio must be less than 1. This is the key to the reasoning approach used in Method 2 of Examples 4-1 through 4-6 in the text.

Knowing how pressure and volume are related, you can predict whether the volume will increase or decrease and set up the pressure ratio accordingly.

Work through Examples 4-1 and 4-2 of the text, paying close attention to the Method 2 solutions.

4-3 Temperature effects: Charles' law

1. Charles' law problems

Charles' law problems can be worked by the same approach as Boyle's law problems. Reasoning out temperature, pressure, or volume ratios to calculate changes is possible in most problems. Using the formula (Method 1 in the text) is just as valid and you should use the method that suits you best. If you understand both methods, so much the better.

One very important fact must be remembered when using Charles' law, whether you use the formula method or the ratio method. The temperature must be in kelvins rather than degrees Celsius. If the temperature is given in degrees Celsius it must be converted to kelvins before the problem can be worked.

• EXAMPLE 1

Problem: A 5.00-liter sample of gas has its temperature raised from 10 to 40°C at constant pressure. What is the new volume?

Solution: Will the final volume be more or will it be less than 5.00 liters? Since an increase in temperature causes an increase in volume, the final volume is greater than the initial.

Would the ratio $\frac{10}{40}$ or $\frac{40}{10}$ be used to multiply the initial volume? Be careful. Neither of these temperature ratios is correct because the ratio must be in kelvins, not degrees Celsius.

$$T_1 = 273 + 10 = 283 \text{ K}$$

$$T_2 = 273 + 40 = 313 \text{ K}$$

Now, is the ratio $\frac{283}{313}$ or $\frac{313}{283}$ correct? Since the volume must increase, we select the ratio greater than 1.

$$V_2 = V_1 \left(\frac{313}{283}\right)$$

$$V_2 = 5.00 \text{ liters} \left(\frac{313}{283}\right) = 5.53 \text{ liters}$$ •

Parallel Problem: A sample of gas occupies 15 liters at 220°C. What would be its volume at 25°C?
Ans: 9.1 L

Now work through examples 4-3 and 4-4 in the text.

2. *Combined law problems*

Combined law problems are approached exactly as Boyle's law and Charles' law problems. The difference is that two variables change instead of one. A separate ratio can be set up for each changing variable and both ratios are used as multipliers to find the final conditions.

• EXAMPLE 2

Problem: A helium-filled weather balloon has a volume of 325 liters at 9.0 kPa and 25°C. It is released and rises through the atmosphere to an altitude where the pressure is 25 kPa and the temperature is –30°C. What is the volume of the balloon at that altitude?

Solution: First we convert the temperature to kelvins.

$$T_1 = 273 + 25 = 298 \text{ K}$$

$$T_2 = 273 - 30 = 243 \text{ K}$$

Now we reason through the problem to set up the required ratios. Since the pressure decreases, the volume will increase, so the pressure ratio mut be greater than 1 or $\frac{90}{25}$. The temperature decreases and this will cause a decrease in volume, so the temperature ratio must be less than 1.

$$V_2 = 325 \text{ liters} \left(\frac{90}{25}\right)\left(\frac{243}{298}\right) = 950 \text{ liters} \bullet$$

Parallel Problem: A sample of gas occupies 10 liters at one atmosphere pressure and 25°C. What would be its volume at 10 atmospheres and 300°C?
Ans: 1.9 L

Now work Examples 4-5 and 4-6 in the text.

4-4 The ideal-gas law

1. *Using the ideal-gas law in calculation*

Watch for problems that are tailor-made for using the ideal-gas law. There are four variables in the equation $PV = nRT$: pressure, volume, temperature, and number of moles. When a problem gives three of the four variables P, V, T, and n and asks for the value of the fourth, use the ideal-gas law. Problems that ask for a gas density or molecular weight can also be solved by the ideal-gas law. Be sure you use consistent units. The units of all variables must be consistent with the units of R.

$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

so volume must be in liters, temperature in kelvins, and pressure in atmospheres. Work through Examples 4-8 and 4-9 in the text for experience with this type of problem.

2. *Calculation of the density of a gas*

Let us try a variation of the ideal-gas law problem.

• EXAMPLE 3

Problem: What is the density of hydrogen at 30°C and 1.00 atm?

Solution: Density = mass/volume. We can find the number of moles of hydrogen from the ideal-gas law, convert the moles to grams, and find the density. The volume is not given in the problem, but we are interested in the number of moles or grams per liter so we choose 1 liter of gas as the basis for calculation. Then *n* will be the number of moles in 1 liter. Solve the ideal-gas law for number of moles.

$$T = 273 + 30 = 303\text{ K}$$

$$n = \frac{PV}{RT} = \frac{1.00\text{ atm}(1.00\text{ liter})}{0.0821\text{ liter atm mol}^{-1}\text{ K}^{-1}(303\text{ K})} = 0.0402$$

Now find the number of grams in the liter.

$$\text{No. of g} = n \times \text{mol. mass.}$$

$$= 0.0402\text{ mol }(2.00\text{ g mol}^{-1}) = 0.0804\text{ g}$$

Since this is the grams per liter, it is also the density.

$$\text{Density} = \frac{\text{grams}}{V} = \frac{0.0804\text{ g}}{1.00\text{ liter}} = 0.0804\text{ g liter}^{-1}$$ •

Parallel Problem: What is the density of argon gas at 100°C and 0.50 atm?
Ans: 0.065 g L^{-1}

3. Calculation of molecular weight from gas density

A common variation in applying the ideal-gas law is to find the molecular mass of a gas from an experimentally measured density. Example 4-10 in the text illustrates this calculation.

4-5 Other properties of the ideal gas

Dalton's law of partial pressure states that the total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

$$P_{\text{total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}}$$

If oxygen gas were collected by displacement of water from a container there would be two gases present in the container, oxygen and water vapor. The total pressure would be:

$$P_{\text{total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

• EXAMPLE 4

Problem: Calculate the partial pressure of oxygen collected by displacement of water on a day when barometric pressure is 90.0 kPa and the temperature is 25°C. The vapor pressure of water at 25°C is 3.17 kPa.

Solution: We will assume that the total pressure of the gas is the same as atmospheric pressure. Dalton's law can be solved for the partial pressure of oxygen.

$$P_{O_2} = P_{\text{total}} - P_{H_2O}$$
$$= 90.0 \text{ kPa} - 3.17 \text{ kPa} = 86.8 \text{ kPa} \bullet$$

Parallel Problem: What is the partial pressure of hydrogen collected by displacement of water if barometric pressure is 1.000 atm and the water temperature is 21°C? The vapor pressure of water is 21°C is 18.65 mm Hg.
Ans: 0.975 atm

Now try Examples 4-12 and then 4-11 in the text.

4-7 Gas stoichiometry

When gases are involved in chemical reactions, we sometimes want to know the volume of the gases involved. The principles of Chapter 4 enable us to make these calculations.

• EXAMPLE 5

Problem: Oxygen was discovered by the decomposition of mercury(II) oxide, HgO.

$$2\ HgO(s) \rightarrow 2\ Hg(\ell) + O_2(g)$$

What volume of oxygen at STP could be obtained from the decomposition of 50.0 g of HgO?

Solution: We can determine the moles of O_2 from regular stoichiometry and use the molar volume at STP to find the volume.

$$\text{mol } O_2 = 50.0 \text{ g HgO} \times \frac{1 \text{ mol HgO}}{217 \text{ g HgO}} \times \frac{1 \text{ mol } O_2}{2 \text{ mol HgO}} = 0.115 \text{ mol } O_2$$

Since 1 mol of any gas at STP occupies 22.4 liters we can find the volume at STP in 0.115 mol O_2.

$$\text{liters } O_2 = 0.115 \text{ mol } O_2 \times \frac{22.4 \text{ liters}}{1 \text{ mol}} = 2.58 \text{ liters} \bullet$$

Parallel Problem: Carbon dioxide is evolved from the thermal decomposition of magnesium carbonate. What volume of carbon dioxide gas at STP could be obtained from the decomposition of 35.0 g of magnesium carbonate?
Ans: 9.30 L

If more than one gas is involved in the reaction, unit factors for volume ratios of reacting chemicals can be set up directly from the stoichiometric coefficients.

• EXAMPLE 6

Problem: Nitric oxide, NO, is produced during the combustion of gasoline in an automobile engine. It rapidly reacts with oxygen to form nitrogen dioxide, NO_2, which is responsible for the brown haze common during air pollution episodes in many cities. If 10.0 liters of NO_2, measured at STP, are produced from NO, how many liters of O_2, also measured at STP, would be consumed?

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

Solution: Since all the gases are measured under the same conditions, the number of moles reacting is directly proportional to the volumes. The coefficients of the equation can be used to give the volume ratios.

$$\text{liters } O_2 = 10.0 \text{ liters } NO_2 \times \frac{1 \text{ liter } O_2}{2 \text{ liter } NO_2} = 5.0 \text{ liters } O_2$$ •

Parallel Problem: How many liters of chlorine gas at STP could be prepared from 15 liters of hydrogen chloride gas also measured at STP. The chemical reaction is:

$$4\,HCl(g) + O_2(g) = 2\,H_2O(g) + 2\,Cl_2(g)$$

Ans: 7.5 L

We can extend our gas stoichiometry problems beyond the STP conditions to any temperature, pressure, and volume with the ideal-gas law.

• EXAMPLE 7

Problem: How many liters of hydrogen measure at 80.0 kPa and 20°C are required to react with chlorine to produce 15.0 g HCl?

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

Solution: First we will find the number of moles of HCl produced. Use the chemical equation to find how many moles of H_2 are required, and then use the ideal-gas law to determine the volume of the hydrogen.

$$\text{mol HCl} = 15.0 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 0.411 \text{ mol HCl}$$

$$\text{mol } H_2 = 0.411 \text{ mol HCl} \times \frac{1 \text{ mol } H_2}{2 \text{ mol HCl}} = 0.206 \text{ mol } H_2$$

Now the volume of HCl is found from the ideal-gas law.

$$V = \frac{nRT}{P}$$

$$= \frac{0.206 \text{ mol}(0.0821)(\text{L atm mol}^{-1}\text{ K}^{-1})(293 \text{ K})}{(80.0 \text{ kPa})\frac{1 \text{ atm}}{101.3 \text{ kPa}}}$$

$$= 6.27 \text{ L}$$ •

Parallel Problem: How many liters of chlorine gas at 0.780 atm and 35°C could be prepared from 25.0 g of HCl? See the previous Parallel Problem for the chemical reaction.
Ans: 11.1 L

Now try Example 4-15 in the text.

4-8 Real gases

1. *The van der Waals equation*

There are many equations of state for gases besides the ideal-gas law. You will be expected to solve for pressure and temperature of a gas using the van der Waals equation.

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

In this equation *P*, *V*, *n*, *R*, and *T* have the same meanings and units as in the ideal-gas law. The constants *a* and *b* have different values for each gas. Some of these values are included in Table 4-5 in the text. Be sure your units are consistent as you use the equation.

2. *Calculation of pressure or temperature of a gas using the van der Waals equation*

The van der Waals equation can be solved for pressure to give

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

or for temperature to give

$$T = \frac{1}{nR}\left(P + \frac{n^2a}{V^2}\right)(V - nb)$$

• EXAMPLE 8

Problem: Oxygen is often sold in high-pressure cylinders containing 28.5 lb of O_2 at a pressure of 2200 lb in^{-2}. The cylinder has a volume of 60 liters. Calculate the temperature of the oxygen using (a) the ideal-gas law and (b) the van der Waals equation.

Solution:

$$P = 2200 \text{ lb in}^{-2}\left(\frac{1 \text{ atm}}{14.7 \text{ lb in}^{-2}}\right) = 150 \text{ atm}$$

$$V = 60 \text{ liters}$$

$$n = 28.5 \text{ lb } (454 \text{ g lb}^{-1})\left(\frac{1 \text{ mol } O_2}{32 \text{ g}}\right) = 404 \text{ mol } O_2$$

(a) Solving the ideal-gas law for *T* and substituting the given values

$$T = \frac{PV}{nR} = \frac{150 \text{ atm } (60 \text{ liters})}{404 \text{ mol } (0.082 \text{ L atm mol}^{-1} \text{ K}^{-1})} = 272 \text{ K or } -1^{\circ}\text{C}$$

(b) Now solve the van der Waals equation for *T* and substitute the given values. The constants *a* and *b* are found in Table 4-5 in the text.

$$a = 1.36 \text{ L}^2 \text{ atm mol}^{-2} \qquad b = 0.0318 \text{ L mol}^{-1}$$

$$T = \frac{1}{nR}\left(P + \frac{n^2a}{V^2}\right)(V - nb)$$

$$T = \frac{1}{404 \text{ mol } (0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})} \left\{ 150 \text{ atm} + \frac{(404 \text{ mol})^2 \, (1.36 \text{ L}^2 \text{ atm mol}^{-2})}{(60 \text{ L})^2} \right\}$$
$$\{60 \text{ L} - (404 \text{ mol})(0.0318 \text{ L mol}^{-1})\}$$

$$T = 301 \text{ K} \qquad \text{or} \qquad 28^\circ\text{C} \; \bullet$$

Example 4-17 in the text illustrates the calculation of pressure using the van der Waals equation.

KEY TERMS

4-1 Variables used for describing gas behavior

Atmosphere: A unit of pressure equal to 1.01325×10^5 pascal.

Kelvin temperature scale: An absolute temperature scale in which the unit is the kelvin. A kelvin is 1/273.16 of the difference between absolute zero (0 K) and the triple point of water.

Manometer: A device used to measure the pressure of gas in a container.

Millimeter of mercury: (mm Hg) A unit of pressure equal to 1/760 atmosphere.

Pascal: The SI unit of pressure equal to one newton per square meter.

Pressure: The force on a surface divided by the area of that surface or force per unit area.

Torr: A unit of pressure essentially equal to one millimeter of mercury.

4-2 Pressure-volume relationship: Boyle's law

Boyle's law: At constant pressure the volume of a gas is inversely proportional to its pressure, or $P_1V_1 = P_2V_2$

4-3 Temperature effects: Charles' law

Charles' law: At constant pressure the volume of a gas is directly proportional to its absolute temperature, or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Combined gas law: For any change in pressure, volume, and temperature of a gas, the ratio of PV to T remains constant, or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

4-4 The ideal-gas law

Avogadro's principle: Equal volumes of different gases at the same temperature and pressure contain equal numbers of molecules.

Equation of state: An algebraic equation relating the pressure, volume temperature, and number of moles of a gas.

Gay Lussac's law of combining volumes: When measured at the same temperature and pressure, the volumes of gaseous reactants and products of a reaction can be expressed as ratios of small integers.

Ideal gas: A gas whose behavior is described by the ideal-gas law.

Ideal-gas constant: The constant of proportionality in the ideal-gas law, $R = 0.0821$ L atm mol^{-1} K^{-1}.

Ideal-gas law: An equation relating the pressure, volume, temperature, and number of moles of an ideal gas, $PV = nRT$.

Molar volume: The volume occupied by one mole of a substance. For an ideal gas at STP, $V_m = 22.4$ L mol^{-1}.

Standard temperature and pressure: (STP) For gases, standard temperature is 0°C, standard pressure is one atmosphere.

4-5 Other properties of the ideal gas

Dalton's law of partial pressures: The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

Diffusion: The passage of one substance through another.

Effusion: The passage of a substance through a pinhole orifice.

Graham's law of diffusion: The rate of diffusion of a gas is inversely proportional to the square root of its density.

Graham's law of effusion: The rate of effusion of a gas through a pinhole orifice is inversely proportional to the square root of its molecular mass.

Partial pressure: The pressure a gas in a mixture would exert if it were alone in the container.

Vapor pressure: The pressure of a gas in equilibrium with its liquid in a closed container.

4-6 Kinetic-molecular theory

Brownian motion: The rapid zigzag motion of small particles due to collision with high-speed molecules.

Kinetic-molecular theory: A model of ideal-gas behavior based on the assumptions that molecules of gas do not interact with each other except on collision and they have essentially no volume.

4-8 Real gases

Adiabatic process: A process in which no heat is exchanged between the system and surroundings.

Free expansion: Expansion into a vacuum.

Inversion temperature: Temperature above which free expansion of a gas is exothermic.

Real gas: An actual gas characterized by departure from ideal-gas behavior.

van der Walls equation: An equation of state which simulates real-gas behavior more closely than the ideal-gas equation.

SELF TEST

True or False

_____ 1. The product of the pressure and volume of a fixed amount of gas is constant.

_____ 2. When a gas is compressed the number of moles increases.

_____ 3. The absolute temperature of a gas is directly proportional to its volume at constant pressure.

_____ 4. Avogadro's principle states that equal masses of different gases at STP contain the same number of molecules.

_____ 5. One mole of any ideal gas occupies 22.4 liters at STP.

_____ 6. In a mixture of two gases A and B, the total pressure is 680 mm Hg. The partial pressure of A is 340 mm Hg. We are sure that half the molecules in the mixture are gas A.

_____ 7. The volume ratio of gases participating in a chemical reaction is always a small whole number.

_____ 8. Nitrogen gas will diffuse faster than oxygen gas at a fixed temperature and pressure.

_____ 9. The kinetic-molecular theory successfully explains most of the experimentally observed behavior of gases.

_____ 10. The total pressure of a sample of hydrogen collected over water is equal to the partial pressure of hydrogen minus the partial pressure of the water vapor.

_____ 11. If a sample of gas in a container at 100°C and 2.0 atm pressure is heated to 200°C at constant volume, the pressure will double.

_____ 12. According to Boyle's law, the pressure of a gas is directly proportional to its volume at constant pressure.

_____ 13. All ideal gases have the same density, measured in grams per liter, under the same conditions of temperature, pressure, and volume.

_____ 14. Departure from ideal-gas behavior is most pronounced at high pressures and low temperatures.

_____ 15. Most gases cool during a free adiabatic expansion because the molecules expend energy to overcome intermolecular forces of attraction.

Completion

16. The mathematical expression of the ideal-gas law is ____________________.

17. Pressure is equal to force per __________________.

18. In the gas laws temperature is always used in __________________ units.

19. If the temperature of a gas at constant pressure increases, the volume ____________________.

20. If the pressure of a gas at constant temperature increases, the volume ____________________.

21. The volume of a gas at STP is ______________ than the volume at 80 kPa and 300 K.

22. The pressure of a gas alone in a container is the _______________.

23. According to Graham's law the relative rate of diffusion of two gases is inversely proportional to the square root of their ________________________.

24. The value of the ideal-gas constant is _______________ liter atm mol^{-1} K^{-1}.

25. An 11.2 liter sample of an ideal gas at STP has a mass of 32 grams. The molecular mass of the gas is __________________.

26. A gas becomes hotter during expansion if it is above its ______________ temperature.

27. The rate of diffusion of hydrogen gas is four times that of ________________.

28. The process by which gas molecules escape a container by passing through a small opening is called __________________.

29. The process by which molecules of one gas mix with molecules of another gas is called ________________.

30. If a sample of nitrogen occupies a volume of 4.00 liters at 0°C, it will occupy a volume of ______________ liters at 80°C if the pressure remains constant.

Multiple Choice

31. If a gas occupies 8.0 liters at 60 kPa, what volume will it occupy at 80 kPa if the temperature remains constant?
(a) 3.0 L (b) 6.0 L (c) 10.7 L (d) 12.0 L

32. If a gas occupies 8.0 liters at 0°C, what volume will it occupy at 273°C? The pressure remains constant.
(a) 2.2 L (b) 4.0 L (c) 4.4 L (d) 16 L

33. The proper ratios of temperature and pressure to find the volume of a gas initially at 100°C and 90 kPa after its pressure and temperature are changed to 50 kPa and 150°C are:
(a) $\frac{50}{90}, \frac{100}{150}$ (b) $\frac{90}{50}, \frac{150}{100}$ (c) $\frac{90}{50}, \frac{423}{373}$ (d) $\frac{50}{90}, \frac{373}{423}$

34. A sample of a gas has a volume of 5.0 liters. If the pressure is doubled and the absolute temperature is increased by a factor of four, the final volume of the gas will
(a) increase by a factor of 8
(b) increase by a factor of 2
(c) decrease by a factor of 1/2
(d) decrease by a factor of 2

35. The density of a gas at 0°C and two atm pressure is 1.3 g L^{-1}. What will be the density of the gas at STP?
(a) 0.65 g L^{-1} (b) 1.3 g L^{-1} (c) 2.6 g L^{-1}
(d) insufficient information to tell

36. The density of a gas at STP is
(a) the molar volume divided by the molar mass
(b) the molar mass multiplied by 0.0821 liter atm mol^{-3} K^{-1}
(c) the molar mass divided by the molar volume
(d) the molar mass divided by the number of moles

37. The reaction for formation of ammonia from nitrogen and hydrogen is the basis for a large fertilizer industry. $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$
What volume of hydrogen, measured at STP, is required to produce a metric ton of ammonia for use as fertilizer? (one metric ton = 1000 kg)
(a) 1.98×10^6 L (b) 1.31×10^6 L
(c) 8.82×10^4 L (d) 990 L

38. Which one of the following is not a property of an ideal gas?
(a) It consists of tiny particles in constant, random motion.
(b) Energy is exchanged between particles as they collide.
(c) There are no forces of attraction or repulsion between the particles.
(d) The volume of the particles is negligible compared to the volume of the container.

39. Which one of the following gases will have the greatest density at STP?
(a) H_2 (b) CH_4 (c) Cl_2 (d) Ar

40. Which one of the following is false for one mole of gas?

(a) For an ideal gas $\frac{PV}{RT} = 1$

(b) the deviation of $\frac{PV}{RT}$ from 1 is a measure of the nonideal behavior of a gas.

(c) For real gases, $\frac{PV}{RT}$ approaches 1 as pressure increases.

(d) For real gases, $\frac{PV}{RT}$ approaches 1 as temperature increases.

41. Real gases approach ideal behavior at

(a) low pressure and low temperature
(b) low pressure and high temperature
(c) high pressure and high temperature
(d) high pressure and low temperature

42. What is the pressure of 2.00 mol of ammonia gas in a 1.00-liter container at 25°C as predicted by the van der Waals equation? (For ammonia, $a = 4.17$ L^2 atm mol^{-2} and $b = 0.0371$ L mol^{-1}.)

(a) 21.1 atm (b) 36.1 atm (c) 44.5 atm (d) 48.9 atm

43. It is found that 1.43 g of an unidentified gas fills a 1.00-liter container at STP. Which of the following is most likely to be the gas?

(a) H_2 (b) CH_4 (c) O_2 (d) SO_2

44. It is found that a sample of an unidentified gas effuses through a small opening half as fast as helium. Which of the following is most likely to be the gas?

(a) H_2 (b) CH_4 (c) O_2 (d) SO_2

45. What volume of O_2 is consumed by complete combustion of 10 liters of CH_4 at 500°C and 90 kPa?

(a) 30 L (b) 20 L (c) 10 L (d) 5 L

Chapter 5

THE ATOM

CHAPTER OVERVIEW

5-1 Early models of the atom

Our present concepts of the structure of atoms are so widely accepted and applied that it is difficult to imagine how matter was visualized before the discoveries described in this section. Dalton's theory of the atom showed amazing insight for his time. Compare his 1803 ideas with your present understanding of atoms. His theory successfully explained the chemical observations of his day and still account for the basic aspects of chemical behavior as we understand it today. His ideas were the beginning of modern atomic theory.

Several other important discoveries followed Dalton in the nineteenth century. Faraday found a basic relationship between matter and electricity, which meant that understanding the behavior of electrons became imporant to understanding matter. The experiments of Crookes, Thomson, and Millikan established two basic properties of electrons: their charge and mass. Further experiments with Crookes tubes revealed a relation between negative and positive electrical charges in matter.

5-2 The nuclear atom

Our present idea of atomic structure in which a nucleus is surrounded by electrons originated with Rutherford's experiment. Study Figures 5-5 and 5-6 in the text until you understand how these observations showed the Thomson model for the structure of an atom could not be correct. Rutherford interpreted his observations as evidence of a small, dense, positively charged nucleus surrounded by space containing the electrons.

Further work showed the nucleus is composed of protons and neutrons. There are some important facts to be remembered from Section 5.2

1. The atomic number is the positive charge on the nucleus of an atom and is equal to the number of protons in the nucleus.
2. The number of protons in the nucleus equals the number of electrons in the extranuclear region of a neutral atom.
3. The mass number is equal to the number of neutrons plus protons in the nucleus.
4. Isotopes are atoms with the same number of protons but different numbers of neutrons in the nucleus. They account for atomic masses being nonintegral numbers.

5-3 Atomic masses

Elements exist in nature as a mixture of isotopes. Since different isotopes of any given element have different masses, we use an average of these isotope masses for the atomic mass. The average is based on the isotope abundance found in nature for each element. The mass and abundance of the isotopes are determined by mass spectrometry as shown in Figure 5-8 in the text. Text Example 5-1 shows how the mass and abundance values from mass spectrometry are used to calculate atomic mass. Note the difference between mass number and atomic mass pointed out in the last paragraph of the section.

5-4 Electrons in atoms

1. The noncollapsing atom

The first ideas about behavior of electrons in the space around the nucleus were unsatisfactory right from the start. They were (1) the electron was moving and (2) the electron was not moving. Strange as it may seem, neither of these alternatives was possible. If the electron were stationary, the electrostatic attraction of its negative charge to the positive charge of the nucleus would cause the atom to collapse. On the other hand, according to classical physics, an electron changing its direction, as in a circular orbit, must emit radiation. Electrons emitting radiation would lose energy and slow down and gradually spiral into the nucleus and the atom would collapse. Rutherford suggested that electrons in atoms travel in trajectories round the nucleus, much as planets travel around the sun, but could not explain why this structure would not collapse.

Either Rutherford's ideas of atomic structure were wrong, or classical physics did not apply to the atom. A new kind of physics was needed to explain atomic structure. This new physics was introduced by Niels Bohr. It is called quantum mechanics and is based on an application of wave theory to electrons and radiant energy.

2. Radiant energy

Radiant energy is often called electromagnetic energy or light energy. The text discusses several characteristics of radiant energy:

1. Radiant energy travels by wave motion much like waves on a surface of water.
2. The frequency, ν, of a wave is the number of crests (or troughs) passing a point per second and is measured in hertz.
3. The wavelength, λ, is the distance between successive corresponding points (crests or troughs).
4. The velocity of a wave is the product of its frequency and wavelength: $c = \nu\lambda$, where c is the velocity of light in a vacuum, 3×10^8 m sec^{-1}.
5. Radiant energy in the form of light can be refracted, or separated by a prism into its different wavelengths. The pattern of wavelengths is called a spectrum. Figure 5-12 in the text illustrates a spectrum.

3. Atomic spectroscopy

When atoms are sufficiently excited by receiving radiant energy, they emit a line spectrum which consists of only certain, discrete wavelengths. The spectral pattern is distinctive for each element, much like a fingerprint. Figure 5-13 in the text shows a line spectrum of hydrogen. The wavelengths observed in the hydrogen spectrum can be calculated very accurately from the Rydberg equation. Note how atoms with more electrons than hydrogen give a more complex line spectrum as shown in Figure 5-14 in the text.

4. The Bohr atom

Bohr's application of wave theory to radiant energy led to the development of quantum mechanics and the concept of quantization. This simply means that energy comes in specific discrete amounts. When this idea is applied to electrons, it means the electron is restricted to only certain energy values. It turns out that the differences between these energy values are numerically the same as the radiant energies of the lines observed in atomic spectra. Thus, there is a basic connection between the energy of electrons and the wavelength of light emitted by an atom. Planck and Einstein showed how to relate the energy of a photon to its wavelength, and Bohr showed the connection between photon energy or wavelength and the energy levels of electrons in atoms. It appeared that electrons behave like waves.

The Bohr model of an atom consists of electrons moving around the nucleus in circular orbits much as planets revolve around the sun. Electrons can change orbits by absorbing or emitting photons which have exactly the same energy as the difference in energy between the two electron orbits. Since the emitted energy is quantized (has a fixed value), the wavelength of the energy is fixed and gives a single line in the spectrum of the atom. In a given atom, many different transitions between different energy levels are possible for an electron, giving rise to the total line spectrum.

The values of energies of the observed line spectrum for hydrogen agree very well with energies calculated from the Bohr model, but agreement between energies calculated from the Bohr model and experimental energies from observed spectra is poor for atoms other than hydrogen.

LEARNING OBJECTIVES

As a result of studying Chapter 5, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 92 of this *Study Guide*.

5-1 Early models of the atom

1. List four ideas of modern atomic theory that came from John Dalton. (Text Prob. 5-1) (Self Test 1, 31)
2. List the important discoveries made from observations of gas discharge tubes. (Text Probs. 5-2, 5-7, 5-10) (Self Test 2, 3, 4, 16, 1, 7, 32)
3. Explain how the mass and charge of the electron were determined. (Self Test 6, 33)

5-2 The nuclear atom

1. Make a sketch illustrating how Rutherford showed that the atom consists of a small, heavy, positively charged nucleus surrounded by extranuclear electrons. (Text Probs. 5-4, 5-5)
2. List three contributions of Rutherford's experiment to the theory of atomic structure. (Text Prob. 5-6) (Self Test 18, 34)
3. Make a table showing the relative characteristics (mass and charge) of the three subatomic particles: proton, neutron, and electron. (Text Probs. 5-8, 5-11, 5-20)
4. Explain the difference between mass number and atomic mass. (Self Test 7, 23, 36, 39)
5. List three items of information about the structure of an atom conveyed by the atomic number. (Text Prob. 5-12) (Self Test 5, 19)
6. Define and use the term *isotope*. (Self Test 9, 21, 22, 36, 42)
7. Determine the number of protons, electrons, and neutrons in the nucleus of an element from its atomic number and mass number. (Text Probs. 5-12, 5-13) (New Skills Examples 1 to 3; Self Test 8, 12, 35, 40, 41, 43)

5-3 Atomic masses

1. Calculate atomic masses from isotope masses and isotope abundances. (Text Example 5-1; Text Probs. 5-16, 5-17, 5-23, 5-29) (New Skills Example 4; Self Test 6, 44)
2. Understand the operation and significance of a mass spectrometer. (Self Test 24)

5-4 Electrons in atoms

1. Explain how application of classical physics to electrons in atoms leads to predictions of collapsing atoms. (Self Test 37)
2. Use the relationship between the speed of a wave, its frequency, and its wavelength in calculations. (Text Probs. 5-24 to 5-26) (New Skills Example 5; Self Test 14, 25, 27, 38)
3. Illustrate the difference between continuous and line spectra. (Self Test 28, 30)

4. Show how line spectra arise from transition of electrons between available energy levels in the atom. (Text Prob. 5-27) (Self Test 11)
5. Explain why new concepts in physics, replacing classical mechanics, were needed to explain the observations of Rutherford. (Self Test 13)
6. Know how the work of Bohr, Planck, and Einstein led to quantum mechanics to replace classical mechanics in explaining the behavior of small particles. (Text Prob. 5-20) (Self Test 26)
7. Calculate the energy of a photon from its frequency using $E = h\nu$, or from its wavelength using $E = hc/\lambda$. (Text Prob. 5-22)
8. Understand the concept of quantized energy. (Self Test 26)
9. Describe the Bohr model of an atom. (Text Probs. 5-18, 5-21) (Self Test 10, 15, 29)
10. Make calculations that show how the energies calculated from the Bohr model (Rydberg equation) agree with the energies of the observed line spectrum for hydrogen. (Text Prob. 5-19)
11. Use the Rydberg equation to calculate wavelengths of lines in the hydrogen spectrum. (Text Prob. 5-28) (New Skills Example 6; Self Test 45)

NEW SKILLS

5-2 The nuclear atom

1. Atomic numbers and mass numbers

The atomic number and mass number give valuable information about the structure of the atom. The atomic number indicates the number of protons in the nucleus and the number of electrons surrounding the nucleus in a neutral atom. The mass number is the number of protons plus neutrons in the nucleus and is designated by a superscript before the atomic symbol. For example, ^{23}Na signifies the isotope of sodium with mass number 23. The atomic number can be found from the periodic table on the inside front cover of the text and is included in the symbol as $^{23}_{11}$Na. However, since sodium can have only one atomic number, 11, this information is already specified by the atomic symobl, Na.

2. The use of atomic numbers and mass numbers to determine the number of protons, neutrons, and electrons in atoms

• EXAMPLE 1

Problem: How many protons and neutrons are present in the nucleus of ^{208}Pb? How many electrons are in the neutral atom?

Solution: The atomic number of Pb is found from the periodic table on the inside front cover of the main text to be 82, so there are 82 protons in the nucleus. We find the number of neutrons as follows:

$$\text{Mass number} = \text{number of protons} + \text{number of neutrons}$$

$$\text{Number of neutrons} = \text{mass number} - \text{number of protons}$$

$$= 208 - 82 = 126$$

The number of electrons is always equal to the number of protons in a neutral atom, so there are 82 electrons in Pb. •

Parallel Problem: How many protons and neutrons are present in the nucleus of ^{243}Pu? How many electrons are in the neutral atom?
Ans: 94 protons, 149 neutrons, 94 electrons

• EXAMPLE 2

Problem: How many protons, neutrons, and electrons are present in $^{208}Pb^{2+}$?

Solution: The mass number and atomic number are the same for ^{208}Pb and $^{208}Pb^{2+}$, so the number of protons and neutrons is the same as in Example 1. The atom has acquired a +2 charge by losing two electrons. The two electrons took their negative charge with them, so the atom was left with two more protons than electrons, hence the +2 charge. The number of electrons remaining is 82 – 2 = 80 •

Parallel Problem: How many protons, electrons, and neutrons are present in $^{65}Zn^{2+}$?
Ans: 30 protons, 28 electrons, 35 neutrons

• EXAMPLE 3

Problem: Complete the following table:

Symbol	Mass number	Atomic number	Protons	Neutrons	Electrons
^{27}Al					
$^{27}Al^{3+}$					
	200	80			
			17	20	
	84		36		

Solution:

Symbol	Mass number	Atomic number	Protons	Neutrons	Electrons
^{27}Al	27	13	13	14	13
$^{27}Al^{3+}$	27	13	13	14	10
^{200}Hg	200	80	80	120	80
^{37}Cl	37	17	17	20	17
^{84}Kr	84	36	36	48	36

•

Parallel Problem: Complete the following table:

Symbol	Mass number	Atomic number	Protons	Neutrons	Electrons
^{108}Ag					
$^{108}Ag^+$					
	28	14			
			25	30	
	80			45	

Ans:

Symbol	Mass number	Atomic number	Protons	Neutrons	Electrons
^{108}Ag	108	47	47	61	74
$^{108}Ag^+$	108	47	47	61	46
^{28}Si	28	14	14	14	14
^{55}Mn	55	25	25	30	25
^{80}Br	80	35	35	45	35

5-3 Atomic masses

Most elements found in nature are composed of mixtures of isotopes. The atomic mass of an element is the average of the masses of the isotopes in the element. The average is weighted, or adjusted for the percent abundance of the isotopes. The percent abundance and masses of the isotopes are determined by mass spectrometry, and atomic masses are calculated from these data. You need to be able to perform these calculations, so the method is illustrated in the following example.

• EXAMPLE 4

Problem: A naturally occurring sample of lithium was analyzed in a mass spectrometer and found to consist of two isotopes: 92.75 percent of the sample was ^{7}Li (mass 7.01 amu) and 7.25 percent was ^{6}Li (mass 6.01 amu). What is the average atomic mass of Li for this sample?

Solution: Each isotope contributes mass to the sample in proportion to its percent abundance. For the mass of 100 atoms:

$$\begin{array}{lcr} ^7\text{Li contributes} & 92.75\%\ (7.01\text{ amu}) = & 650\text{ amu} \\ ^6\text{Li contributes} & 7.25\%\ (6.01\text{ amu}) = & \underline{43.6\text{ amu}} \\ & & 694\text{ amu} \end{array}$$

The mass of 100 atoms of Li is 694 amu, so the mass of an atom of Li (the atomic mass) is:

$$\frac{694\text{ amu}}{100} = 6.94\text{ amu}\ \bullet$$

Parallel Problem: Vanadium is a metal used to make alloy steels. It occurs in two isotopes in nature with a distribution of 0.24% for ^{50}V (mass 50.52836 amu) and 99.76% for ^{51}V (mass 51.56038). What is the atomic mass of vanadium for this natural sample?
Ans: 51.43664

Now do Example 5-1 in the text.

5-4 Electrons in atoms

1. The wavelength of radiant energy

The speed, frequency, and wavelength of a wave are related by the equation:

$$\text{Speed} = \nu\lambda$$

In chemical applications we are interested in electromagnetic waves. These are the waves by which radiant energy travels. They behave in a manner analogous to water waves, but travel at the speed of light, designated by c and equal to 3.00×10^8 m s^{-1}. For radiant energy, or light waves, the product of the frequency ν and wavelength λ is equal to the speed of light

$$c = 3.00 \times 10^8 \text{ m s}^{-1} = \nu\lambda$$

This relation can be used to find the frequency of radiation if the wavelength is known, or to find the wavelength if the frequency is given.

• EXAMPLE 5

Problem: The wavelength of red light is 650 nm. What is its frequency?

Solution: 650 nm is 650 nanometers or 650×10^{-9} m. Solve the equation $c = \nu\lambda$ for ν and use $c = 3.00 \times 10^8$ m s^{-1}.

$$\nu = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{\lambda}$$

$$= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{650 \times 10^{-9} \text{ m}} = 4.6 \times 10^{14} \text{ s}^{-1} \bullet$$

Parallel Problem: The crossbar on a TV antenna is designed so that its length is about equal to the wavelength of the station signal being received. If the crossbar is 120 cm long, what frequency of wave will it receive best?
Ans: 2.5×10^9 s^{-1}

Example 5-2 and Probs. 5-24 to 5-26 in the text are very similar to these problems.

2. Calculation of wavelengths using the Rydberg equation

You may be asked to calculate the wavelength of a line in the hydrogen spectrum using the Rydberg equation. Let us see how this is done. Equation 5-1 in the text is the Rydberg equation:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where λ is the wavelength of lines in the hydrogen spectrum, R is the Rydberg constant (1.10×10^{-2} nm^{-1}) and n_1 and n_2 are integers. If $n_1 = 1$, the equation gives the Lyman series; if $n_1 = 2$, the Balmer series; and if $n_1 = 3$, the Paschen series of hydrogen spectra lines. In all cases n_2 is an integer larger than n_1. We will investigate the significance of the values of n in Chapter 6.

We can generate several equations for each series by giving different values to n_2.

• EXAMPLE 6

Problem: Calculate the wavelength of the line in the Lyman series of the hydrogen spectrum for which $n_2 = 2$.

Solution: The Rydberg equation for the Lyman series is

$$\frac{1}{\lambda} = 1.10 \times 10^{-2}\ \text{nm}^{-1}\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

For $n_2 = 2$ the equation becomes

$$\begin{aligned}\frac{1}{\lambda} &= 1.10 \times 10^{-2}\ \text{mn}^{-1}\left(1 - \frac{1}{2^2}\right)\\ &= 1.10 \times 10^{-2}\ \text{nm}^{-1}\ (1 - \tfrac{1}{4})\\ &= 8.25 \times 10^{-3}\ \text{nm}^{-1}\\ \lambda &= \frac{1}{8.25 \times 10^{-3}}\ \text{nm} = 121\ \text{nm}\ \bullet\end{aligned}$$

Parallel Problem: Calculate the wavelength of the line in the Lyman series of the hydrogen spectrum for which $n_2 = 4$.
Ans: 97.0 nm

Now try Problem 5-28 in the text.

KEY TERMS

5-1 Early models of the atom

Canal ray: The stream of positively charged particles leaving the anode in a gas discharge tube.

Cathode ray: The stream of electrons leaving the cathode in a gas discharge tube.

Crookes tube: A vacuum tube with two electrodes used to investigate the behavior of electrical discharges in gases at low pressure.

Dalton's atomic theory: Observations by John Dalton in 1803 that known chemical behavior could be explained by assuming that matter is composed of atoms.

Electron: A subatomic particle with very small mass and a unit negative electrical charge.

Thomson atom: An early model of the atom based on electrons imbedded in a positively charged sphere.

5-2 The nuclear atom

Atomic number: The number of protons in the nucleus of an atom.

Extranuclear: Associated with an atom but outside the nucleus.

Isotope: Atoms with the same number of protons but different numbers of neutrons in the nucleus.

Mass number: The total number of nucleons in the nucleus of an atom.

Neutron: An electrically neutral subatomic particle of similar mass to a proton.

Nucleon: A proton or neutron in the nucleus of an atom.

Nucleus: The tiny center of an atom which comprises all the positive charge and nearly all the mass of an atom.

Proton: A subatomic particle carrying a unit positive electrical charge.

5-3 Atomic masses

Atomic mass: The weighted (by abundance) average of the masses of the isotopes of an element.

Mass spectrometer: An instrument which separates and measures the relative abundance of isotopes.

5-4 Electrons in atoms

Balmer series: A series of lines in the hydrogen spectrum with wavelength in the visible region.

Bohr atom: A model of the atom in which electrons are in circular orbits around the nucleus similar to planets in the solar system.

Electromagnetic energy: Same as radiant energy.

Exicted state: The state of an atom when electrons have been raised to higher energy levels by the absorption of energy.

Frequency: The number of waves passing a point per second, expressed in cycles per second (hertz).

Ground state: The lowest energy state available to a particle.

Hertz: One cycle per second, a measure of frequency.

Ionization: Loss of an electron.

Line spectrum: A set of discrete lines produced by light of discrete wavelengths.

Lyman series: A series of lines in the hydrogen spectrum with wavelengths in the ultraviolet region.

Paschen series: A series of lines in the hydrogen spectrum with wavelengths in the infrared region.

Photon: A quantum of electromagnetic energy.

Plank's constant: The constant of proportionality between the energy and frequency of electromagnetic radiation.

Quantized: Restricted to specific values.

Radiant energy: Energy traveling by wave motion.

Rydberg equation: An algebraic relation between the wavelength of lines in the hydrogen spectrum and a series of integers.

Spectroscopy: The process of obtaining a spectrum.

Spectrum: The array resulting from the orderly separation of wavelengths or mass.

Speed of light: The rate at which electromagnetic radiation travels. In a vacuum it is 3.00×10^8 m sec^{-1}.

Wavelength: The distance between successive points on a wave.

SELF TEST

True or False

_____ 1. John Dalton proposed that all matter is composed of identical atoms.

_____ 2. Cathode rays are attracted to a positive charge.

_____ 3. Electrons are present in all matter.

_____ 4. Removal of an electron from an atom leaves the atom with a positive charge.

_____ 5. The atomic number gives the number of protons in the nucleus and number of extranuclear electrons in an atom.

_____ 6. Millikan measured the charge on an electron in his famous "oil drop experiment."

_____ 7. The mass number is the number of protons plus electrons in an atom.

_____ 8. There are 24 protons and 26 neutrons in the nucleus of $^{52}_{24}\mathrm{Cr}$.

_____ 9. All atoms of the same element are alike in mass and size.

_____ 10. Bohr's theory states that electrons travel in well-defined orbits around the nucleus.

_____ 11. Line spectra result when electrons in an atom move from higher energy levels to lower energy levels and release the excess energy as a photon.

_____ 12. $^{110}\mathrm{Cd}$ has fewer neutrons than protons.

_____ 13. Classical physics cannot account for the behavior of electrons in atoms.

_____ 14. The velocity of a wave is the product of its frequency and wavelength.

_____ 15. The Bohr model of an atom consisting of electrons moving around the nucleus in circular orbits gives a good correlation between calculated energies and energies calculated from experimentally observed spectra for most atoms.

Completion

16. The cathode ray in a discharge tube is made up of particles called ______________.

17. Cathode rays are repelled by _____________ charges.

18. Rutherford showed the atom has a dense massive ___________________ surrounded by ____________________.

19. The _______________________ number gives the number of electrons in orbit around the nucleus of a neutral atom.

20. The three subatomic particles of interest to chemists are the _______________, _________________, and __________________.

21. Atoms of an element can have different numbers of ________________ in the nucleus and still be the same element.

22. Atoms of a particular element which have the same atomic _____________ but different atomic mass are called _________________.

23. The sum of protons and neutrons in an atom is its _______________.

24. The mass of an isotope can be determined by a technique known as _____________.

25. A hertz is the same as a ___________________.

26. Energy in certain permitted amounts is said to be _______________.

27. The velocity of all types of electromagnetic waves is equal to _________________.

28. White light dispersed by a prism forms a _______________ spectrum.

29. The model of an atom consisting of electrons in circular orbits around a nucleus is called the ________________.

30. Many energy transitions are possible for the electrons in an atom and these transitions are observed as a _________________ spectrum.

Multiple Choice

31. Which of the following was not part of Dalton's theory of the atom?
(a) Atoms can be neither created nor destroyed.
(b) All atoms of a given element have identical properties.
(c) Compounds are composed of atoms of elements in fixed ratios.
(d) The center of the atom is a small, dense nucleus containing the positive charge.

32. Which of the following does not pertain to cathode rays?
(a) They are emitted from the cathode of a gas discharge tube.
(b) They are attracted toward a positive charge.
(c) They are radiant energy.
(d) They carry a negative charge.

33. The charge on the electron was determined by
(a) Thomson simultaneously applying an electric and a magnetic field to cathode rays.
(b) Goldstein's measurement on canal rays
(c) Millikan's oil drop experiment
(d) Rutherford's gold foil experiment

34. The concept that the nucleus of an atom contains the positive charge and most of the mass and is surrounded by extranuclear electrons was originated by
(a) Planck and Einstein (b) Dalton
(c) Bohr (d) Rutherford

35. Which of the following is not given by the atomic number of an atom?
(a) The number of neutrons in the nucleus.
(b) The number of protons in the nucleus.
(c) The number of extranuclear electrons.
(d) The mass number minus the number of neutrons.

36. The mass number of an element is the number of
(a) nucleons (b) neutrons (c) protons (d) electrons

37. According to classical physics an atom will
(a) consist of a nucleus and stationary electrons
(b) collapse
(c) fly apart because of centrifugal force on the electron
(d) emit a line spectrum

38. Channel 19 on CB radios broadcasts at 27.185 megahertz (MHz). What is the wavelength of Channel 19?
(a) 11.0 m (b) 8.10×10^{16} m
(c) 0.0900 m (d) 81.0 m

39. Which atom has the greatest mass?
(a) ^{12}C (b) ^{14}N (c) ^{18}O (d) ^{10}Be

40. Which atoms in the following pairs have the same number of neutrons?
(a) ^{28}Si and ^{29}P (b) ^{39}K and ^{40}K
(c) ^{20}Ne and ^{22}Na (d) ^{32}S and ^{32}Cl

41. Which atoms have the same number of neutrons?
(a) ^{10}Be and ^{10}B (b) ^{10}Be and ^{11}B
(c) ^{10}B and ^{11}B (d) ^{10}Be and ^{14}N

42. Which atoms are isotopes?
(a) ^{10}Be and ^{10}B (b) ^{10}Be and ^{11}B
(c) ^{10}B and ^{11}B (d) ^{10}Be and ^{14}N

43. Which atom has a charge of +4 on its nucleus?
(a) ^{10}Be (b) ^{10}B (c) ^{11}B (d) ^{14}N

44. Potassium occurs naturally as a mixture of two isotopes: ^{39}K (mass 38.96 amu) and ^{41}K (mass 40.96 amu). The relative abundance of ^{39}K is 93.0 percent. What is the atomic mass of K?
(a) 39.098 (b) 39.1 (c) 40.0 (d) 40.1

45. The Balmer series of the hydrogen spectrum falls in the visible region of electromagnetic waves. What is the wavelength for the transition of an electron from $n_2 = 4$ to $n_1 = 2$ in the Balmer series?
(a) 2.06×10^{-3} nm (b) 2.75×10^{-3} nm
(c) 364 nm (d) 485 nm

Chapter 6

ELECTRONS

CHAPTER OVERVIEW

A particle consisting of electrons flying around a nucleus in well-defined paths is the popular presentation of an atom. This picture is easy to visualize and agrees with our experience and observations of matter in the macroscopic world, but it is incorrect. The microscopic world of atoms is governed by an entirely different set of rules. To gain true insight into the behavior of atoms we must set aside our experience with matter on the macroscale and learn a whole new set of rules based on probability, quantized energy, and particles that behave like waves. Chapter 6 presents these new rules and applies them to atoms. Let the notion that electrons behave like little particles take a back seat for a while. Instead, think of electrons as waves of energy and the quantum-mechanical picture of an atom will begin to make sense.

6-1 The quantum-mechanical model and electronic energies

The Heisenberg uncertainty principle showed that the Bohr model is not an accurate description of the atom. The application of wave theory or quantum mechanics to electrons gives a more realistic picture of the atom. In the microscopic world, particles can behave like waves and waves exhibit properties of particles. The fact that electrons can be diffracted provides the most convincing evidence that electrons are waves, or at least behave like waves. De Broglie's equation relates the wavelength of microscopic particles to their mass and velocity. The application of quantum mechanics to behavior of electrons involves very difficult mathematics so only the results are presented in the text. This quantum-mechanical approach gives a systematic method of classifying electronic energy levels and helps us understand how electrons are distributed in an atom.

Figures 6-2 to 6-4 in the text summarize the electronic orbital classification scheme. The pattern of distribution of electrons in the orbitals of an atom is described in Figures 6-2 to 6-5 in the text. There are two methods of showing this distribution pattern: electronic configurations and orbital diagrams. The electronic configuration of each element is shown in Table 6-1 in the text.

The last half of the section emphasizes the Aufbau procedure for adding electrons to orbitals of lowest energy to determine ground-state electronic configurations of the atoms. The Aufbau filling sequence is shown in Figure 6-5 in the text. You should become familiar enough with this filling sequence to write the electronic configurations for the elements given only the atomic number. The electronic configurations resulting from the Aufbau process are shown in Table 6-1 of the text. The configuration consisting of full *s* and *p* subshells in the highest energy shell is very stable. We will see how this configuration, sometimes called the noble-gas configuration, is important in predicting general chemical behavior of the elements.

6-2 Waves and particles

Under certain conditions electrons behave like particles; under other conditions they behave like waves. Davisson and Germer reported the diffraction of electrons as shown in Figure 6-6 of the text. This was conclusive evidence of the wave nature of electrons. The de Broglie equation relates the particle-wave dual nature of electrons and allows us to calculate the wavelength of an electron. Further application of wave theory to electrons through the techniques of *quantum mechanics* has given a very satisfactory description and explanation of electron behavior in atoms.

6-3 Standing waves

The text introduces wave behavior in one dimension and shows how the nodes and antinodes become more complex in two and three dimensions, and how quantum numbers are used to describe the mode of vibration.

Nodes in two-dimensional standing waves are along lines. While the mode of vibration in one dimension could be described by a single quantum number, description of the wave motion in two dimensions requires two quantum numbers, one to describe the frequency of vibration and one to specify its orientation.

Extending the one- and two-dimensional concepts of the previous sections into three dimensions gets us into the wave description of electrons. Nodes in three dimensions become surfaces and describe the boundary limits for electrons in atoms.

6-4 The wavelike properties of electrons

The Schrodinger equation applies quantum mechanics to electrons in atoms. Solutions to the Schrodinger equation are called wave functions, Ψ. The square of the wave function, Ψ^2, represents the probability of finding the electron within a tiny volume of space. Where Ψ^2 is large, the probability of finding the electron is high. Where Ψ^2 is small, the probability of finding the electron is low. *Electron cloud* and *probability density* are terms used to represent the probability concept. In the quantum mechanical model of an atom, the Bohr orbits are replaced with atomic orbitals. Orbitals are regions of space within the atom which have a high probability (typically 90%) of containing the electron. We can expect the electron to be found within the orbital 90% of the time. Each atomic orbital has a characteristic shape and energy. Figures 6-17, 6-23, and 6-26 in the text show the geometry of the *s*, *p*, and *d* orbitals.

6-5 Quantum numbers

Quantum numbers arise from solutions to the Schrödinger equation. They serve as identification tags for electrons in atoms. Each electron can be assigned specific values of the four quantum numbers and no two electrons in an atom have the same values for all four quantum numbers. Table 6-3 in the text summarizes the basic information concerning quantum numbers.

LEARNING OBJECTIVES

As a result of studying Chapter 6, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 107 of this *Study Guide*.

6-1 The quantum-mechanical model and electronic energies

1. Show why the notion of an atom consisting of electrons flying around the nucleus in well-defined paths is not correct. (Self Test 1)
2. Show why quantum mechanics replaced classical mechanics to explain the behavior of subatomic particles.
3. Explain why it is impossible to know the velocity and position of an electron simultaneously. (Text Prob. 6-4)
4. Illustrate the organization of electron energy levels in an atom into shells, subshells, and orbitals. (Text Figs. 6-4; Text Probs. 6-8, 6-9) (New Skills Example 1; Self Test 2, 6, 7, 11, 14, 18, 31, 38)

5. Determine the number of paired or unpaired electrons in an atom. (Text Prob. 6-34) (New Skills Example 5; Self Test 3, 23, 32)
6. Predict whether or not an atom is paramagnetic. (Text Probs. 6-10, 6-13) (New Skills Example 6; Self Test 19)
7. Write Hund's rule. (Text Prob. 6-31)
8. Illustrate the filling order of electrons for the Aufbau procedure. (Text Fig. 6-5; Text Prob. 6-11) (New Skills Section 6-1:2; Self Test 4, 12)
9. Write the electronic configuration and orbital diagram for elements with atomic numbers 1 through 36. (Text Examples 6-1, 6-2; Text Probs. 6-6, 6-7, 6-12, 6-21) (New Skills Examples 2 to 4; Self Test 8, 15, 17, 20, 21, 33, 35, 37, 40, 42)

6-2 Waves and particles

1. Show how diffraction of electrons is experimental evidence that electrons behave like waves. (Text Prob. 6-1)
2. Calculate the de Broglie wavelength of a particle. (Text Probs. 6-2, 6-3, 6-5) (Self Test 16, 41)

6-3 Standing waves

1. Represent a one-dimensional standing wave by a vibrating string and identify the nodes and antinodes. (Text Probs. 6-18, 6-25, 6-38) (Self Test 5)
2. Understand why certain modes of vibration are allowed while others are forbidden. (Text Prob. 6-19)
3. Understand how standing wave vibrations are quantized because only certain, specific modes of vibration are possible and how quantum numbers can serve as labels for the allowed vibrational modes. (Text Prob. 6-31)
4. Understand that when the concept of the vibrating string is expanded to two dimensions, the nodes become more complex and a second quantum number is required to describe the orientation of the wave.
5. Understand how a three-dimensional wave represents an electron in an atom.
6. Relate the nodes and antinodes of three-dimensional waves to boundary surfaces for electron contours. (Text Probs. 6-19, 6-25, 6-27, 6-28, 6-31) (Self Test 10)
7. Relate the lobes of three-dimension waves to orbitals of the electrons.

6-4 The wavelike properties of electrons

1. Understand how wave motion is described by the Schrodinger equation and relate the solutions of this equation to the wave function (Ψ).
2. Relate the square of the wave function (Ψ^2) to the probability of finding an electron in a particular region of space, and to the shape of the orbital lobes. (Text Probs. 6-22, 6-23) (Self Test 26)
3. Draw sketches of the *s*, *p*, and *d* orbitals (Text Figs. 6-17, 6-21, 6-26; Text Probs. 6-14 to 6-17, 6-20, 6-21, 6-24, 6-26, 6-36, 6-37, 6-39) (Self Test 25, 36)

6-5 Quantum numbers

1. List the names, symbols, information provided, and possible values of the four quantum numbers. (Text Table 6-3; Text Probs. 6-29, 6-30, 6-32, 6-35) (New Skills Section 6-5:1; Self Test 13, 28, 30, 34, 39)
2. Write quantum numbers for electrons in atoms. (Text Table 6-4; Text Prob. 6-33) (New Skills Examples 7, 8; Self Test 22, 24, 27, 29, 43, 44, 45)

3. Describe the overall shape of an atom in terms of the sum of the electron charge clouds. (Text Prob. 6-24)
4. State the Pauli exclusion principle. (Self Test 28)
5. Relate the principal quantum number to the total nodes in the charge cloud and the azimuthal quantum number to the angular nodes. (Text Probs. 6-27, 6-28, 6-31)

KEY EQUATIONS

6-2 Waves and particles

Energy of a particle: $E = mc^2$

where E = Energy of a particle

m = mass of particle

c = speed of light in a vacuum = $3.00 \times 10^8\ \text{ms}^{-1}$

Energy of a wave: $E = h\nu$

where h = Planck's constant = $6.63 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}$

ν = wave frequency

de Broglie equation:

$$\lambda = \frac{h}{mv}$$

where λ = de Broglie wavelength of a particle

v = velocity of particle

NEW SKILLS

6-1 The quantum-mechanical model and electronic energies

1. Classification of electron energy levels or shells

The electronic energy levels in an atom are organized into shells, subshells, and orbitals according to the following scheme:

1. The principal division of energy levels is into shells designated by the letters K, L, M, N, O , ... or specified by the number *n* of the shell where *n* is some integer, roughly equivalent to the Bohr atom integers. A shell represents a general region in space around the nucleus where the electron is found. Shells get progressively larger and have higher energy going through the sequence K, L, M, N, O.
2. Each shell consists of one or more subshells representing characteristic regions in space and designated *s, p, d, f* . . . .
3. Subshells are divided into orbitals which indicate the orientation of the subshell in space. Each orbital can hold two electrons.
4. Two electrons in an orbital always spin in opposite directions around their own axis.

• EXAMPLE 1

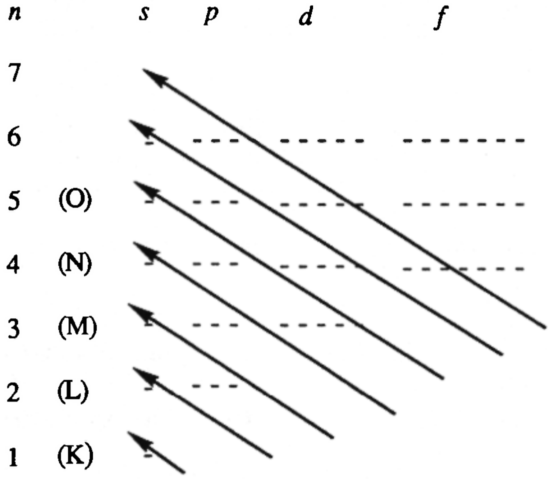
Problem: List the possible subshells in the fourth main energy level. How many orbitals are in each subshell? What is the maximum electron population possible for this level?

Solution: The fourth main energy level is the N shell. The number of subshells in a shell is equal to the shell number. Therefore, there are four subshells. They are the *s, p,* *d*, and *f* subshells. There is one orbital in the *s* subshell, three in the *p* subshell, five in the *d* subshell, and seven in the *f* subshell, a total of 16 orbitals. Each orbital holds a maximum of two electrons so the total possible electrons in the fourth energy level is 32. Note that if n is the number of a main level, there are n^2 orbitals and $2n^2$ possible electrons in the energy level. •

Parallel Problem: List the possible subshells for the third main energy level. How many orbitals are in each subshell? What is the maximum electron population possible for this level?
Ans: Subshells: *s*, *p*, *d*; Orbitals: 9; Possible electrons: 18

2. *The Aufbau filling process*

The Aufbau procedure for building up the electronic configuration of elements consists of assigning electrons to orbitals according to a systmatic filling order. The diagram below will make it easy to remember the Aufbau filling order. Just follow the arrows beginning at the bottom (lowest energy). See Text Fig. 6-5.



3. *Electronic configurations*

An electronic configuration shows the number of electrons in each occupied orbital of an atom. The only information needed to write an electronic configuration is the atomic number of the element and the Aufbau filling order.

• EXAMPLE 2

Problem: Write the electronic configuration for the element with atomic number 32.

Solution: The atomic number 32 signifies 32 electrons that need to be placed in orbitals. We place electrons in orbitals in order of increasing energy, remembering that there is a maximum of two electrons per orbital. Each *s* orbital holds two electrons. There are three *p* orbitals and five *d* orbitals, so the *p* subshell holds six electrons and the *d* subshell holds ten. Starting with the lowest energy level (K) we have:

$$1s^22s^22p^63s^23p^64s^23d^{10}4p^2$$

The electrons up to and including the 3*p* sublevel can be denoted by the symbol [Ar], which represents the configuration for argon. This shortens the configuration to:

$$[\mathrm{Ar}]3d^{10}4s^24p^2$$ •

Parallel Problem: Write the electronic configuration for the element with atomic number 57.
Ans: $[Xe]5d^16s^2$

Electronic configurations of other elements are written in the same fashion. The only exceptions to the Aufbau filling diagram occur when it is possible to half fill *d* or *f* subshells. Table 6-1 in the text shows that an electron is taken from a higher-energy-level *s* orbital in these cases.

• EXAMPLE 3

Problem: Write electronic configurations for the following particles: Ba, Ba^{2+}, I^-, and Xe.

Solution: The atomic number of Ba is 56, so it has 56 electrons. Ba^{2+} has lost two electrons so it has 54. I^- has one additional electron besides the 53 indicated by its atomic number for 54 total electrons. Xe has 54 electrons. The electronic configurations are:

Ba	(Z = 56)(56 electrons)	$[Xe]6s^2$
Ba^{2+}	(Z = 56)(54 electrons)	[Xe]
I^-	(Z = 53)(54 electrons)	[Xe]
Xe	(Z = 54)(54 electrons)	[Xe]

Ba^{2+}, I^-, and Xe all have the same electronic configuration and are called isoelectronic particles. •

Parallel Problem: Write the electronic configurations for the following substances: Se, Se^{2-}, Rb^+, As^{3-}.
Ans: Se: $[Ar]3d^{10}4s^24p^4$; Se^{2-} : [Kr]; Rb^+: [Kr]; As^{3-}: [Kr]

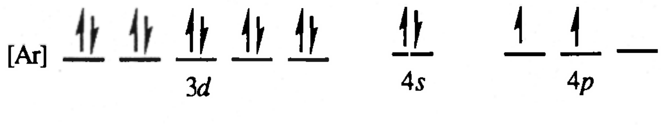
4. Orbital diagrams

An alternative method of depicting electron distribution in atoms is by orbital diagrams. These diagrams show the distribution of electrons among the orbitals of the higher energy subshells.

• EXAMPLE 4

Problem: Write the orbital diagram for the element in Example 2 above.

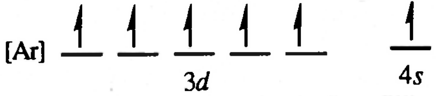
Solution: The orbital diagram is:



The two electrons in the 4*p* subshell are placed in separate orbitals with parallel spins (both arrows point in the same direction) in accordance with Hund's rule. •

Parallel Problem: Write the orbital diagram for element with atomic number 24.

Ans.



(Note the exception to the Aufbau filling order for half-filled *d* and *f orbitals.)*

5. Unpaired electrons

Lone electrons in an orbital are called unpaired electrons. Atoms containing unpaired electrons are attracted to a magnetic field and are said to be paramagnetic.

• EXAMPLE 5

Problem: How many unpaired electrons does the element in Example 4 contain?

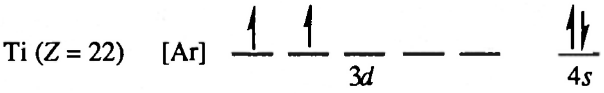
Solution: The two 4*p* electrons occupy separate orbitals so they are unpaired. There are two unpaired electrons. •

Parallel Problem: How many unpaired electrons does the element in the previous Parallel Problem have?
Ans: 6

• EXAMPLE 6

Problem: Is titanium paramagnetic?

Solution: An atom is paramagnetic if it has unpaired electrons. An orbital diagram will show if unpaired electrons are present; the orbital diagram is:



The two 3*d* electrons are unpaired according to Hund's rule, so titanium is paramagnetic. •

Parallel Problem: Is chromium paramagnetic?
Ans: yes

6-5 Quantum numbers

1. Information indicated by quantum numbers

Quantum numbers are identification tags for electrons in atoms. There are four quantum numbers.

1. The first quantum number is called the principal quantum number and given the symbol n. It tells the shell or main energy level of an electron and is a measure of its average distance from the nucleus. The allowed values for n are 1, 2, 3, 4, 5, . . .
2. The second quantum number is called the azimuthal quantum number and has the symbol l. It specifies the subshell *s*, *p*, *d*, or *f* containing the electron. The allowed values of l are integers from 0 to $(n - 1)$.

3. The third quantum number is the magnetic quantum number and is represented by the symbol m_l, it specifies the directional orientation of the subshell in space. m_l has integral values from $-l$ to $+l$.
4. The fourth quantum number is the spin quantum number represented by m_s. It specifies the direction of spin of the electron about its own axis and has values of $+\frac{1}{2}$ or $-\frac{1}{2}$.

The names, possible values, and information signified by the four quantum numbers are summarized in Table 6-3 in the text.

2. Assigning quantum numbers to electrons in atoms

The following rules can be used to determine the quantum numbers of electrons in specific orbitals.

1. n is the number of the main energy level
2. $l = 0$ for *s* electrons, $l = 1$ for *p* electrons, $l = 2$ for *d* electrons, and $l = 3$ for *f* electrons
3. m_l has any integral value from $-l$ to $+l$, including 0
4. m_s is either $+\frac{1}{2}$ or $-\frac{1}{2}$.

• EXAMPLE 7

Problem: What are the possible quantum numbers for the last two Aufbau electrons in Si?

Solution: The last two Aufbau electrons in Si are the $3p^2$ electrons. Applying the rules for assigning quantum numbers gives:

$$n = 3 \qquad l = 1 \qquad m_l = 1, 0, \text{or} +1 \qquad m_s = +\frac{1}{2} \text{or} -\frac{1}{2}$$

The three $3p$ orbitals corresponding to $m_l = -1, 0$, and $+1$ are all equivalent and the $3p^2$ electrons could be in any of them. The electrons must have parallel spin, so m_s must be either $+\frac{1}{2}$ or $-\frac{1}{2}$ for both electrons. The six possible quantum numbers are:

$3, 1, -1, +\frac{1}{2}$	$3, 1, 0, +\frac{1}{2}$	$3, 1, 1, +\frac{1}{2}$
$3, 1, -1, -\frac{1}{2}$	$3, 1, 0, -\frac{1}{2}$	$3, 1, 1, -\frac{1}{2}$

Any two of these in which both electrons have the same sign for m_s represent the allowable quantum numbers. •

Parallel Problem: What are the possible quantum numbers for the last Aufbau electron in potassium?
Ans: 4, 0, 0, +1/2 or 4, 0 0, –1/2

• EXAMPLE 8

Problem: Which of the following sets of quantum numbers are possible in an atom?

(a) $1, 1, 0, +\frac{1}{2}$ (b) $2, 1, 1, -\frac{1}{2}$ (c) $3, 1, -2, -\frac{1}{2}$ (d) $4, 0, 1, +\frac{1}{2}$

(e) $5, 4, 3, +\frac{1}{2}$

Solution: The quantum numbers are always given in the order, n, l, m_l, and m_s. (a) Not possible: l can only have values up to $n - 1$. (b) Possible. (c) Not possible: m_l can only have values up to $\pm l$. (d) Not possible: m_l must be 0 if $l = 0$. (e) Possible. •

Parallel Problem: The following pairs of quantum numbers are for electrons in the same atom. Which of these combinations violates the Pauli exclusion principle?

(a)	1: $n = 3$	$l = 1$	$m_l = 1$	$m_s = \frac{1}{2}$
	2: $n = 3$	$l = 1$	$m_l = 1$	$m_s = -\frac{1}{2}$
(b)	1: $n = 3$	$l = 1$	$m_l = 1$	$m_s = \frac{1}{2}$
	2: $n = 3$	$l = 1$	$m_l = -1$	$m_s = \frac{1}{2}$
(c)	1: $n = 3$	$l = 1$	$m_l = -1$	$m_s = \frac{1}{2}$
	2: $n = 3$	$l = 1$	$m_l = -1$	$m_s = \frac{1}{2}$
(d)	1: $n = 3$	$l = 1$	$m_l = 0$	$m_s = \frac{1}{2}$
	2: $n = 3$	$l = 1$	$m_l = 0$	$m_s = -\frac{1}{2}$

Ans: (c)

KEY TERMS

6-1 The quantum-mechanical model and electronic energies

Antiparallel spins: Electron spins in opposite directions.

Aufbau procedure: A procedure for "building" atoms by adding electrons to the lowest available energy level.

Classical mechanics: A system of physics which describes the behavior of objects much larger than atoms.

Electron spin: Property of an electron related to its interaction with a magnetic field.

Electronic configuration: The arrangement of electrons in atomic orbitals for an atom.

Filling diagram: An orderly arrangement of electronic subshells according to energy of the subshell. Used in assigning electrons in the Aufbau procedure.

Ground-state electronic configuration: Arrangement of electrons in an atom where the electrons occupy the lowest available energy levels.

Heisenberg uncertainty principle: It is impossible to determine simultaneously both the position and the momentum of a particle exactly.

Hund's rule: Electrons remain unpaired and in separate orbitals as far as possible.

Noble-gas electron core: That portion of the electronic configuration of an atom which can be represented by the configuration of the noble gas with atomic number closest to but less than the atom under consideration.

Orbital: An energy level available to an electron in an atom.

Orbital diagram: A method of showing the electronic configuration of atoms.

Parallel spin: Electron spins in the same direction.

Paramagnetism: Attraction to a magnetic field resulting from unpaired electrons in an atom.

Quantum mechanics: The branch of physics which describes the behavior of electrons by treating them as waves. Same as wave mechanics.

Quantum number: A number used to describe the state of an electron in an atom.

Shell: A principle set of electronic energies in an atom designated by K, L, M, N, . . . or by the principle quantum numbers 1, 2, 3, 4, . . .

Spectroscopic notation: Representation of electronic configuration by listing the occupied subshells with their electron populations.

Subshell: A subset of electronic energy levels in an atom, designated *s*, *p*, *d*, *f*, . . . or by the azimuthal quantum number, $l = 0, 1, 2, 3, \ldots$

Wave mechanics: Same as quantum mechanics.

6-2 Waves and particles

Diffraction: The bending or reflection of waves by a diffraction grating.

Diffraction grating: A transparent plate with very closely space lines ruled on its surface.

Electron diffraction: The reflection of electrons from a diffraction surface. Used to show the wave nature of electrons.

6-3 Standing waves

Angular node: Nodes of standing waves vibrating in two dimensions. These nodes form straight lines at specific angles with each other.

Antinode: Region of maximum displacement of a standing wave.

Node: Region at which no motion occurs in a standing wave and where $\psi^2 = 0$.

Standing wave: A wave fixed in space.

6-4 The wavelike properties of electrons

Boundary surface: A surface of constant electron probability density.

Contour diagram: A two-dimensional cross section of a boundary surface which represents a contour of constant probability density.

Electronic charge cloud: A region in space representing a high probability density for an electron orbital.

Orbital lobe: Parts of a nonspherical electronic orbital separated by an angular node.

Probability density: The probability per unit volume of finding an electron in a given region, ψ^2.

Radial node: A node extending in all directions in a standing wave.

Schrödinger wave equation: A wave equation which describes an electron in a hydrogen atom.

Wave equation: A mathematical equation describing the motion of a wave.

Wave function: A solution to a wave equation.

6-5 Quantum numbers

Azimuthal quantum number: l. A quantum number which specifies a subshell for an electron in an atom.

Magnetic quantum number: m_l. A quantum number which indicates the orbital occupied by an electron.

Pauli exclusion principle: No two electrons in an atom can have the same values for all four quantum numbers.

Principle quantum number: n. A quantum number which specifies a shell for an electron in an atom.

Spin quantum number: m_s. A quantum number which specifies the spin of an electron in an atom.

SELF TEST

True or False

_____ 1. Electrons move around the nucleus in well-defined paths called orbits.

_____ 2. No matter what energy level it is in, each orbital can hold two electrons.

_____ 3. Paired electrons have parallel spins.

_____ 4. The filling sequence of orbitals by the Aufbau procedure follows a fixed order.

_____ 5. A stretched string may vibrate in many different modes.

_____ 6. The third main energy level holds a maximum of 18 electrons.

_____ 7. A 3*d* subshell and a 4*d* subshell contain the same number of orbitals.

_____ 8. The element with atomic number 27 has an electronic configuration of $[\mathrm{Ar}]3d^7 4s^2$.

_____ 9. In some ways electrons behave like particles, in other ways they behave like waves.

_____ 10. The boundaries of electron orbitals are similar to nodes in a three-dimensional wave.

_____ 11. Ground state is the lowest energy available for electrons in an atom.

_____ 12. An electron in a 3*d* orbital is usually at a lower energy level than in a 4*s* orbital.

_____ 13. The possible values of the magnetic quantum number are determined by the magnitude of *l*.

_____ 14. The *d* sublevel consists of a set of four orbitals.

_____ 15. The electronic configuration for nitrogen can be written as $1s^2 2s^2 2p^3$

Completion

16. The de Broglie wavelength of an electron with mass of 9.11×10^{-28} grams traveling at a velocity of 6.00×10^{8} cm s^{-1} is ______________________ nanometers.

17. The element that has atoms with ground-state electron configuration of $[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$ is ______________________.

18. The N shell has ______________ (number) subshells and ____________ orbitals.

19. Unpaired electrons cause an interaction with a(an) ____________ field.

20. An atom of carbon has __________ (number) electron(s) in a $1s$ orbital, _________ electron(s) in a $2s$ orbital, and ________ electron(s) in each of __________ different $2p$ orbitals.

21. The electronic configuration of the element with atomic number 22 is ____________________.

22. The smallest principal quantum number of an electron for which the magnetic quantum number is +3 is ____________.

23. The number of unpaired electrons in manganese (atomic number 25) is(are) ________.

24. All electrons in a $3d$ subshell have quantum number n equals to _____________.

25. There are __________ (number of) lobes on a $2p$ orbital and ______________ on a $3d$ orbital.

26. The square of a wave function is the _______________ of finding an electron in a given region of space.

27. The atomic number of the element for which the last electron added in the Aufbau procedure has $n = 3$, $l = 1$, $m_l = -1$, and $m_s = -\frac{1}{2}$ is _______________.

28. Two electrons in the same orbital must have different _______________.

29. All electrons in a p subshell have quantum number l equal to _______________.

30. There are ____________ (number) different possible orientations in space for orbitals having $l = 3$.

Multiple Choice

31. The maximum number of electrons in the energy level with $n = 4$ is
(a) 4 (b) 16 (c) 32 (d) 50

32. Which of the following has the most unpaired electrons?
(a) $_{7}N$ (b) $_{13}Al$ (c) $_{17}Cl$ (d) $_{24}Cr$

33. Which of the following is the electronic configuration for Mn?
(a) $[Ar]3d^7$ (b) $[Ar]3d^54s^2$ (c) $[Ar]3d^64s^1$
(d) $[Ar]3p^64s^1$

34. Which quantum number designates the orientation in space of electron orbitals?
(a) principal (b) azimuthal (c) magnetic (d) spin

35. Which element has its 3*d* orbitals half full of electrons?
(a) $_{23}V$ (b) $_{42}Mo$ (c) $_{29}Cu$ (d) $_{24}Cr$

36. The shape of an *s* orbital is
(a) like a four leaf clover
(b) like a squashed set of dumbbells
(c) very complex
(d) spherical

37. What is the atomic number of the element whose electronic configuration is $[Ar]3d^{10}4s^24p^1$?
(a) 11 (b) 13 (c) 21 (d) 31

38. In which of the following subshells would an electron have the lowest energy?
(a) 4*d* (b) 4*f* (c) 5*s* (d) 5*p*

39. How many different values of the magnetic quantum number are possible for azimuthal quantum number $l = 2$?
(a) one (b) three (c) five (d) ten

40. Which of the following does not represent a possible electronic configuration for an atom in its ground state?
(a) $1s^22s^22p^6$ (b) $1s^22s^22p^63s^1$ (c) $[Ar]4s^13d^3$ (d) $[Ar]4s^13d^5$

41. What is the wavelength in meters of a proton (mass = 1 amu) traveling at $\frac{1}{1000}$ of the speed of light? ($c = 3.00 \times 10^8$ m s^{-1})
(a) 1.33×10^{-12} (b) 1.33×10^{-15} (c) 2.21×10^{-39} (d) 3.67×10^{-63}

42. Which is the correct electronic configuration for zirconium?
(a) $[Kr]4d^25s^2$ (b) $[Ar]4d^25s^2$ (c) $[Kr]4d^26s^2$
(d) $[Kr]4d^35s^2$

43. What are the quantum numbers of the last electron added in the Aufbau procedure for the element with atomic number 18?
(a) $3, 0, 0, +\frac{1}{2}$ (b) $3, 1, 0, +\frac{1}{2}$ (c) $3, 1, 1, +\frac{1}{2}$ (d) $3, 1, -1, -\frac{1}{2}$

44. Which of the following sets of quantum numbers could describe an electron in an orbital in a hydrogen atom?

	n	l	m_l	m_s
a.	3	2	–3	$\frac{1}{2}$
b.	2	3	0	$-\frac{1}{2}$
c.	2	1	0	$-\frac{1}{2}$
d.	1	2	1	$\frac{1}{2}$

45. Which choice is a possible set of quantum numbers for the last electron added to make up an atom of gallium (Ga) in its ground state?

	n	l	m_l	m_s
a.	4	2	0	$-\frac{1}{2}$
b.	4	1	0	$\frac{1}{2}$
c.	4	2	–2	$-\frac{1}{2}$
d.	3	1	+1	$\frac{1}{2}$

Chapter 7

CHEMICAL PERIODICITY

CHAPTER OVERVIEW

There are 109 elements which interact to form millions of compounds. Each of these compounds has characteristic physical and chemical properties. If we were to approach chemistry in a haphazard manner and start learning about these compounds one by one, we would not get very far in a lifetime.

The concepts presented in this chapter make possible a systematic study of chemical trends and behavior of groups of elements. The periodic table organizes an immense amount of information to make the study of chemistry and chemicals meaningful and possible.

7-1 The discovery of the periodic law

Several attempts to correlate the behavior of elements before 1870 went largely unnoticed, but when Meyer and Mendeleev published their periodic tables, they predicted the existence of unknown elements and accurately estimated their properties. These predictions were soon verified and the periodic table became a standard tool of chemists.

When elements are arranged in order of increasing atomic number, certain properties are seen to repeat at definite intervals. This repetition is the periodic law and forms the basis for the modern periodic table shown as Figure 7-2 in the text. Using the periodic table to understand and predict chemical behavior is what Chapter 7 is all about. Elements in groups or columns have similar chemical properties, so we can learn the chemistry of the group rather than studying each element individually. The noble gases, alkali metals, and halogens are groups whose numbers show striking similarities in their properties.

7-2 Periodicity in electronic configurations

The correlation of electronic configuration with position in the periodic table is at least as important as the correlation of observable properties. Study Figure 7-5 to see the relationship between the Aufbau orbital-filling process and the periodic table. You should be able to correlate the electronic configuration of the last Aufbau filling orbital with the position of elements in the periodic table. The divisions of the periodic table shown in Figure 7-5 are very important and should be learned.

7-3 Periodicity in atomic properties

One of the main uses of the periodic table is the correlation of trends in several physical and chemical properties of the elements. The text shows periodic correlations for atomic radius, ionization energy, electron affinity, density, and melting point by presenting data in six Figures and six Tables. You do not need to memorize these data, but you should see the trends, recognize the exceptions to the trends, and learn the reasons for the trends and the exceptions.

The trends in size are easy to remember if you correlate what we have already learned about electronic configurations with the periodic chart. Each new period in the chart adds a new shell so, logically, each period is larger than the one(s) before it. Electrons added to the same shell across a period are approximately the same distance from the nucleus. The increasing nuclear charge pulls the entire shell closer, so size trends correlate beautifully with what we have learned about electronic structure. Notice how even the exceptions in trends are predicted by the stability of half-filled subshells.

Trends in ionization energy showing strong periodic behavior (Figure 7-7 in the text) can be closely correlated to electronic configuration and nuclear charge. Again, the irregularities in the trends are expected from the stability of filled or half-filled subshells. Electron affinity also shows general trends but the irregularities here are not so easily explained in terms of simple electronic configuration.

7-4 Periodicity in physical properties

All of the physical properties mentioned in the text show strong periodic trends, and plots like Figures 7-10 and 7-11 in the text could be made for any of them.

7-5 Periodicity in chemical properties

The chemical definition of a metal is any element which loses electrons to form a positive ion in a chemical reaction. Nonmetals gain electrons to form negative ions when they react. Note how the number of electrons gained or lost by an element and the amount of metallic or nonmetallic character it has can be predicted from its position on the periodic table.

The stepped, diagonal line from boron to astatine in Figure 7-12 in the text divides the periodic table into two important divisions. Metals lie to the left and nonmetals to the right of this diagonal line. Elements close to the diagonal line are called metalloids.

We visit the world of chemical nomenclature again in this chapter. The "ous-ic" endings for multivalent metal ions and the preferred Stock system of nomenclature are shown in text Table 7-8. The "ide" ending applies to nonmetals only. A special ion having the "ide" ending is OH^-, the hydroxide ion. Some bases containing the OH^- ion are shown in text Table 7-9. Note that acids containing oxygen have the OH group. We shall see that there are significant differences between the OH group in acids and that in bases. The dissociation of acids to give H^+ ion and bases to give OH^- ion generally takes place in a water solution. Metals react with water to produce bases; nonmetals react with water to produce acids.

In Chapter 8 we will see how the position of elements in the periodic table can be used to determine the formulas of simple ionic compounds. An understanding of the relationship between electronic configuration and the periodic table is essential for effective use of the table in predicting chemical formulas.

LEARNING OBJECTIVES

As a result of studying Chapter 7, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 118 of this *Study Guide*.

7-1 The discovery of the periodic law

1. Explain how the concept of periodic behavior was discovered and why it was so successful. (Text Probs. 7-3, 7-4) (Self Test 9)
2. Write the periodic law and give three examples of periodic behavior.
3. Identify periods and groups on the periodic table. (Text Probs. 7-5, 7-20) (Self Test 10, 16, 22, 26, 27, 28)
4. Identify the alkali metals, halogens, noble gases, and transition metals on the periodic table. (Text Probs. 7-6, 7-27) (Self Test 6, 7, 18, 35)

7-2 Periodicity in electronic configurations

1. Predict electronic configurations from the position of an element in the periodic table. (Text Probs. 7-8, 7-9, 7-39, 7-41)
2. Determine the number of valence-shell electrons from the position of an atom in the periodic table. (Text Probs. 7-10, 7-42) (Self Test 1, 21, 24, 25, 31, 42)

7-3 Periodicity in atomic properties

1. Predict the trends in atomic radius, ionic radius, ionization energy, and electron affinity among atoms in the same group or period. (Text Probs. 7-14, 7-17, 7-18, 7-29, 7-33, 7-34, 7-35) (Self Test 2, 3, 8, 13, 14, 17, 19, 20, 33 to 39, 43)
2. Explain the trends in atomic radius and ionization energy in terms of electronic configurations and nuclear charge. (Text Probs. 7-11, 7-12, 7-16)
3. List irregularities of trends in atomic radius and ionization energy for second-period elements and justify these irregularities on the basis of electronic configuration and nuclear charge.
4. Explain why second-period elements often behave differently from other members of their group.
5. Explain why the chemical behavior and physical properties of the transition elements, lanthanides, and actinides show strong similarities. (Self Test 32)
6. Using a halogen atom as an example, clearly distinguish between ionization energy and electron affinity. (Text Prob. 7-15)

7-4 Periodicity in physical properties

1. Predict trends in density and melting point among adjacent atoms in the periodic table. (Text Probs. 7-13, 7-19) (Self Test 4, 41)

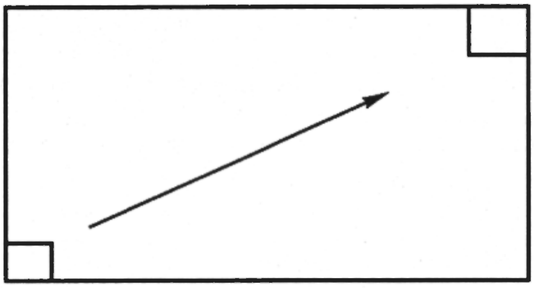
7-5 Periodicity in chemical properties

1. List some advantages of studying chemical behavior by groups of elements rather than individually. (Self Test 4, 40)
2. Define metal and nonmetal in a chemical sense. (Text Prob. 7-21)
3. Identify elements as metals, nonmetals, or metalloids from their position in the periodic table. (Text Probs. 7-20, 7-22) (Self Test 5, 11, 15, 23)
4. Write balanced chemical equations for reactions of metals with water, metals with nonmetals, and nonmetals with nonmetals. (Text Probs. 7-24, 7-36) (Self Test 44, 45)
5. Give correct "ous-ic" and Stock names for multivalent metal ions and their compounds. (Text Probs. 7-25, 7-26, 7-37, 7-38) (Self Test 12, 29)
6. Identify the electrons in the outermost shell of an atom or ion called valence electrons. (Text Prob. 7-41) (Self Test 21, 24, 25, 31)
7. Write dissociation reactions for hydroxo compounds in water. (Text Probs. 7-23, 7-40) (Self Test 30)

NEW SKILLS

7-3 Periodicity in atomic properties

If we represent the periodic table by a rectangle, it becomes easy to represent the general trends in atomic properties by remembering values of the properties for two corners of the periodic table.



Smallest atomic radius, highest ionization energy, highest electron affinity

Largest atomic radius, lowest ionization energy, lowest electron affinity

The diagonal points in the direction of decreasing atomic size and increasing ionization energy and electron affinity.

The correlations of atomic properties among groups and periods may be summarized as follows:

1. The atomic radius of elements decreases from left to right in a period and increases from top to bottom in a group.
2. The ionization energy of elements increases from left to right in a period and decreases from to top bottom in a group.
3. Electron affinity shows the same trend as ionization energy.

KEY TERMS

7-1 The discovery of the periodic law

A groups: The eight long columns on the periodic table consisting of five or six elements each.

Actinides: Elements with atomic numbers 90 through 103.

Alkali metals: Elements in the first column of the periodic table, group IA.

Alkaline earth metals: Elements in the second column of the periodic table, group IIA.

B groups: The ten short columns in the center of the periodic table.

Chalcogens: Elements in group VIA of the periodic table.

Group: Elements in the same vertical column in the periodic table.

Halogens: Elements in group VIIA in the periodic table.

Lanthanides: Elements with atomic numbers 58 through 71.

Main groups: Same as A groups.

Noble gases: Elements in the last column of the periodic table, group 0.

Period: Elements in the same horizontal row of the periodic table.

Periodic law: When elements are listed sequentially in order of increasing atomic number, a periodic repetition in properties is observed.

Periodic table: An arrangement of elements based on the periodic law.

Representative elements: Elements in the representative or A groups.

Representative groups: Same as A groups.

Transition elements: Elements in the B groups.

Transition groups: Same as B groups.

7-2 Periodicity in electronic configurations

Octet rule: The valence-shell electronic configuration, ns^2np^6, in an atom is especially stable.

Valence shell: The outermost shell (highest principal quantum number) of electrons in an atom.

7-3 Periodicity in atomic properties

Atomic radius: One half of the distance between the nuclei of two adjacent atoms in the solid state of an element.

Electron affinity: The enthalpy change when a gaseous, isolated atom gains an electron.

Ionization energy: The energy required to remove an electron from a gaseous, isolated atom.

Lanthanide contraction: The gradual decrease of atomic radius of lanthanide elements with increasing atomic number.

Periodicity: The regular recurrence of properties of elements at specific intervals of atomic number.

Screening effect: The shielding of valence electrons by inner-core electrons from the electrical attraction of the nucleus. It moderates the effect of periodic trends in properties.

7-4 Periodicity in physical properties

Metal: An element that loses electrons in a chemical reaction.

Metalloid: An element that has properties intermediate between metals and nonmetals.

Nonmetal: An element that gains electrons in chemical reactions.

7-5 Periodicity in chemical properties

Amphoteric: Compounds that can react as either acids or bases.

Anions: A negatively charged ion.

Cation: A positively charged ion.

Hydroxo compound: A compound containing the OH group of atoms in its structure.

SELF TEST

True or False

_____ 1. The concept that a completed valence shell is a very stable electronic configuration is called the octet rule.

_____ 2. The atomic radii decrease from left to right in a period.

_____ 3. The atomic radii decrease from top to bottom in the representative groups.

_____ 4. Chemical properties generally obey the periodic law but physical properties do not.

_____ 5. Metals are on the left of the periodic table and nonmetals are on the right.

_____ 6. Group IA elements are called the alkaline earth elements.

_____ 7. Group VIIA elements are called the halogens.

_____ 8. For any given period in the periodic table the ionization energy generally increases as the atomic number increases.

_____ 9. Mendeleev is given credit for establishing that properties of the elements are periodic functions of atomic number.

_____ 10. A horizontal row in the periodic table is called a group.

_____ 11. In any given period of elements the most metallic elements are on the left.

_____ 12. A correct name for $FeCl_3$ is ferric(III) chloride.

_____ 13. The minimum energy required to remove an electron from a gaseous, ground-state atom is the ionization energy.

_____ 14. Electron affinity is the energy released when a gaseous, ground-state atom gains an electron.

_____ 15. Gallium is a nonmetal.

Completion

16. In the periodic table elements having similar chemical and physical properties appear together in _______________.

17. Ionization energy and ___________________show similar trends in the periodic table.

18. Elements whose differentiating electrons are in the *d* subshell of an energy level below the valence shells are called ___________________.

19. The first ionization energy of an element is always ____________ (less, greater) than the second ionization energy.

20. Sodium is ______________ (smaller, larger) than the atom just under it in the periodic table.

21. The number of valence electrons is the same as the ______________ for A group elements.

22. The element that follows lanthanum in the periodic table is ______________.

23. The elements that show both metallic and nonmetallic behavior are called ____________.

24. The alkali metals have ___________ (number of) electron(s) in their valence shell.

25. The halogens have _________________(number of) electron(s) in their valence shell.

26. Each B group has _______________ (number of) elements.

27. The _________________ and __________________ groups appear outside the main body of the conventional periodic table.

28. Elements whose differentiating electrons are in the *f* subshell two energy levels below the valence shell are called ________________ and _________________.

29. A correct name for CuF is _______________________.

30. The dissociation reaction which occurs when $Mg(OH)_2$ dissolves in water is __________________.

Multiple Choice

31. The electrons in the highest energy level comprise which shell?
(a) transition (b) valence (c) periodic (d) main

32. The size change associated with filling the 4*f* subshell is called the
(a) atomic radius trend (b) electron screening
(c) lanthanide contraction (d) actinide contraction

33. The element with the largest atomic radius is located in which part of the periodic table?
(a) upper left (b) upper right (c) lower left (d) lower right

34. The element with the highest ionization potential is located in which part of the periodic table?
(a) upper left (b) upper right (c) lower left (d) lower right

35. The group of elements at the far right of the periodic table are the:
(a) alkali metals (b) alkaline-earth metals
(c) halogens (d) noble gases

36. The element with the highest electron affinity is located in which part of the periodic table?
(a) upper left (b) upper right (c) lower left (d) lower right

37. Which of the following has an atomic radius less than that of sulfur?
(a) Na (b) P (c) Ar (d) K

38. Which of the following are arranged in order of increasing ionization energy?
(a) Na, K, Rb (b) Cl, Ar, K (c) O, F, Ne (d) Ne, Cl, Se

39. Which of the following are arranged in order of increasing atomic radius?
(a) B, C, N (b) F, Ne, Na (c) Kr, Ar, Ne (d) Li, Na, K

40. Which of the following would be expected to have chemical properties similar to sulfur?
(a) Cl (b) P (c) Si (d) Se

41. Which of the following has a melting point and boiling point similar to Ca?
(a) Mg (b) Sc (c) Co (d) K

42. Which of the following has the same number of valence electrons as Br?
(a) Mn (b) Kr (c) Cl (d) Se

43. Which element has the highest electron affinity?
(a) Li (b) He (c) F (d) At

44. A correct chemical equation representing the reaction of lithium metal with excess water is:
(a) $Li + H_2O = LiOH_2$
(b) $Li + H_2O = LiO + H_2$
(c) $2\,Li + 2\,H_2O = 2\,LiOH + H_2$
(d) $4\,Li + 2\,H_2O = 4\,LiH + O_2$

45. A correct chemical equation for the reaction of calcium metal with bromine is
(a) $Ca + Br = CaBr$
(b) $Ca + Br_2 = CaBr + Br$
(c) $Ca + Br_2 = CaBr_2$
(d) $2\,Ca + Br = Ca_2Br$

Chapter 8

CHEMICAL BONDING

CHAPTER OVERVIEW

In Chapters 5, 6, and 7 we studied the electronic structure and properties of atoms. In Chapter 8 we investigate the forces that bond atoms together into molecules. The two general types of bonds are ionic and covalent. Each type is formed by a specific process and gives unique properties to a molecule. The opening paragraph of the text emphasizes that actual bonds are usually intermediate between these two idealized bond types.

Polyatomic ions are held together by covalent bonds, and their structures are determined by the manner of distribution of valence electrons among the atoms. We will investigate this electron distribution in considerable detail. Chemical properties of a molecule are related to the charge distribution and we will see how this distribution is described by oxidation numbers of the atoms.

8-1 Ionic bonding

An ionic bond is the electrostatic force of attraction between particles with opposite electrical charges. It is formed by the transfer of one or more electrons from a metal to a nonmetal. Metals tend to lose electrons and nonmetals gain electrons to attain a noble-gas electronic configuration called a stable octet. The ionic charge for representative elements can be found by inspection from their position in the periodic table. Since molecules are always electrically neutral, positive and negative ions combine in ratios determined by their charges. The total positive and negative charges always balance in a molecule. When one atom has a low ionization energy (metal) and another has a high electron affinity (nonmetal), an electron transfer takes place to form an ionic bond. The overall process releases energy, so the ionic product is energetically more stable than the original atoms. This process is illustrated for NaCl in Figure 8-4 in the text.

8-2 Covalent bonding

When two atoms with similar tendencies to gain or lose electrons interact, electrons are shared between the atoms to form a covalent bond. Sharing of two or three pairs of electrons between two atoms gives double or triple covalent bonds. The distribution of valence electrons in covalent compounds is conveniently shown by Lewis structures.

Although electrons are shown on specific atoms in Lewis structures, in reality all electrons in a molecule are indistinguishable. Lewis structures are only a bookkeeping technique and they fail to show a true picture of bonding when resonance is possible. Then, the actual molecule is a resonance hybrid of the different Lewis structures. However, drawing Lewis structures helps to predict how atoms combine to form molecules and what geometry these molecules will have. We will use Lewis structures as an aid to understanding molecular geometry throughout the text, so you should learn the rules for drawing them. Examples 8-4 through 8-7 in the text illustrate Lewis structures. Much of the material on chemical bonding and structure in the next few chapters is based on the Lewis structure concept, so learning the basis for these structures and how to draw them will be an important foundation for these next chapters.

8-3 Electronegativity

Electronegativity is the tendency of a bonded atom to attract additional electrons. The electron pair in a covalent bond responds to differences in electronegativities between the bonded atoms. When atoms of equal electronegativity are bonded, the electrons are shared equally and the bond is nonpolar. When atoms of different electronegativity are bonded, the atom with higher electronegativity attracts the electron pair more strongly, resulting in unequal sharing of the electrons. The atom with higher electronegativity becomes the negative end of the bond, leaving the other end positive and making a polar covalent bond. Most bonds exhibit a mixture of ionic and covalent characteristics and so are polar to some extent. Bonds with a high degree of ionic character are called ionic; those with a high degree of covalent character are called covalent or polar covalent. The amount of ionic character of a bond can be estimated from the difference in electronegativities of the bonding atoms. Atoms in the upper left of the periodic table have highest electronegativities; atoms in the lower left corner have the lowest electronegativities.

8-4 Bond energies

Bond energy is the term given to the energy necessary to break a bond in a molecule. The stronger the bond, the higher the bond energy. Formation of a new bond releases an amount of energy equal to the bond energy. Since chemical reactions involve breaking bonds and forming new bonds, the energy changes during reactions can be calculated from bond energies. The energy required to break all bonds in the reactants minus the energy released when the product bonds are formed is the enthalpy of reaction. When a given type of bond (such as the C—H bond) is found in several different compounds, an average value for the bond energy is generally used in calculations.

8-5 Electronic bookkeeping, part I: formal charges

Formal charges give a convenient model and description of the charge or electron distribution in molecules. Three simple rules for assigning formal charges are given in the text and New Skills section of this *Study Guide*. One of the main uses of formal charges is to help select the correct structure when more than one Lewis structure is possible for a molecule.

8-6 Electron-pair repulsion

An important aspect of a covalent molecule is its geometry, or the physical arrangement of its atoms in space. Several terms from basic geometry will be used to describe the shape of molecules. Refer to a dictionary or geometry text if you need help understanding these terms. Atoms tend to arrange themselves to minimize the repulsion between electron pairs and maximize the electron-nucleus attractions. The VSEPR (pronounced "vesper") method is a way to predict the orientation of atoms most favorable for strong covalent bonding.

The steps in using the VSEPR method are outlined in Section 8-6. First draw the Lewis structure, then determine the steric number, and see Table 8-6 to find the general geometry of the molecule. Tables 8-6 and 8-7 apply the VSEPR method for you if you know the steric number and number of lone pairs on the central atom. These are quickly seen from the Lewis structure. Remember that the geometrical shape of a molecule is found by connecting the nuclei of the outside atoms by straight lines. Lone pairs on the central atom are not included in the overall geometry of the molecule.

8-7 The polarity of molecules

Another important aspect of covalent molecules is their polarity. Often molecules contain polar bonds, but the shape of the molecule causes the bond dipoles to cancel each other so the overall molecule is nonpolar. When an imaginary plane can be passed through the center of mass and separate the center of positive charge from the center of negative charge, the molecule is polar.

LEARNING OBJECTIVES

As a result of studying Chapter 8, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 134 in this *Study Guide.*

8-1 Ionic bonding

1. Explain how an ionic bond results from the electrostatic attraction between ions formed by transfer of electrons from an atom with low ionization energy to one with a high electron affinity. (Text Prob. 8-3) (Self Test 31)
2. Draw Lewis structures for simple ionic compounds and ions. (Text Examples 8-1, 8-2; Text Probs. 8-20, 8-22) (Self Test 8, 19, 21)
3. Identify lone-pair and shared-pair electrons in Lewis structures. (Self Test 10)
4. Write empirical formulas for ionic compounds given the charges on the cation and anion. (Text Example 8-3; Text Probs. 8-1, 8-2, 8-11, 8-45) (New Skills Example 1; Self Test 5, 7, 16, 17)
5. Predict the number of electrons an atom will lose or gain (hence its ionic charge) from the number of valence electrons as determined by its position in the periodic table. (Text Prob. 8-15) (Self Test 1, 3, 6)
6. Calculate energies associated with ionization processes using a Born-Haber type of calculation. (Text Prob. 8-4)

8-2 Covalent bonding

1. Explain how covalent bonds are formed between atoms by sharing electrons. (Text Prob 8-5) (Self Test 1, 13, 18, 25)
2. Explain the change in potential energy and electron probability density which occurs as separated atoms are brought together to form a covalent bond.
3. Draw Lewis structures for molecules or polyatomic ions with covalent bonds. (Text Examples 8-4 to 8-7; Text Probs. 8-6, 8-7, 8-12, 8-21 to 8-23, 8-41, 8-42, 8-49 to 8-51) (New Skills Examples 2 to 4; Self Test 20, 22, 38)
4. Give examples showing the limitations of the octet rule and Lewis structures for large atoms, resonance hybrids, and odd-electron compounds. (Text Probs. 8-42, 8-44) (Self Test 11, 45)
5. Draw the contributing structures for resonance hybrid molecules. (Text Prob. 8-12)

8-3 Electronegativity

1. Define electronegativity and electron affinity and relate the general trend of electronegativity to the position of atoms in the periodic table. (Text Prob. 8-13) (Self Test 4, 12, 23, 28, 30, 35)
2. Predict whether a bond will be normal covalent, polar covalent, or ionic by using the difference in electronegativity between the bonded atoms. (Text Probs. 8-14, 8-17 to 8-19) (Self Test 13, 24, 26, 36, 39)

3. Relate the electronegativity value of an atom to metallic or nonmetallic behavior. (Self Test 4)

8-4 Bond energies

1. Distinguish between *bond dissociation energy* and *average bond energy*. (Text Probs. 8-24, 8-25)
2. Relate the magnitude of bond dissociation energies to bond strengths and bond lengths. (Text Probs. 8-26, 8-27)
3. Calculate enthalpies of reaction from bond dissociation energies. (Text Example 8-8; Text Probs. 8-28, 8-29) (New Skills Example 5)
4. Recognize that most tabulated bond energies are averages from several different atomic environments; therefore enthalpies of reaction determined in this manner must be regarded as approximate. (Text Prob. 8-28)

8-5 Electronic bookkeeping, part I: formal charges

1. Use formal charges to predict the distribution of valence electrons among atoms in a molecule. (Self Test 5)
2. Show why formal charges are not identical to the electrical charges in an ion.
3. Assign formal charge to each atom in a molecule or polyatomic ion. (Text Examples 8-9, 8-10; Text Probs. 8-30, 8-31, 8-41) (New Skills Example 6; Self Test 27, 37, 44)

8-6 Electron-pair repulsion

1. Use the four steps of the VSEPR method to predict molecular geometry by minimizing electron-pair repulsion. (Text Example 8-11; Text Probs. 8-36, 8-37) (New Skills Examples 7, 8; Self Test 15, 29, 40, 41)
2. Determine the steric number of a central atom in a molecule or ion. (Text Table 8-6; Text Examples 8-11, 8-12; Text Prob. 8-32) (News Skills Examples 7, 8; Self Test 14, 34, 42)
3. Make sketches similar to those in Table 8-6 in the text showing the arrangement of electron pairs and multiple bonds around a central atom in a molecule or ion which result in the fewest lone-pair electron repulsions. (Text Examples 8-11, 8-12; Text Probs. 8-33, 8-34) (New Skills Examples 7, 8; Self Test 43)
4. Relate the structure with fewest lone-pair electron repulsions to the geometry of the molecule or ion given in Table 8-7 in the text. (Text Examples 8-11, 8-12; Text Prob. 8-35) (New Skills Examples 7, 8; Self Test 15)
5. Make sketches of the arrangements of atoms for each of the geometries listed in Table 8-6 in the text.

8-7 The polarity of molecules

1. Define dipole moment.
2. Predict whether or not a molecule is polar by passing an imaginary plane through the center of mass and determining if there is a separation of positive and negative charges. (Text Fig. 8-23; Text Probs. 8-38 to 8-40, 8-47, 8-52, 8-53) (Self Test 9)

NEW SKILLS

8-1 Ionic bonding

1. Writing Lewis structures for ionic compounds

Lewis structures (sometimes called electron-dot formulas) are an important aid to understanding the kind of bonding in a molecule. In the following chapters we will use them in writing structures for resonance hybrids, determining bond polarity, and predicting geometry of molecules and types of hybrid bonds. Although electrons are shown as belonging to or coming from specific atoms in Lewis structures, in reality all electrons are indistinguishable, and Lewis structures are only a bookkeeping technique.

Examples 8-1 and 8-2 in the text show how to write the Lewis structure for the ionic compound calcium chloride. Since all ionic compounds must be electrically neutral (you do not get an electrical shock when you touch a chemical), they combine in the ratio of one calcium ion to two chloride ions. Notice that in Lewis structures brackets and ionic charges are added to the chemical symbol and all the electrons in the original valence shell are shown. The number of chloride ions or oxide ions is indicated by a coefficient in the Lewis structure and by a subscript in the chemical formula.

2. Writing chemical formulas from ionic charges

Chemical formulas of binary ionic compounds can be written easily if the charges on the ions are known. Charges of the representative elements in binary ionic compounds are determined from their position in the periodic table. Group IA, IIA, and IIIA metals have one, two, and three valence electrons, respectively. They lose these electrons to form their respective ions and so have ionic charges of +1, +2, and +3, respectively. Therefore, the group number is the charge for elements in the first three groups. When elements in Groups VA, VIA, and VIIA form binary ionic compounds they gain three, two, and one electrons, respectively, to complete their valence octets. Their resulting charges are –3, –2, and –1, respectively. Thus we have

Group	IA	IIA	IIIA	VA	VIA	VIIA
Ionic charge	+1	+2	+3	–3	–2	–1

We can determine ionic charges from the group number of the representative elements. Transition elements usually have ionic charges of +2 or +3.

• EXAMPLE 1

Problem: What is the chemical formula for the ionic compound between strontium and nitrogen?

Solution: Strontium is in Group IIA and nitrogen is in Group VA, so they have charges of +2 and –3, respectively. Strontium must lose two valence electrons and nitrogen must gain three electrons for each to satisfy the octet rule. The number of electrons a metal loses is the same as its periodic table group number, IIA in the case of strontium. The number of electrons a nonmetal gains is the difference between its group number and 8. In the case of nitrogen, 8 – 5 = 3. Since nitrogen gains three electrons to form a nitride ion, the ion has an ionic charge of –3. A neutral compound can be formed by combining three strontium ions with two nitride ions to give a total +6 charge for three strontium ions and –6 charge for three nitride ions. The formula is Sr_3N_2. •

Parallel Problem: Write the chemical formula for the ionic compounds between potassium and phosphorus using only the periodic table.
Ans: K_3P

Now try Example 8-3 in the text.

8-2 Covalent bonding

1. Lewis structures

Lewis structures are more informative for covalent compounds than for ionic; however, before the Lewis structure can be drawn the geometry of the molecule must be known or determined. The procedure for writing a Lewis structure for a compound in which the elements follow the octet (or duet) rule is as follows:

1 Write the symbol for each atom in a position showing the geometry of the molecule. In most cases the arrangement of atoms will be obvious; if it is not, you may need to try several arrangements to find one that works.
2 Determine the total number of valence electrons in the molecule. Add an electron for each negative charge or subtract an electron for each positive charge if the particle is an ion.
3 Assign a pair of electrons to each bond between adjacent atoms.
4 Assign the remaining electrons to complete the octet for each atom except hydrogen. This may require sharing of two or three pairs of electrons between atoms.

You will usually be given the geometrical (spatial) position of atoms relative to each other in the molecule. If you are not given this information, and there are three or more atoms in the molecule, remember that oxygen and hydrogen atoms are usually bonded to a central atom. The central atom is the one closest to the lower left-hand corner of the periodic table. Remember that carbon has four covalent bonds, and almost never has a lone pair of electrons.

The completed Lewis structure should show:

1 Which atoms in the molecule are bonded together
2 How the valence electrons are assigned in the molecule
3 Which pairs of electrons are bonding and which are lone pairs
4 Any double or triple bonds in the molecule

• EXAMPLE 2

Problem: Write the Lewis structure for N_2.

Solution: Each nitrogen atom contributes its five valence electrons to the Lewis structure, giving ten electrons to be distributed around the two nitrogen nuclei. It should be obvious that some of the ten electrons must be shared by both nitrogen atoms in order to give each nitrogen atom eight electrons. The only way to arrange ten electrons around two atoms and satisfy the octet rule is by sharing three pairs of electrons:

$$:N:::N:$$

Each bonding pair of electrons is replaced by a line representing the covalent bond to give the Lewis structure:

$$:N\equiv N: \quad \bullet$$

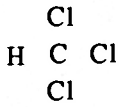
Parallel Problem: Write the Lewis structure for Cl_2.

Ans: $\cdot\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}—\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\,:$

• EXAMPLE 3

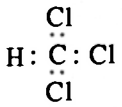
Problem: Write the Lewis structure of chloroform, $CHCl_3$.

Solution: No information or hints were given about the geometry of the molecule, so we resort to the general observation that carbon usually serves as the central atom and other atoms are bonded to it. The carbon atom must have four bonds. The geometry is:



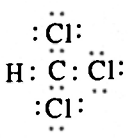
$$\begin{array}{ccc} & \mathrm{Cl} & \\ \mathrm{H} & \mathrm{C} & \mathrm{Cl} \\ & \mathrm{Cl} & \end{array}$$

The position of H and Cl around the carbon is arbitrary; the H can be exchanged with any Cl and the geometry is still the same. Next we need to determine the total number of valence electrons. From their positions in the periodic table we see that H has one valence electron, C has four, and each Cl has seven for a total of 1 + 4 + 3 (7) = 26 valence electrons. Eight of these are required for the four bonds on the carbon.



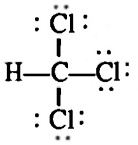
$$\begin{array}{ccc} & \mathrm{Cl} & \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & :\mathrm{Cl} \\ & \mathrm{Cl} & \end{array}$$

Note how the shared pairs needed for bonding satisfy the need for two electrons to fill hydrogen's valence shell and eight to fill carbon's shell. There are 26 – 8 = 18 additional electrons to be distributed among the chlorine atoms. This gives six more electrons to each Cl, just the right amount to complete the octet on each Cl and finish the Lewis structure for $CHCl_3$. •



$$\begin{array}{ccc} & :\ddot{\mathrm{Cl}}: & \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \\ & :\underset{\cdot\cdot}{\mathrm{Cl}}: & \end{array}$$

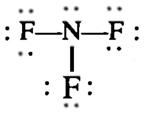
or



$$\begin{array}{ccc} & :\ddot{\mathrm{Cl}}: & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \\ & | & \\ & :\underset{\cdot\cdot}{\mathrm{Cl}}: & \end{array}$$

Parallel Problem: Write the Lewis structure for NF_3.

Ans:



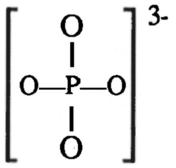
$$\begin{array}{ccc} :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}- & \ddot{\mathrm{N}} & -\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: \\ & | & \\ & :\underset{\cdot\cdot}{\mathrm{F}}: & \end{array}$$

Now let us try a Lewis structure for a charged particle (ion).

• EXAMPLE 4

Problem: Write the Lewis structure for the phosphate ion, PO_4^{3-}.

Solution: In this ion the four oxygens are bonded to the central phosphorus atom.

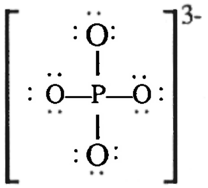


$$\left[\begin{array}{ccc} & \mathrm{O} & \\ & | & \\ \mathrm{O}- & \mathrm{P} & -\mathrm{O} \\ & | & \\ & \mathrm{O} & \end{array}\right]^{3-}$$

The total valence electrons are five from phosphorus, six from each of the four oxygens, and three for the 3– charge on the ion.

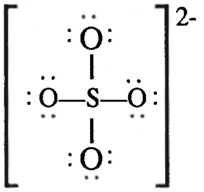
$$5 + 4(6) + 3 = 32$$

There is only one way the 32 electrons can be distributed so each atom obeys the octet rule.

 •

Parallel Problem: Write the Lewis structure for SO_4^{2-}.

Ans:



Now try Examples 8-4 through 8-7 in the text.

8-4 Bond energies

Bond energies can be used to calculate the enthalpy of gas-phase reactions if enthalpy of formation data are not available. The actual bond energies of the individual C—H bonds in CH_4 are not exactly the same as the average bond energy, but we can use average bond energies to calculate an approximate value for enthalpy changes of gas-phase reactions.

• EXAMPLE 5

Problem: Estimate the enthalpy of combustion of methane, CH_4, using average bond energies.

Solution: The gas-phase equation for the combustion of methane is:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

In order for the reaction to occur, we must break all the bonds in the reactants and form all the bonds in the products. The enthalpy of reaction is:

$$\Delta H_{Rxn} = \Sigma\,BE_{(reactants)} - \Sigma\,BE_{(products)}$$

$$\Delta H_{Rxn} = [4\,BE\,(C—H) + 2\,BE\,(O{=}O)] - [2\,BE\,(C{=}O) + 4\,BE\,(O—H)]$$

Using average bond energy values from Tables 8-4 and 8-5, the equation becomes:

$$\Delta H_{Rxn} = [4\,(416) + 2\,(498)] - [2\,(799) + 4\,(463)] = 2660 - 3450 = -790\text{ kJ}$$

If we use the values of standard enthalpies of formation given in Table 3.2 of Chapter 3 in the text for comparison, we get:

$$\Delta H_{Rxn} = -802.3 \text{ kJ}$$

It should be recognized that enthalpies of reaction calculated from average bond energies are only approximate values. •

Parallel Problem: Estimate the enthalpy of reaction for: $Cl_2(g) + 3\ F_2(g) \rightarrow 2\ ClF_3(g)$
Ans: –965 kJ

8-5 Electronic bookkeeping, part I: formal charges

When more than one Lewis structure is possible for a molecule, formal charges can be used to decide which Lewis structure is correct. The true Lewis structure will have formal charges consistent with charges predicted from known valence electrons for the atoms in the molecule.

We can assign formal charges to each atom in a Lewis structure using these 4 steps:

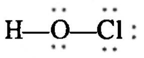
1 Assign both electrons of a lone pair to its atom.
2 Split all bonding pairs of electrons so that each bonded atom is assigned one electron.
3 Determine the number of apparent valence electrons for each bonded atom by adding all the electrons assigned in steps 1 and 2.
4 Determine the formal charge on each atom by subtracting the apparent valence electrons for each atom as determined in step 3 from the actual valence electrons present in each isolated, nonbonded atom.

$$\text{Formal charge} = \begin{matrix}\text{No. of actual valence electrons}\\ \text{in the isolated atom}\end{matrix} - \begin{matrix}\text{No. of apparent valence electrons}\\ \text{in the bonded atom}\end{matrix}$$

• EXAMPLE 6

Problem: Assign formal charges to each atom in the molecule, HOCl, hydrogen hypochlorite.

Solution: We must determine the Lewis structure before we can apply the formal charge rules.



$$H{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!:$$

Applying the steps for determining formal charge we get:

apparent valence electrons in bonded atoms
H = $1\ e^-$
O 4+2 = $6\ e^-$
Cl 6+1 = $7\ e^-$

actual valence electrons in isolated atoms

H	$1\ e^-$
O	$6\ e^-$
Cl	$7\ e^-$

$$\text{Formal charge on each atom} = \text{No. of actual valence electrons in the isolated atom} - \text{No. of apparent valence electrons in the bonded atom}$$

$$\begin{array}{l} \mathrm{H}\ 1-1 = 0 \\ \mathrm{O}\ 6-6 = 0 \\ \mathrm{Cl}\ 7-7 = 0 \end{array}$$

The formal charges may be designated as:

$$\overset{0}{\mathrm{H}}—\overset{0}{\mathrm{O}}—\overset{0}{\mathrm{Cl}}$$ •

Parallel Problem: Assign formal charges to each atom in an alternate Lewis structure for HOCl where chlorine is the central atom.

Ans: $\mathrm{H—\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:}$

$$\overset{0}{\mathrm{H}}—\overset{+1}{\mathrm{Cl}}—\overset{-1}{\mathrm{O}}$$

Note that the structure giving the lower formal charges (the structure in Example 6) is the correct structure. Now work Examples 8-9 and 8-10 in the text.

8-6 Electron-pair repulsion

Predicting the shape of molecules from Lewis structures by the VSEPR method

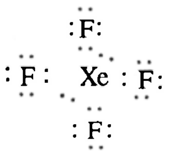
The valence-shell electron-pair repulsion theory (designed VSEPR and pronounced "vesper") is a way of determining the geometry or shape of a molecule from the Lewis structure. The VSEPR method is based on the idea that electron pairs repel each other so that the most stable shape for a molecule is one that allows the electron pairs to get as far apart as possible.

Tables 8-6 and 8-7 in the text make the VSEPR method easy to use. The first step is using the Lewis structure to determine the number of lone electron pairs on the central atom and the steric number of that central atom. Steric number is the total atoms bonded to the central atom plus the number of lone electron pairs. After this information is determined you can use text Tables 8-6 and 8-7 to find the geometry and bond angles for several combinations of steric numbers and lone pairs. Double or triple bonds count as only one electron pair when determining the steric number.

• EXAMPLE 7

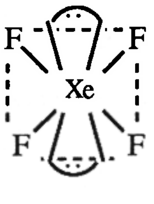
Problem: Predict the geometry (shape) of the XeF_4 molecule.

Solution: We will apply the steps in the VSEPR method as given in Section 8-6 of the text. First we write a Lewis structure. The molecule is symmetrical, with the four fluorines arranged around Xe. There are 8 + 4(7) = 36 valence electrons. The octet rule only allows distribution of 32 valence electrons.



Since there is a total of 36 valence electrons, the valence shell of Xe must be expanded to contain 12 electrons. There are four bonding pairs and two nonbonding pairs on Xe so the steric number is 4 + 2 = 6. Table 8-6 gives octahedral orientation around atoms with a steric number of 6 and shows all bonds are 90° to each other. Note that the two lone pairs occupy points on the octahedron, but that these sites are not part of the overall geometry of the molecule.

Using Table 8-7, we find that a molecule with a steric number of 6 and two lone pairs on the central atom has square planar geometry. All five atoms are in the same plane, with the four fluorine atoms at the corners of a square surrounding Xe. The lone pairs on Xe are oriented at 90° above and below the plane.



Note how the lone pairs help determine the bond directions even though they are not considered part of the overall shape of the molecule. Without the lone pairs, the geometry shape would be tetrahedral. •

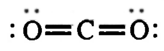
Parallel Problem: Predict the geometry of the AsF_5 molecule.
Ans: trigonal bipyrimidal

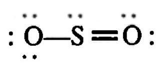
Now try Example 8-11 in the text.

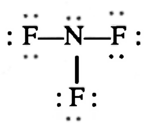
• EXAMPLE 8

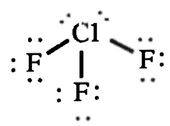
Problem: Predict the geometry of the following using the VSEPR method: (a) CO_2 (b) SO_2 (c) NF_3 (d) ClF_3

Solution: Lewis structures are:


(a)


(b)


(c)


(d)

Compound	Number of atoms bonded to central atom	Lone pairs	Steric number	Molecular geometry
(a) CO_2	2	0	2	Linear
(b) SO_2	2	1	3	Angular
(c) NF_3	3	1	4	Trigonal pyramidal
(d) ClF_3	3	2	5	T-shaped

The Lewis structure is used to determine the steric number and lone pairs, then Table 8-7 in the text gives the geometry having least electron-pair repulsion. •

Parallel Problem: Predict the geometry of the following: (a) SnF_4 (b) IF_2^+ (c) I_3^- (d) PH_3.
Ans: (a) tetrahedral (b) bent (c) linear (d) trigonal pyramidal

KEY TERMS

8-1 Ionic bonding

Chemical bond: The forces that hold atoms together in molecules.

Core: All of the atom except the valence shell of electrons. Same as kernel.

Dissociation: The splitting apart of a molecule to form two fragments. In solution it is the reaction of an electrolyte with a solvent to form ions. Sometimes called ionization.

Energetically favorable: Capable of releasing energy.

Ionic bond: The electrostatic attraction between ions of opposite electrical charge.

Ionization: Same as dissociation.

Kernel: Same as core.

Lattice energy: The energy necessary to separate one mole of a crystalline solid into the gaseous state.

Lewis structure: A depiction of the arrangement of valence electrons by representing them as dots around the atomic symbols. An electron-dot formula.

Sublimation: Direct conversion from solid to gas.

8-2 Covalent bonding

Bond length: The distance between the nuclei of two bonded atoms.

Bonding pair: A pair of electrons shared between two atoms and constituting a covalent bond. Same as shared pair.

Central atom: The principal atom at the center of a Lewis structure. Several other atoms are generally bonded to the central atom.

Coordinate covalent bond: A covalent bond in which both shared electrons appear to have been donated by one atom.

Covalent bond: A bond consisting of a pair of electrons shared between the bonded atoms.

Double bond: Two bonding electron pairs between the same two atoms.

Lone pair: A pair of valence electrons not involved in bonding. Same as unshared pair.

Normal covalent bond: A covalent bond in which each bonded atom contributes one electron to the shared pair.

Resonance: The bonding condition in which two or more Lewis structures differing only in the distribution of electrons can be drawn. The stable structure is intermediate to the Lewis structures.

Resonance hybrid: The intermediate structure of a series of resonance structures.

Shared pair: Same as bonding pair.

Triple bond: Three bonding electron pairs between the same two atoms.

Unshared pair: Same as lone pair.

8-3 Electronegativity

Bond polarity: The degree to which a bonding pair is shared unequally by the bonded atoms.

Electronegativity: The relative tendency of a bonded atom to attract an electron.

Nonpolar: No separation of electrical charges. A bond formed between two atoms with identical electronegativities is nonpolar.

Polar covalent bond: A covalent bond in which the bonding electron pair is not shared equally but is drawn closer to the more electronegative atom.

8-4 Bond energies

Average bond energy: An average of bond dissociation energies from different compounds containing the bond.

Bond dissociation energy: The energy necessary to break a specific bond in a molecule.

8-5 Electronic bookkeeping, part I: formal charges

Formal charge: The charge an atom would have if all of its bonding pairs were shared equally.

8-6 Electron-pair repulsion

Axial: Positions that define the principal axis passing through the top and bottom corners and the center of a geometrical figure.

Equitorial: Positions on the corners of a geometrical figure not on the principal axis.

Steric number: The sum of the number of bonds plus the number of lone pairs around a bonded atom.

Tetrahedral: The shape of a regular four-sided polyhedron.

Trigonal bipyramidal: The shape of two triangular pyramids joined at their bases.

VSEPR: Valence-shell electron-pair repulsion theory.

8-7 The polarity of molecules

Dipole: Same as polar molecule.

Dipole moment: The product of the magnitude of the charge of a dipole times the distance between the opposite charges.

Polar molecule: A molecule in which the centers of positive and negative charge are physically separated. Same as dipole.

SELF TEST

True or False

_____ 1. The octet rule means an atom tends to achieve a full outside energy shell of electrons.

_____ 2. In a normal covalent bond the shared pair of electrons remain exactly equal distances between the two nuclei of the bonded atoms.

_____ 3. When forming ionic compounds, sodium gains one electron.

_____ 4. Electronegativity increases from left to right in a period.

_____ 5. The formula for the ionic compound formed between aluminum and sulfur is AlS.

_____ 6. The tendency of an atom to achieve a noble-gas configuration is called the octet rule.

_____ 7. Any compound formed between an element in Group IA (not including hydrogen) and an element in Group VIIA will be ionic.

_____ 8. The correct Lewis structure for the ionic compound formed between potassium and sulfur is Na:S:Na.

_____ 9. SiH_4 is a polar molecule.

_____ 10. Lone pairs of electrons are not attached to an atom.

_____ 11. Large atoms such as iodine can use vacant *d* orbitals to expand their valence shell.

_____ 12. Electronegativity is the same as electron affinity.

_____ 13. A polar covalent bond is formed by two atoms of similar but different electronegativities.

_____ 14. The steric number is the total number of valence electron pairs in a molecule.

_____ 15. Lone pairs are not included in the designation of the overall geometry of a molecule.

Completion

16. The ionization of aluminum may be represented by the equation ____________________.

17. Element X is in Group IIA and element Y is in Group VA. The chemical formula for an ionic compound between X and Y is ______________.

18. A triple bond requires the sharing of _____________ (number of) electrons.

19. The Lewis structure for $MgCl_2$ is _______________________.

20. The Lewis structure for NCl_3 is _______________________.

21. A chloride ion has a stable valence shell of __________ (number of) electrons.

22. The Lewis structure for SO_2^{2-} is ________________________.

23. The tendency of a bonded atom to attract electrons is indicated by its ___________.

24. The bonding in CsBr is _________________ (covalent or ionic).

25. A shared electron pair between two atoms is called a(n) ____________________.

26. When electrons are shared unequally by two atoms, the bond between the atoms is said to be __________________________.

27. The formal charges on the atoms in the ion SO_2^{2-} are ______________ for sulfur and _______________ for oxygen.

28. Arrange the atoms K, Rb, Na in order of increasing electronegativity. __________________________________.

29. The NH_3 molecule has a _____________________ shape.

30. The most electronegative elements are located in the ______________________ part of the periodic table.

Multiple Choice

31. Ionic bonds are formed when
    (a) a metal atom gains electrons and a nonmetal atom loses electrons
    (b) a metal atom loses electrons and a nonmetal atom gains electrons
    (c) a metal atom shares electrons with a nonmetal atom
    (d) two nonmetal atoms share electrons

32. Lewis structures
    (a) have eight electrons around all atoms
    (b) do not show lone-pair electrons
    (c) show the distribution of electrons on atoms
    (d) accurately describe the structure of a resonance hybrid

33. The total number of valence electrons in CO_3^{2-} is
    (a) 12 (b) 14 (c) 24 (d) 26

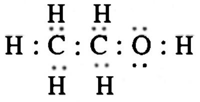
34. The total number of shared pairs of electrons in CO_2 is
    (a) one (b) two (c) three (d) four

35. Which element has the greatest electronegativity?
    (a) F (b) I (c) Li (d) Cs

36. Which of the following bonds is most polar?
    (a) H—C (b) F—F (c) Cs—F (d) Na—Cl

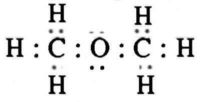
37. The formal charge on S in the ion SO_4^{2-} is
    (a) 0 (b) +2 (c) –2 (d) +4

38. The correct Lewis structure(s) for the compound C_2H_6O is(are)



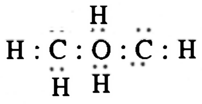
$H:\overset{H}{\underset{H}{C}}:\overset{H}{\underset{H}{C}}:\ddot{\underset{..}{O}}:H$

(A)



$H:\overset{H}{\underset{H}{C}}:\ddot{\underset{..}{O}}:\overset{H}{\underset{H}{C}}:H$

(B)



$H:\underset{H}{C}:\overset{H}{\underset{H}{O}}:\ddot{\underset{..}{C}}:H$

(C)

    (a) A, B, and C (b) A (c) A and B (d) B and C

39. Which of the following is polar?
    (a) CO_2 (b) $BeCl_2$ (c) NH_4^+ (d) NH_3

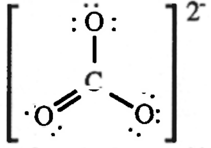
40. Which of the following is not essential to the VSEPR method?
    (a) Drawing a Lewis structure
    (b) Determining the steric number
    (c) Minimizing the repulsion between lone pairs
    (d) Minimizing the repulsion between bonding pairs

41. Which of the following has a tetrahedral shape?
    (a) H_2O (b) NH_3 (c) C_2H_2 (d) SiH_4

42. The steric number of XeF_2 is
    (a) 2 (b) 3 (c) 4 (d) 5

43. How many lone pairs of electrons are present in H_2Se?
    (a) zero (b) one (c) two (d) four

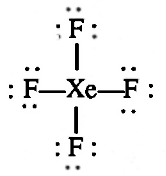
44. What are the formal charges on oxygen in the following Lewis structure?



(a) −2 and −1 (b) −2 and +1 (c) −1 and +2 (d) 0 and −1

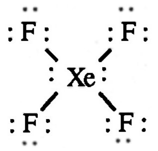
45. The correct Lewis structure for the compound XeF_4 is:

(a)



(b) $Xe^{+4} + 4\,:F:^{-}$

(c)



(d) Lewis structures are not possible for the noble gases or their compounds.

Chapter 9

SOLIDS

CHAPTER OVERVIEW

9-1 Solids: some preliminary observations

In a true solid, the atoms or particles are arranged in an orderly array. The geometry and type of particles determine the properties of the solid and we will see how they fall into definite groups or types. Sometimes the external appearance of a large crystal gives clues to the internal structure of the crystal, but there are also powerful techniques that reveal the microstructure of crystals.

9-2 X-ray diffraction

Crystals diffract x rays into a pattern of spots or rings which can be analyzed to determine the internal microstructure and bonding in the crystal. The mathematics of analyzing x-ray diffraction patterns is based on the Bragg relation. It relates the angle of diffraction and wavelength of x rays to the spacing of atoms in parallel plans in the crystal.

$$n\lambda = 2d \sin \theta$$

The variables in this equation are defined in the text and in the New Skills section. The term sin θ is a trigonometric function. It can be determined from θ by looking in a table of trigonometric functions in any mathematics or chemical handbook or by using most pocket calculators. Laue patterns or Debye-Sherrer diffraction patterns are often recorded on film. Values of θ can be measured directly from the film and d values can be calculated with the Bragg relation. You should be able to make this calculation. (See Example 9-1 in the text.)

9-3 The crystal lattice

The unit cell is the key to understanding the geometry of any crystal lattice since the entire crystal is generated by repeating the unit cell. Of the six different crystal types shown in Figure 9-14, you should become familiar with the cubic and hexagonal structures. Learn the differences and similarities of the three types of cubic structures: primitive, face-centered, and body-centered. Most of the problems and calculations you will do are based on these three types.

9-4 Close packing

There are two types of close-packed crystal structures: cubic close-packed and hexagonal close-packed. They differ only in the way layers of atoms are stacked upon each other. These stacking sequences are illustrated in Figures 9-19 through 9-23 in the text. It should be apparent that face-centered cubic and cubic close-packed are different names for the same structure. Close-packed structures are important because all the noble gases and about 40 metals crystallize in these structures.

The concept of tetrahedral holes and octahedral holes in close-packed structures will not be difficult to understand if you examine Figure 9-24 in the text closely. These void spaces are often occupied by atoms or ions that are the right size to fit into the space. Size relations of atoms play an important part in determining the type of crystal structure of a compound. Many ionic compounds crystallize with one ion in a close-packed structure pattern and the other in tetrahedral or octahedral holes in the structure.

9-5 Bonding and the properties of solids

The four types of solids have different physical properties as a result of the different crystal structures and types of particles. You should become very familiar with the physical properties of each type of solid (summarized in Table 9-1 in the text.)

Van der Waals forces are much weaker than the ionic and covalent bonds we have studied previously, but they are important in determining the structure of solids. There are two types of van der Waals or intermolecular forces: (1) dipole-dipole forces between polar molecules, illustrated in Figure 9-28 in the text, and (2) London forces (also called dispersion forces) illustrated in Figure 9-29.

The concept of delocalized electrons, or electron gas, is important in explaining the high thermal and electrical conductivity of metallic solids.

9-6 Lattice energy

Lattice energy is an indication of the strength of bonds in a crystal. It is usually quite difficult to measure experimentally and so is calculated from other experimental measurements by a Born-Haber calculation. You will become familiar with this type of calculation in several problems in the text.

9-7 Defects in crystals

Imperfections in the crystal lattice are called defects. The two main types of defects are line defects and point defects. Line defects are edge or screw dislocations of the normal crystal pattern and tend to weaken the crystal structure. Point defects give rise to changes in color and conductivity in crystals and are used to make semiconductors and transistors. Figure 9-33 in the text shows how point defects or impurities are intentionally introduced into certain crystals to make semi-conductors. Impurity defects can change the physical properties of alloys and metals dramatically. For instance, carbon in the interstices of iron crystals makes steel hard, but sulfur or hydrogen in the same positions greatly weakens the iron structure.

LEARNING OBJECTIVES

As a result of studying Chapter 9, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 148 of this *Study Guide*.

9-1 Solids: some preliminary observations

1. Define a solid in terms of the internal arrangement of its particles in a crystal structure. (Text Prob. 9-5) (Self Test 14)
2. Describe the difference between a true solid and an amorphous substance. (Text Prob. 9-1) (Self Test 16)
3. Relate the properties of a solid to its crystal structure. (Text Probs. 9-2, 9-3) (Self Test 9)

9-2 X-ray diffraction

1. Make a sketch showing the diffraction of x rays from layers in a crystal lattice. (Text Prob. 9-7)
2. Use the Bragg equation to calculate spacing between layers when the angle of diffraction and wavelength of an x ray are given. (Text Example 9-1; Text Probs. 9-8 to 9-10, 9-41) (Self Test 17, 34)
3. Describe how the geometry and dimension of a unit cell are obtained from x-ray diffraction patterns. (Self Test 17, 40)

9-3 The crystal lattice

1. Sketch the geometry of simple crystal structures. (Text Probs. 9-6, 9-11, 9-15) (Self Test 2, 6, 7, 13, 25, 33, 42 to 45)
2. Cite the fact that all crystals belong to one of six different crystal systems.
3. Show how the unit cell describes the entire geometry of a crystal. (Text Probs. 9-12 to 9-14) (Self Test 18)
4. Illustrate how the properties and kind of particles determine the type of crystal lattice of a solid.
5. Calculate the length of a unit cell for body-centered or face-centered cubic structures from the atomic radius or density of the substance. (Text Probs. 9-16, 9-17, 9-44) (New Skills Examples 1, 3; Self Test 36, 37)
6. Determine the number of atoms per unit cell and the type of cell for cubic structures given the density and unit cell dimensions. (Text Probs. 9-18, 9-42, 9-43) (New Skills Example 2; Self Test 35)

9-4 Close packing

1. Define packing efficiency. (Self Test 19)
2. Calculate packing efficiency given the type of crystal for simple crystals. (Text Example 9-2)
3. Know which types of crystals have high packing efficiencies. (Text Prob. 9-20) (Self Test 7)
4. Understand the difference in layering sequence between cubic close-packed and hexagonal close-packed structures. (Text Prob. 9-19) (Self Test 1, 27, 33)
5. Understand how tetrahedral and octahedral holes arise in close-packed structures and how these holes are occupied by particles in some substances. (Text Probs. 9-21, 9-22, 9-45, 9-46) (Self Test 3, 4, 12, 28)

9-5 Bonding and the properties of solids

1. Relate the properties of solids to the geometry of the crystal structure, the type of particles, and the kind of bonding. (Text Probs. 9-25, 9-26, 9-29, 9-33, 9-48) (Self Test 9, 22, 23, 38)
2. Make a list of the properties and kind of bonding of the four types of solids. (Text Probs. 9-23, 9-24, 9-28, 9-47) (Self Test 20)
3. Describe the van der Waals forces and London or dispersion forces. (Self Test 5, 21)

9-6 Lattice energy

1. Calculate the lattice energy of a crystal using a Born-Haber type of calculation. (Text Probs. 9-30 to 9-32, 9-34) (New Skills Example 4; Self Test 39, 41)

9-7 Defects in crystals

1. Distinguish between edge dislocation and screw dislocations and explain how they affect the properties of crystals. (Text Probs. 9-35 to 9-37)
2. Show how atoms or ions occupying lattice vacancies or lattice interstitial positions can affect the electrical properties of the crystal. (Text Prob. 9-38) (Self Test 10, 29 to 31)
3. Make a sketch showing how metalloids are doped to make n-type and p-type semiconductors and explain the difference between the two types. (Text Probs. 9-38 to 9-40, 9-50) (Self Test 11, 15, 26, 32)
4. Show how nonstoichiometric compounds result when ions occupy interstices. (Self Test 10, 29 to 31)

NEW SKILLS

9-2 X-ray diffraction

Determining the spacing between layers in a crystal using the Bragg equation

Data taken by x-ray diffraction techniques can be used in the Bragg equation to reveal the micro-structure of crystals. The Bragg equation relates the measured angle of diffraction to the spacing between layers in a crystal.

$$n\lambda = 2d \sin \theta$$

where $\sin \theta$ = sine of the angle between the incoming x ray and the plane of the atoms in the crystal layer

d = distance between two parallel planes
λ = wavelength of the x ray
n = a positive integer

In actual practice the x-ray wavelength and the angle of diffraction can be measured very accurately. Values of d are calculated for several values of n for each measured angle of diffraction and the unit cell is deduced by analyzing the d values through geometric relations. Each substance has a unique set of diffraction angles called a diffraction pattern that can be used to easily identify complex compounds and minerals.

We will carry this process only as far as determining the distance between parallel planes of atoms in the crystal as shown in Example 9-1 in the text. The Bragg relation can be used to solve for any of the variables, d, n, λ, or θ if values for the others are known.

9-3 The crystal lattice

A knowledge of the geometry of the unit cell reveals much about the substance. You need to be able to analyze several different aspects of the unit cell.

1. Calculation of dimensions of a unit cell when the type of cell and atomic radius of the substance are given

If the type of cell and the atomic radius of the substance are known, the dimensions of the unit cell can be determined.

• EXAMPLE 1

Problem: The atomic radius of gold is 0.144 nm and it crystallizes in the face-centered cubic structure. What is the length of a side of a unit cell for a gold crystal?

Solution: In a face-centered cubic structure, atoms along a diagonal of the face of the cell just touch each other. See Figure 9-15*a* in the text. The length of the face diagonal is four times the radius of the atom, $d = 4r$, where d is the diagonal length and r is the atomic radius. Since the diagonal forms the base of an isosceles triangle with two cell edges, the pythagorean theorem of geometry gives $d^2 = 2l^2$ where d is the hypotenuse of the isosceles triangle and l is the length of the cell edge. Equating these two relations for d gives

$$4r = \sqrt{2}\,l \qquad l = \frac{4}{\sqrt{2}}r$$

For the gold crystal

$$l = \frac{4}{\sqrt{2}}(0.144\text{ nm}) = 0.407\text{ nm}$$ •

Parallel Problem: The atomic radius of argon is 0.088 nm and it crystallizes in the face-centered structure. What is the length of a side of a unit cell for a crystal of solid argon?
Ans: 0.25 nm

2. *Calculation of the number of atoms in a unit cell when the type of cell and density of the substance are given*

Since the unit cell contains a fixed number of atoms, its mass is fixed. It also has a fixed volume, so the mass of a unit cell is actually a mass per unit volume, or density. If we know the type of cell and the density of the substance, we can find the number of atoms or molecules in the unit cell.

• EXAMPLE 2

Problem: The density of silver metal is 10.5 g cm^{-3}. It crystallizes in a cubic structure with a side length of 0.41 nm. How many atoms are there in the unit cell?

Solution: The volume of the unit cell is

$$V = l^3 = (0.41)^3 = 0.069\text{ nm}^3$$

From the density we can determine the mass of the unit cell.

$$\text{Mass of unit cell} = 10.5\text{ g cm}^{-3}\,(0.069\text{ nm}^3)\left(\frac{1\text{ cm}}{10^7\text{ nm}}\right)^3 = 7.2 \times 10^{-22}\text{ g}$$

The atomic mass of silver is 108 g mol^{-1}, so there are

$$7.2 \times 10^{-22}\text{ g}\left(\frac{1\text{ mol}}{108\text{ g}}\right) = 6.7 \times 10^{-24}\text{ mol}$$

in the unit cell. We can use Avogadro's number to find the number of atoms in the unit cell.

$$\left(6.7 \times 10^{-24} \frac{\text{mol}}{\text{unit cell}}\right)\left(6.02 \times 10^{23} \frac{\text{atoms}}{\text{mol}}\right) = 4.0 \frac{\text{atoms}}{\text{unit cell}}$$

Note that the face-centered cubic structure must have four atoms per unit cell, corresponding to the number we calculated. (See Figure 9-15*a* in the text.) •

Parallel Problem: The density of solid oxygen is 1.429 g cm^{-3}. It crystallizes in a cubic structure and the length of a side of the unit cell is 0.265 nm. How many atoms are there in a unit cell of solid oxygen?
Ans: one atom

3. Calculation of unit cell dimensions when the type of cell and density of the substance are given

The reverse of the previous procedure can be used to find the dimensions of the unit cell if the type of crystal structure is known.

• EXAMPLE 3

Problem: The density of platinum is 21.4 g cm^{-3} and it crystallizes in a body-centered cubic structure. What is the length of the unit cell?

Solution: The body-centered cubic structure has two atoms per unit cell. Let us consider the placement of atoms in the unit cell to show how this is so. There is one atom at each corner, but each of these belongs to eight different unit cells (see Figure 9-12 in the text), so $\frac{1}{8}(8) = 1$ atom contributed to a unit cell from the corner positions. The atom in the center of the unit cell belongs entirely to the cell, so each unit cell has, effectively, two atoms. These two atoms comprise the mass of the unit cell.

$$\text{Mass of unit cell} = 195 \text{ g mol}^{-1}\left(\frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}}\right)\left(\frac{2 \text{ atoms}}{\text{unit cell}}\right)$$

$$= 6.48 \times 10^{-22} \text{ g (unit cell)}^{-1}$$

The volume of the cell can be found from the mass of the cell and the bulk density

$$\text{Volume of unit cell} = 6.48 \times 10^{-22} \text{ g (unit cell)}^{-1}\left(\frac{1 \text{ cm}^3}{21.4 \text{ g}}\right)$$

$$= 3.03 \times 10^{-23} \text{ cm}^3 \text{ (unit cell)}^{-1}$$

The length of a cube is the cube root of the volume

$$l = V^{1/3} = (3.03 \times 10^{-23} \text{ cm}^3)^{1/3} = 3.12 \times 10^{-8} \text{ cm}$$

or

$$3.12 \times 10^{-8} \text{ cm}\left(\frac{10^7 \text{ nm}}{1 \text{ cm}}\right) = 0.312 \text{ nm} \bullet$$

Parallel Problem: The density of metallic sodium is 0.97 g cm^{-3}. It crystallizes in a body-centered cubic structure. Calculate the length of a side of the unit cell for metallic sodium.
Ans: 0.43 nm

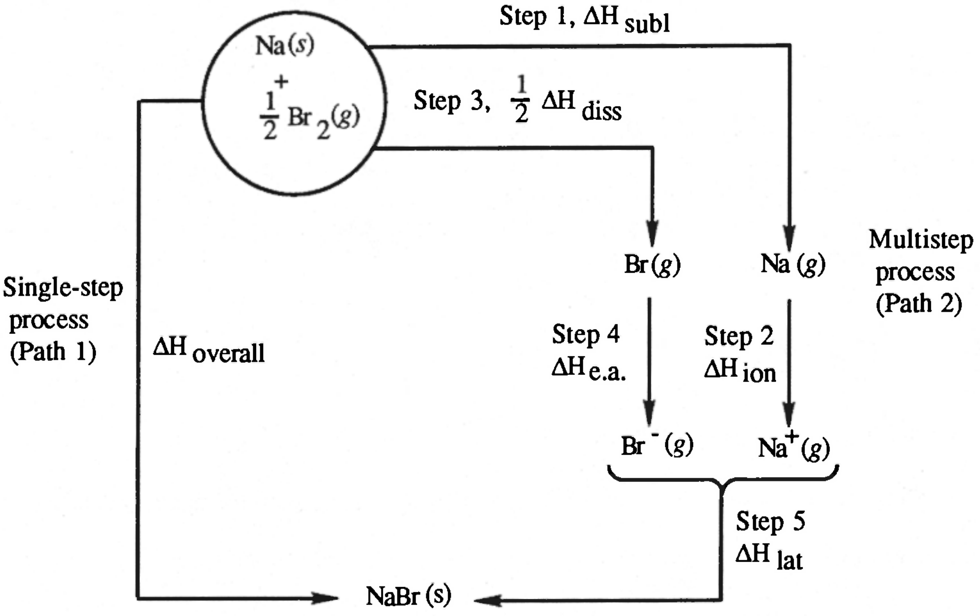
9-5 Bonding and the properties of solids

Born-Haber calculations

The Born-Haber calculation is a method of determining the energy released when a crystal lattice is formed from gaseous ions. This quantity is difficult to measure experimentally, but the enthalpy change between reactants and products in a reaction is always the same regardless of the path or sequence of steps by which the reaction proceeds. The figure below shows two possible paths for forming an NaBr crystal. Since both paths start with the same reactants and end with the same products, the overall enthalpy change must be the same for the two paths. The enthalpy change for the multistep path on the right is the sum of the enthalpy change for each step.

$$\Delta H_{\text{overall}} = \Delta H_{\text{step 1}} + \Delta H_{\text{step 2}} + \Delta H_{\text{step 3}} + \Delta H_{\text{step 4}} + \Delta H_{\text{step 5}}$$

Since all of the enthalpy changes except the lattice energy ($\Delta H_{\text{step 5}}$) can be measured experimentally, the lattice energy can be calculated.



• EXAMPLE 4

Problem: Calculate $\Delta H_{\text{lattice}}$ of sodium bromide from the following experimental data. ΔH of formation of NaBr from the elements is –360 kJ mol^{-1}, ΔH_{subl} of Na is 108 kJ mol^{-1}, ΔH_{diss} of Br_2 is 112 kJ mol^{-1}, ΔH_{ion} of Na is 496 kJ mol^{-1}, and $\Delta H_{\text{e.a.}}$ of Br is –330 kJ mol^{-1}.

Solution: The lattice energy is the enthalpy of the reaction

$$Na^+(g) + Br^-(g) \rightarrow NaBr(s)$$

The lattice energy can be determined by a Born-Haber calculation which incorporates the lattice energy as part of the overall reaction path.

Step 1	$Na(s)$	→	$Na(g)$	$\Delta H_1 = \Delta H_{subl}$	=	108 kJ
Step 2	$Na(g)$	→	$Na^+(g) + e^-$	$\Delta H_2 = \Delta H_{ion}$	=	496 kJ
Step 3	$1/2\,Br(g)$	→	$Br(g)$	$\Delta H_3 = 1/2\Delta H_{diss}$	=	56 kJ
Step 4	$e^- + Br(g)$	→	$Br^-(g)$	$\Delta H_4 = \Delta H_{e.a.}$	=	–330 kJ
Step 5	$Na^+(g) + Br^-(g)$	→	$NaBr(s)$	$\Delta H_5 = \Delta H_{lat}$		
Overall	$Na(s) + 1/2Br_2(g)$	→	$NaBr(s)$	$\Delta H_{overall} = \Delta H_{form}$	=	–360 kJ

The overall chemical reaction is the algebraic sum of the reactions for steps 1 through 5. To find the enthalpy change for an overall reaction, we sum the enthalpy changes for the individual steps in the same manner as the chemical reactions for the steps were combined to give the overall reaction and equate the enthalpy change for the two paths.

$$\Delta H_{overall} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

Solving for ΔH_{lat}

$$\Delta H_5 = \Delta H_{lat} = \Delta H_{overall} - (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4)$$

Now we can substitute numerical values and solve for ΔH_{lat}.

$$\Delta H_{lat} = -360\text{ kJ} - (108\text{ kJ} + 496\text{ kJ} + 56\text{ kJ} - 330\text{ kJ}) = -690\text{ kJ mol}^{-1} \;\bullet$$

Parallel Problem: Calculate the $\Delta H_{lattice}$ of potassium fluoride from the following data: ΔH of formation of KF is –563 kJ mol^{-1}, ΔH of sublimation for potassium is 89 kJ mol^{-1}, ΔH of dissociation for F_2 is 158 kJ mol^{-1}, ΔH of ionization for potassium is 419 kJ mol^{-1}, and ΔH of electron affinity for fluorine is –333 kJ mol^{-1}.
Ans: 817 kJ mol^{-1}

KEY TERMS

9-1 Solids: some preliminary observations

Coefficient of thermal expansion: Volume change per degree of temperature change.

Crystalline solid: A true solid, one with a regular internal structure.

Solid: A substance that maintains a fixed volume and shape.

9-2 X-ray diffraction

Powder pattern: The x-ray diffraction pattern generated by a powdered sample.

X ray: Electromagnetic radiation with very short wavelength.

X-ray diffraction: The diffraction of x rays of atoms in a crystal lattice.

9-3 The crystal lattice

Body-centered cubic: A unit cell with lattice points at the corners and center of a cube.

Bravais lattice: One of 14 fundamental lattice types.

Crystal lattice: The regular, repeating arrangement of particles in a crystal.

Face-centered cubic: A unit cell with lattice points at the corners and in the center of each face of a cube. Same as cubic-close packed.

Lattice point: The location of particles in a unit cell.

Primitive cell: A unit cell with lattice points only at the corners.

Simple cubic cell: A primitive cubic unit cell.

Unit cell: The smallest repeating portion of a crystal lattice that can be used to generate the entire lattice.

9-4 Close packing

Close-packed: Arrangement of atoms in a crystal lattice with the maximum possible packing efficiency.

Cubic-close packed: Same as face-centered cubic.

Hexagonal-close packed: A crystal lattice with repeating layers in the sequence ABABAB.

Octahedral hole: A space in a close-packed structure which is bounded by six spheres located at the corners of an octahedron.

Packing efficiency: A measure of the fraction of the volume of a unit cell which is occupied by the atoms.

Tetrahedral hole: A space in a close-packed structure which is bounded by four spheres located on the corners of a tetrahedron.

9-5 Bonding and the properties of solids

Covalent solid: A solid in which atoms are bonded covalently to form a giant extended network.

Dipole-dipole force: Force between polar molecules.

Dispersion force: A weak force between atoms or molecules due to momentary fluctuations in their electronic charge-cloud distributions. Same as London forces.

Electron gas: The delocalized electrons in a metal. Same as free electron.

Free electron: Same as electron gas.

Ionic solid: A solid composed of anions and cations in its lattice.

London force: Same as dispersion force.

Metallic solid: Solids which have positive ions at all lattice points surrounded by an electron gas.

Molecular solid: Solids which have molecules at each lattice point.

van der Waals force: Weak forces between atoms or molecules including dispersion and dipole-dipole forces.

9-6 Lattice energy

Lattice energy: The amount of energy required to separate the component particles in one mole of a solid.

9-7 Defects in crystals

Color center: A kind of point defect in a crystal giving rise to colors in an otherwise colorless crystal.

Crystal defect: Irregularities in the structure of a crystal lattice.

Diode: An electronic component that is a combination of n- and p- type semiconductors.

Dislocation defect: A structural irregularity that follows a line in a crystal. Same as line defect.

Doping: Enhancing a semiconductor by carefully adding an impurity to an intrinsic semiconductor.

Edge dislocation: A structural irregularity resulting when a layer of particles stops within a crystal instead of continuing all the way to the crystal surface.

Impurity center: A foreign particle at a lattice point.

Interstitial: A space between the atoms in a crystal.

Intrinsic semiconductor: A pure substance that has semiconductor properties.

Lattice vacancy: A structural irregularity resulting from a missing particle in the crystal lattice.

Line defect: Same as dislocation defect.

n-type semiconductor: A semiconductor in which the charge carriers are weakly bound electrons.

p-type semiconductor: A semiconductor in which the charge carriers are holes caused by missing electrons.

Point defect: A structural irregularity at a single point in a crystal lattice.

Screw dislocation: A dislocation in which layers of particles in a crystal are warped around the axis of a screw.

Semiconductor: A substance whose electrical conductivity increases with increasing temperature.

SELF TEST

True or False

_____ 1. Cubic close-packed and hexagonal close-packed structures differ only in layering sequence.

_____ 2. Face-centered cubic structures have four particles per unit cell.

_____ 3. All close-packed structures have both tetrahedral and octahedral holes.

_____ 4. Atoms often occupy tetrahedral or octahedral holes and expand the original close-packed structure.

_____ 5. Van der Waals forces are electrostatic and form a strong ionic bond.

_____ 6. There are four particles in the unit cell of a body-centered cubic structure.

_____ 7. Body-centered cubic crystal structure is the most densely packed type of cubic crystal structure.

_____ 8. Lattice defects are common in solids.

_____ 9. Ionic compounds generally have large lattice energies.

_____ 10. Positions between layers in crystals are called interstitial positions.

_____ 11. When the impurity has more electrons than atoms in the pure lattice, an n-type semiconductor is formed.

_____ 12. Tetrahedral holes are surrounded by four atoms.

_____ 13. The body-centered lattice has lattice points at the corners and at the center of each unit cell.

_____ 14. Crystals are characterized by flat faces that intersect at certain characteristic angles.

_____ 15. The presence of As as an impurity in Ge leads to a p-type semiconductor.

Completion

16. Rubber and glass are examples of ____________________.

17. The Bragg relation allows calculation of ____________________ from the x-ray wavelength and diffraction angle.

18. The small portion of a crystal structure that can be used to generate the entire structure is called a ________________.

19. ____________________ is a measure of ratio of volume of spheres to the volume of a unit cell.

20. There are four types of solids. They are __________, __________, ___________, and ___________.

21. The two types of van der Waals forces are ____________ and ____________.

22. Ionic solids are ___________ (good, poor) conductors of electricity.

23. Molecular solids have ___________ (high, low) melting points.

24. Imperfections in crystals are called ______________.

25. The body-centered cubic crystal contains _________ (number) atoms per unit cell.

26. Impurities are added to pure silicon to form _________________.

27. The sequence ABABAB is found in _________________ type crystals while the sequence ABCABC is found in ________________ type crystals.

28. Two types of holes in ionic crystals are ______________ and _______________.

29. Defects caused by cations being moved from their normal lattice sites to interstitial positions are called ___________________.

30. Defects occurring when cation or anion sites are left vacant are called _______________.

31. Impurity defects consist of
(a) interstitial atoms
(b) foreign atoms present at lattice sites
(c) vacant lattice sites
(d) a pair of lattice vacancies of opposite charge

32. Semiconductors are substances
(a) with F centers in the crystal lattice
(b) which have point defects known as color centers
(c) whose electrical conductivity increases as temperature increases
(d) are examples of nonstoichiometric compounds

33. How many atoms surround each atom in a hexagonal close-packed structure?
(a) 4 (b) 6 (c) 8 (d) 12

34. X-rays of wavelength 1.54 nm are diffracted from a crystal at an angle of 35° 30'. If this is a first-order diffraction, what is the spacing of the planes of atoms responsible for the diffraction?
(a) 2.65 nm (b) 1.34 nm (c) 1.32 nm (d) 0.758 nm

35. An ionic compound crystallizes with the positive ions (M) in a close-packed cubic pattern and the negative ions (X) occupying all the tetrahedral holes of the positive ion lattice. What is the formula for the compound?
(a) M_2X (b) MX (c) MX_2 (d) MX_4

36. The density of tungsten (W) is 19.3 g cm^{-3}. It crystallizes in a body-centered cubic structure. What is the volume of a unit cell for tungsten?
(a) 0.0158 nm (b) 0.0316 nm^3 (c) 0.331 nm^3 (d) 11.8 nm^3

37. Referring to the unit cell for tungsten from Problem 36, what is the radius of the tungsten atom in nanometers?
(a) 0.112 (b) 0.137 (c) 0.274 (d) 0.316

38. Which of the following types of solids ordinarily have low melting points?
(a) ionic (b) molecular (c) covalent (d) metallic

39. Given that the enthalpy of formation of LiF is –612 kJ mol^{-1}, the enthalpy of sublimation of Li is 155 kJ mol^{-1}, the enthalpy of dissociation of F_2 is 79 kJ mol^{-1}, the enthalpy of ionization of Li is 520 kJ mol^{-1}, and the electron affinity of F is –333 kJ mol^{-1}, what is the lattice energy of LiF in kilojoules per mole?
(a) –994 (b) –1034 (c) –1660 (d) –1700

40. Experimental evidence for the orderly arrangement of atoms in crystals is given by:
(a) polymorphism (b) the unit cell
(c) x-ray diffraction patterns (d) electrical conductivity measurements

41. The lattice energy of an ionic solid is equal to
(a) its enthalpy of formation from the elements
(b) its enthalpy of vaporization
(c) its enthalpy of ionization
(d) its enthalpy of formation from gaseous ions
(e) the enthalpy of formation of its ions from the elements

42. In a face-centered cubic lattice an atom lying in a face of a unit cell is shared equally by how many unit cells?
(a) one (b) two (c) eight (d) four
(e) sixteen

43. In a cubic lattice the number of unit cells that can share a corner atom equally is
(a) 1/4 (b) 1 (c) 2 (d) 4
(e) 8

44. The number of atoms in contact with the one at the cube center in a body-centered cubic cell is
(a) 2 (b) 6 (c) 8 (d) 12

45. The number of nearest neighbors around each particle in a face-centered cubic lattice is:
(a) 4 (b) 6 (c) 8 (d) 12

Chapter 10

LIQUIDS AND CHANGES OF STATE

CHAPTER OVERVIEW

10-1 Liquids

Liquids contain particles that are close together but have neither the orderly arrangement characteristic of solids nor the randomness of gases. Liquids have physical properties quite different from gases or solids. Study the concepts of viscosity, diffusion, surface tension, and evaporation, as applied to liquids. Note how evaporation rate is related to temperature.

10-2 Equilibrium and vapor pressure

Note the difference between boiling point and normal boiling point. The appearance of gas bubbles as a liquid is heated does not always signify boiling since dissolved gases often appear as vapor bubbles as they come out of solution.

There is no model of an ideal liquid comparable to an ideal gas, so we cannot analyze the behavior of liquids in the same way we analyze gases. Nonideal behavior of liquids is observed as superheating during boiling and supercooling during freezing. The text discusses some problems in making experimental measurements of boiling and melting points that arise from these effects.

10-3 The variation of vapor pressure with temperature

The Clausius-Clapeyron equation relates vapor pressure of a liquid to temperature and the molar heat of vaporization. There are three kinds of calculations normally carried out with this equation and they are covered later in the New Skills section.

10-4 Solid-liquid equilibria

Note that freezing point and melting point are identical temperatures for pure substances. Highly supercooled liquids are called glasses.

10-5 Changes of state

Figure 10-7 in the text shows what happens when heat is added to a substance. You are familiar with an increase in temperature of a substance as it is heated. This is an increase in the kinetic energy or speed of movement of the molecules. An increase in the kinetic energy of molecules is just another way of saying the temperature increases. There are instances, however, when adding heat to a substance does not change its temperature or kinetic energy. This occurs at the melting point and the boiling point. It is important to note that changes of state (solid to liquid or liquid to vapor) occur at constant temperature. Even though heat is added to a substance during a change of state, the temperature does not change. When heat is removed during a change of state (condensation or freezing), the temperature does not change. Heat added during a change of state breaks the forces between molecules and increases their potential energy rather than their kinetic energy. The kinetic energy and temperature remain constant.

10-6 Equilibrium and Le Châtelier's principle

The text presents solid-liquid, solid-vapor, and liquid-vapor equilibrium data for water in Figure 10-14. These data are combined in Figure 10-15 to give a phase diagram. Phase diagrams can be used to determine what phases are present at a given pressure and temperature.

Many chemical reactions do not give a complete transformation of reactants into products. Instead, these reactions appear to stop before they reach completion. At the end of the reaction the ratio of products to reactants attains some constant value. We say the reaction has reached equilibrium. The importance of this simple concept in chemistry will become increasingly apparent in the next few chapters. The concept of equilibrium is one of the foundations of several topics coming up. Pay close attention to the text discussion of Le Châtelier's principle. We will encounter this effect several times as we study shifts in equilibrium.

10-7 Phase diagrams

Here are some important things to learn about phase diagrams. A line represents the pressure-temperature conditions where two phases are in equilibrium. The intersection of lines represents the only point (triple point) at which all three phases coexist in equilibrium. The area between the lines represents single-phase conditions. Phase diagrams can become quite complicated when several polymorphs exist in the solid state or when more than a single compound is present.

LEARNING OBJECTIVES

As a result of studying Chapter 10, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 159 of this *Study Guide.*

10-1 Liquids

1. Compare the structure of liquids to those of solids and gases. (Text Probs. 10-1, 10-19)
2. Explain why liquids have higher viscosity than gases.
3. Compare the rates of diffusion of liquids and gases.
4. Explain the cause and effects of surface tension. (Text Prob. 10-2) (Self Test 27, 30)
5. Describe the process of evaporation. (Text Prob. 10-4)

10-2 Equilibrium and vapor pressure

1. Define boiling point, normal boiling point, and vapor pressure. (Self Test 1, 20, 22, 36)
2. Relate the different types of intermolecular forces and types of molecules to vapor pressure of a liquid. (Text Probs. 10-3, 10-5, 10-6) (Self Test 4, 5, 25)
3. Explain the cause, results, and cure of superheating in liquids. (Text Probs. 10-7 to 10-9) (Self Test 16, 40)

10-3 The variation of vapor pressure with temperature

1. Show how temperature affects vapor pressure. (Text Probs. 10-12, 10-40) (Self Test 23)
2. Use the Clausius-Clapeyron equation to calculate vapor pressure as different temperatures, to determine the normal boiling point of a liquid, or to determine the molar heat of vaporization given sufficient vapor pressure and temperature information. (Text Examples 10-1 to 10-3; Text Probs. 10-13 to 10-15, 10-37 to 10-39) (New Skills Example 5; Self Test 7, 8, 37 to 39, 45)

10-4 Solid-liquid equilibria

1. Define freezing point and heat of fusion. (Self Test 2, 24)
2. Explain the cause and result of supercooling in liquids. (Text Probs. 10-16, 10-17) (Self Test 11, 40, 42)
3. Explain why the structure of glass is more like a liquid than a solid. (Text Probs. 10-10, 10-11) (Self Test 17)

10-5 Changes of state

1. Cite the changes of state that take place as a substance is heated and explain why the temperature is constant during a change of state. (Text Probs. 10-18, 10-20, 10-21) (Self Test 2, 9, 13, 31)
2. Give an example showing how potential energy varies while kinetic energy remains constant during changes of state. (Text Probs. 10-20, 10-22, 10-23) (Self Test 9, 15, 32)

10-6 Equilibrium and Le Châtelier's principle

1. Give an illustration that shows the concept of equilibrium in changes of state. (Text Probs. 10-26, 10-28, 10-29) (Self Test 3, 21)
2. Apply Le Châtelier's principle to shifts in equilibrium and use the principle to predict what will happen as the equilibrium of a system is shifted. (Text Probs. 10-26 to 10-30, 10-43) (Self Test 18)
3. Use the Clausius-Clapeyron equation to calculate molar heat of vaporization, molar heat of sublimation, and equilibrium vapor pressure of a phase change. (Text Probs. 10-24, 10-41)
4. Compare the behavior of a substance above and below its critical temperature. (Text Probs. 10-25, 10-42, 10-44) (Self Test 6, 41)

10-7 Phase diagrams

1. Use a phase diagram to predict what phases exist at equilibrium in a system at a given temperature and pressure. (Text Probs. 10-34, 10-36) (Self Test 19, 34, 43)
2. Make a sketch of a phase diagram showing how areas, lines, and points on the diagram relate to the number of phases present. (Text Prob 10-45) (Self Test 10, 26, 29, 33, 44)
3. Use a phase diagram to predict what changes of phase will be encountered as a substance is heated or cooled at constant pressure. (Text Probs. 10-33, 10-34) (Self Test 12, 35)
4. Use a phase diagram to predict what changes of phase will be encountered as the pressure on a substance is changed at constant temperature. (Text Probs. 10-31, 10-32, 10-47) (Self Test 14, 19, 28)
5. Draw a simple phase diagram using information obtained from cooling curves. (Text Probs. 10-34, 10-46, 10-48)

NEW SKILLS

10-3 The variation of vapor pressure with temperature

One of the most important relations in physical chemistry is the Clausius-Clapeyron equation. It relates equilibrium vapor pressure to temperature and the enthalpy of vaporization. You will find its most useful form to be

$$\ln \frac{P_1}{P_2} = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The Clausius-Clapeyron equation makes three kinds of calculations possible.

1. Calculation of ΔH_{vap} when the vapor pressure is given at two different temperatures

Example 10-1 in the text illustrates this calculation. ΔH_{vap} changes somewhat with temperature and 42.2 kJ mol^{-1} is an average value for temperatures between 20 and 60°C.

2. Use the Clausius-Clapeyron equation to find the vapor pressure at one temperature when ΔH_{vap} and the vapor pressure at a second temperature are known

This calculation is illustrated in text Example 10-2.

3. Use the Clausius-Clapeyron equation to find the temperature at which a liquid has a certain vapor pressure if ΔH_{vap} and the vapor pressure at some other temperature are known.

• EXAMPLE 1

Problem: Calculate the temperature at which the vapor pressure of water is 1.50 atm given that ΔH_{vap} is 40,700 J mol^{-1} at 100°C.

Solution: We will use the normal boiling point for our reference vapor pressure.

T_1 = 100°C + 273 = 373 K
T_2 = ?
P_1 = 1.00 atm
P_2 = 1.50 atm
R = 8.31 J mol^{-1} K^{-1}
ΔH_{vap} = 40,700 J mol^{-1}

Substituting these values into the Clausius-Clapeyron equation gives

$$\ln \frac{1.00 \text{ atm}}{1.50 \text{ atm}} = \frac{-40{,}700 \text{ J mol}^{-1}}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})}\left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)$$

$$\ln 0.667 = -4.90 \times 10^3 \left(2.681 \times 10^{-3} - \frac{1}{T_2}\right)$$

$$-0.405 = -4.90 \times 10^3 \left(2.681 \times 10^{-3} - \frac{1}{T_2}\right)$$

$$2.681 \times 10^{-3} - \frac{1}{T_2} = \frac{-0.405}{-4.90 \times 10^3} = 8.27 \times 10^{-5}$$

$$\frac{1}{T_2} = 2.681 \times 10^{-3} - 8.27 \times 10^{-5} = 2.598 \times 10^{-3}$$

$$T_2 = 385\text{ K} \quad \text{or} \quad 385\text{ K} - 273 = 112^\circ\text{C}$$

Notice how the logarithmic relation between vapor pressure and temperature gives a very large increase in vapor pressure for a small temperature increase. •

Parallel Problem: Calculate the temperature at which the vapor pressure of mercury is 1.0×10^{-3} atm. The ΔH of vaporization for mercury is 52.3 kJ mol^{-1} at 357°C.
Ans: 99°C

The normal boiling point of a liquid can be calculated in the same manner. It is simply the temperature at which the vapor pressure is 1.00 atm. Text Example 10-3 shows this calculation.

KEY TERMS

10-1 Liquids

Evaporation: The change from a liquid phase to a vapor phase. Same as vaporization.

Liquid: The state of matter intermediate between gases and solids characterized by free movements of the molecules among themselves but without the tendency to separate.

Surface tension: A measure of the energy necessary to increase the surface area of a liquid.

Vaporization: Same as evaporation.

Viscosity: The resistance to flow shown by a liquid.

10-2 Equilibrium and vapor pressure

Boiling point: The temperature at which the vapor pressure of a liquid is equal to the external pressure.

Condensation: The change of a vapor into the more dense liquid state.

Equilibrium: A state in which opposing processes or reactions take place at the same rate so that no net change is observed.

Heat of condensation: The energy released when one mole of gas condenses to liquid.

Heat of vaporization: The energy necessary to vaporize one mole of liquid.

Normal boiling point: The temperature at which the vapor pressure of a liquid equals one atmosphere.

Superheating: The heating of a liquid above its boiling point without boiling taking place.

Vapor pressure: The pressure of a gas when it is in equilibrium with its liquid in a closed container.

10-3 The variation of vapor pressure with temperature

Clausius-Clapeyron equation: The algebraic equation relating the vapor pressure of a liquid to its heat of vaporization and temperature.

10-4 Solid-liquid equilbria

Amorphous solid: A substance which appears to be solid but has an internal molecular structure resembling a liquid. A highly supercooled liquid, a glass.

Freezing point: The temperature at which the solid and liquid states are in equilibrium. Same as melting point.

Glass: An amorphous solid.

Heat of crystallization: The quantity of heat released when one mole of substance changes from the liquid to the solid state. Same as heat of solidification and heat of freezing.

Heat of fusion: The quantity of heat necessary to melt (fuse) one mole of a solid. Same as heat of melting.

Melting point: Same as freezing point.

Supercooling: The cooling of a liquid below its freezing point without freezing taking place.

10-5 Changes of state

Cooling curve: A graph of the change of temperature of a substance as heat is removed from it at a constant rate.

Heating curve: A graph of the change of temperature of a substance as heat is added to it at a constant rate.

10-6 Equilibrium and Le Châtelier's principle

Critical point: The temperature and pressure above which the distinction between gas and liquid vanishes.

Critical pressure: The pressure needed to liquify a gas at its critical temperature.

Critical temperature: The highest temperature at which a gas can be liquefied.

Le Châtelier's principle: When a system at equilibrium is subjected to a disturbance or stress, it tends to adjust or shift to reestablish equilibrium and reduce the effect of the disturbance.

Triple point: The temperature and pressure at which solid, liquid, and gaseous phases of a substance exist together at equilibrium.

10-7 Phase diagrams

Phase diagram: A representation of the phases of a substance which exist at equilibrium at different temperatures and pressures.

Polymorphs: Different crystal structures of the same substance.

SELF TEST

True or False

_____ 1. As pressure is decreased, boiling points increase.

_____ 2. The melting point of a pure substance is a little higher than the freezing point.

_____ 3. Dynamic equilibrium is a condition in which two opposing processes occur at exactly the same rate.

_____ 4. The vapor pressure of any liquid increases as atmospheric pressure is increased.

_____ 5. The vapor pressure of any liquid increases as its temperature is increased.

_____ 6. The vapor pressure of butane, C_4H_{10}, at its normal boiling point is the same as that of water at its normal boiling point.

_____ 7. The variables in the Clausius-Clapeyron equation are vapor pressure, enthalpy of vaporization, and temperature.

_____ 8. A plot of ln vapor pressure versus reciprocal temperature gives a straight line with the same slope for all liquids.

_____ 9. Heat of fusion is a measure of the increase in potential energy of the molecules during melting.

_____ 10. Only the solid phase exists at temperatures below the triple point.

_____ 11. Supercooled water could be crystallized by adding a snowflake.

_____ 12. Solid CO_2 melts to liquid CO_2 at 1 atmosphere pressure when heat is added

_____ 13. The temperature remains constant when heat is added to a liquid in equilibrium with its vapor.

_____ 14. When heat is added to a mixture of solid and liquid at equilibrium, the mixture always expands if the pressure is held constant.

_____ 15. The average potential energy of the molecules increases during the melting process.

Completion

16. Superheating and bumping may be controlled by adding ____________________ to the liquid.

17. Glass is an example of a liquid well below its ____________________.

18. Increasing the pressure on a gas-liquid equilibrium mixture causes the system to shift toward the ____________________ phase.

19. Water is different from most substances in that its melting point ________________(increases, decreases) as pressure increases.

20. The temperature at which a liquid boils at one atmosphere pressure is called the ____________________.

21. In a dynamic equilibrium the rate of evaporation is equal to the rate of ______________.

22. The pressure exerted by a gas in equilibrium with its liquid is called the __________________________.

23. The effect of pressure on the freezing point is ________________ (greater, less) than its effect on boiling point.

24. Freezing of a liquid is accompanied by the __________________ (evolution, absorption) of heat.

25. The greater the attractive forces between molecules in liquids, the __________________ (greater, lower) is the vapor pressure.

26. The lines on a phase diagram represent the conditions for equilibrium between _________ (how many) phases.

27. A property of liquids called ____________________ is responsible for the curved surface of the liquid in small tubes.

28. The vapor pressure of a liquid at its critical temperature is called the _________.

29. The ____________________ is the temperature at which solid and liquid are in equilibrium.

30. The surface tension of a liquid ___________________ (increases, decreases) as temperature is increased.

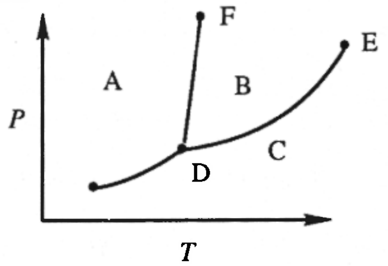
Multiple Choice

31. The change of a substance from the gaseous state to the liquid state is known as
(a) fusion (b) evaporation (c) condensation (d) supercooling

32. The heat of vaporization is a measure of
(a) the increase in kinetic energy when a substance changes from the liquid to the gaseous state
(b) the increase in potential energy when a substance changes from the liquid to the gaseous state
(c) the average potential energy during the vaporization process
(d) the heat of fusion plus the heat of sublimation

33. The triple point is
(a) the temperature at which the vapor pressure of the solid and liquid states are equal
(b) the temperature and pressure at which solid, liquid, and gas are at equilibrium
(c) the temperature at which the gas-liquid equilibrium curve starts
(d) all of the above

34. The sketch shows a simple phase diagram for a pure substance. Which of the following is correct?



(a) A represents solid, B represents liquid, C represents gas, D is the triple point, and E is the critical point.
(b) A represents solid, B represents gas, C represents liquid, D is the triple point, and E is the critical point.
(c) A represents liquid, B represents gas, C represents solid, D is the triple point, and F is the critical point.
(d) A represents gas, B represents liquid, C represents solid, D is the triple point, and F is the critical point.

35. In the phase diagram sketched in Problem 34, if the temperature and pressure are changed from region A to region B, what would be observed?
(a) freezing (b) melting (c) condensation (d) evaporation

36. The boiling point of a liquid can be lowered by
(a) increasing the temperature of a liquid
(b) decreasing the external pressure on the liquid
(c) decreasing the amount of liquid present
(d) establishing an equilibrium vapor pressure

37. Data for the equilibrium vapor pressure of any liquid as a function of temperature can be represented on a straight line by plotting
(a) P against T (b) $\ln P$ against T
(c) P against $1/T$ (d) $\ln P$ against $1/T$

38. The molar heat of vaporization of methane is 8.2 kJ mol^{-1} and its normal boiling point is -162°C. What is the pressure in a closed container of liquid methane at room temperature (25°C)?
(a) 1.01 atm (b) 1.73 atm (c) 2.59 atm (d) 263 atm

39. The molar heat of vaporization of propane is 11.2 kJ mol^{-1}. At room temperature (25°C) it has a vapor pressure of 3.70 atm. What is the normal boiling point of propane?
(a) 0°C (b) –42°C (c) –83°C (d) 231°C

40. Superheating and supercooling are similar departures from ideal behavior in that
(a) both cause bumping of solutions
(b) both lead to the amorphous state
(c) both can be prevented by providing sites for the formation of a new phase
(d) neither can be reproduced

41. The critical temperature is the temperature
(a) below which a gas cannot be liquified
(b) above which a gas cannot be liquified unless sufficient pressure is applied
(c) above which the gas will explode
(d) above which the gas cannot be liquified regardless of pressure
(e) below which the gas cannot be liquified unless sufficient pressure is applied

42. Supercooled water at –10°C can spontaneously warm to 0°C. This is possible because
(a) a small amount of energy is taken from the surroundings
(b) ice is unusual in that it is less dense than liquid water
(c) some of the water freezes and this provides energy
(d) supercooled water needs less energy for change of temperature than ordinary water
(e) supercooled materials do not obey energy conservation laws

43. If a substance becomes less dense on melting, what effect will increased pressure have on its melting point?
(a) It will lower the melting point.
(b) It will raise the melting point.
(c) It will have no effect.
(d) The effect can't be predicted but must be experimentally determined.
(e) No known substance exhibits this behavior.

44. The triple point is
(a) the temperature above which the liquid phase cannot exist
(b) usually found at a temperature very close to the normal boiling point
(c) the temperature at which the vapor pressure of a liquid is three times the value at 25°C
(d) the value of temperature and pressure at which solid, liquid and gas may exist in equilibrium

45. The molar heat of vaporization of propane is 11.2 kJ mol^{-1} and its normal boiling point is –42.1°C. What is the pressure in a closed container of propane at room temperature (25°C)?
(a) 0.27 atm (b) 1.00 atm (c) 3.71 atm (d) 92.0 atm

Chapter 11

SOLUTIONS

CHAPTER OVERVIEW

Chapter 11 is a fairly long chapter and it is full of new and important concepts fundamental to understanding the behavior of solutions. It will require intensive study.

11-1 General properties of solutions

There are many different kinds of mixtures and the classification into heterogeneous or homogeneous is not sharp. Nevertheless, if we cannot distinguish different phases in a mixture on a molecular scale we say we have a homogeneous mixture or a solution.

11-2 Types of solutions

Of the several types of solutions mentioned in the text, most of your attention and study will be centered on solids, gases, and liquids dissolved in water. In fact, the remainder of the chapter deals almost exclusively with aqueous (water) solutions of a solute.

11-3 Concentration units

You will quickly discover there are many different ways of expressing the concentration of the solute. The amount of solute dissolved in the solvent may be expressed qualitatively as dilute, concentrated, weak, or strong; or semiquantitatively as unsaturated, saturated, or supersaturated. These terms only give a relative idea of concentration. Of more importance to you will be an understanding of the quantitative expressions of concentration: mole fraction, mole percent, molarity, molality, and percent by mass. Most of the calculations in this chapter deal with these quantitative terms. Molarity is the most common concentration unit used to describe solutions but, as you will see, each of the other quantitative expressions is also used in calculations. We will work several examples showing the use of each. Study these examples and Examples 11-1 through 11-6 in the text and you should become proficient at handling concentration in any units.

11-4 Solubility

The solvation process is explained and understood best in terms of interactions between solute and solvent molecules. If the solute-solvent attraction is strong enough to overcome solvent-solvent and solute-solute attractions, the substance will be soluble. In certain substances hydrogen bonding takes place and greatly increases the solute-solvent attraction to make these substances more soluble. The adage "like dissolves like" is worth remembering to help predict solubilities. In general, the solubility of solids in water increases as temperature increases, while the solubility of gases decreases, but there are several exceptions. Figure 11-7 in the text shows some solubilities.

Le Châtelier's principle helps predict the effect of temperature on solubility if the sign of ΔH_{soln} is known. Many solids have positive ΔH_{soln} (that is, are endothermic), so their solubility tends to increase as the temperature increases. Figure 11-7 in the text shows how the solubility of some solutes increases with increasing temperature while that of others decreases. The sign of ΔH_{soln} depends on the relative values of ΔH_{lat} and ΔH_{hyd}. A high lattice energy tends to make the solute less soluble while a high hydration energy makes it more soluble.

Most gases have negative ΔH_{soln} so the rule that the solubility of gases decreases as temperature increases generally holds. Pressure has little effect on the solubility of solids but a pronounced effect on the solubility of gases. Use Henry's law to determine the solubility of a gas at a given pressure.

11-5 Colligative properties

Pure liquids have characteristic values of vapor pressure, osmotic pressure, boiling point, and freezing point. When a solute is added, these properties are affected.

Vapor-pressure lowering by a solute is given by Raoult's law. If a solution follows Raoult's law it is said to be an ideal solution; thus, departure from Raoult's law is a measure of nonideal behavior in solutions. Figure 11-12 in the text illustrates this behavior. The direction of deviation from Raoult's law depends on the relative attractions between solute and solvent molecules.

Boiling-point elevation and freezing-point depression are related colligative properties. Remember that if compounds dissociate you get two or more moles of ions from one mole of solute. One mole of ions dissolved in one kilogram of solvent lowers the freezing point by K_f degrees or raises the boiling point by K_b degrees. Values for K_f and K_b are given in Table 11-4 in the text.

Note the similarity between the van't Hoff equation for osmotic pressure and the ideal-gas law. The similarity is coincidental, but it makes the van't Hoff equation easy to remember. Study Figures 11-16 to 11-18. They explain osmosis, osmotic pressure, and reverse osmosis.

An important use of colligative properties is to determine the molecular mass of nonelectrolyte solutes.

11-6 Electrolytes

Electrolytes are solutes that dissociate to give ions when they dissolve. The ions are electrical conductors. Compounds whose solutions do not conduct electricity are called nonelectrolytes. Strong electrolytes are completely dissociated into ions while weak electrolytes are only partially dissociated. Nearly all salts are strong electrolytes. Le Châtelier's principle predicts that dissociation of weak electrolytes will be greater at low concentrations than at high concentrations.

The hydrated proton H_3O^+ is called a hydronium or oxonium ion. Hydronium ions and hydroxide ions are important to aqueous solutions and we will use them extensively in the next few chapters. The Arrhenius definition of acids and bases applies to aqueous solutions and is based on the H^+ and OH^- ions. We will learn other definitions of acids and bases in Chapter 12, so be sure you have a firm understanding of the Arrhenius definition now.

All ions in aqueous solution are hydrated and this often affects their properties. Smaller ions with high charge densities are hydrated to the greatest extent, so the Na^+ hydrated ion is actually larger than the K^+ hydrated ion, exactly the opposite of the size ratio of the corresponding unhydrated ions.

KEY EQUATIONS

11-3 Concentration units

1. Mole fraction $$X_A = \frac{n_A}{n_A + n_B + n_C + \ldots} = \frac{\text{mol A}}{\text{total mol}}$$

2. Mole percent $$\text{mol \% A} = X_A(100) = \frac{\text{mol A}}{\text{total mol}} \times 100$$

3. Molarity $$M_A = \frac{\text{mol solute}}{\text{liters solution}} = \frac{\text{mol}}{\text{liter}} = \frac{n_A}{V}$$

Note that the number of moles of solute is fixed by the molarity and volume of solution.

$$n_A = M_A V$$

4. Molality $$m_A = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{\text{mol}}{\text{kg}} = \frac{n_A}{\text{kg solvent}}$$

5. Percent by mass $$\text{mass \% A} = \frac{\text{mass A}}{\text{total mass}} \times 100$$

6. Solubility of a gas (Henry's law) $$X = KP$$

where X = mole fraction of the dissolved gas
P = partial pressure of the gas above the liquid
K = Henry's law constant (see Table 11-2 in the text)

11-5 Colligative properties

1. Vapor pressure of a solution (Raoult's law) $$P_1 = X_1 P_1^{o}$$

where P_1 = vapor pressure of the solution
P_1^{o} = vapor pressure of pure solvent
X_1 = mole fraction of the solvent

2. Boiling-point elevation $$\Delta T_b = K_b m$$

where ΔT_b = boiling-point elevation
K_b = boiling-point elevation constant (see Table 11-4 in the text)
m = molality of the solute

3. Freezing-point depression $$\Delta T_f = -K_f m$$

where ΔT_f = freezing-point depression
K_f = freezing-point depression constant (see Table 11-4 in the text)
m = molality of the solute

4. Osmotic pressure $\pi V = n_2RT$

where π = osmotic pressure
n_2 = moles of solute
V = volume of solution containing n_2 mol of solute
R = ideal-gas constant
T = temperature in kelvins

LEARNING OBJECTIVES

As a result of studying Chapter 11, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 182 of this *Study Guide*.

11-1 General properties of solutions

1. Tell whether a mixture is heterogeneous or homogeneous. (Self Test 16)

11-2 Types of solutions

1. Describe how different phases combine to make solutions. (Text Prob. 11-2)
2. Relate the properties of a solution to its pure components. (Text Probs. 11-1, 11-18) (Self Test 1)

11-3 Concentration units

1. Write definitions for the terms used to describe concentration. (Text Prob. 11-3) (Self Test 2, 6, 21, 23)
2. Use the quantitative terms for concentration in calculations, that is, calculate the following:
    a) Mole fraction and mole percent, given the mass of solute and solvent. (Text Examples 11-1, 11-2; Text Probs. 11-11 to 11-13) (New Skills Examples 1, 2; Self Test 2, 5, 31, 32)
    b) Molarity, given the mass of solute and volume of solution. (Text Example 11-3; Text Probs. 11-9, 11-40, 11-48) (New Skills Example 3; Self Test 6)
    c) Molarity, given the mass of solute and solvent and density of the solution. (Text Example 11-4; Text Probs. 11-12, 11-13, 11-15, 11-59, 11-61) (New Skills Example 5; Self Test 34)
    d) Molality, given the mass of solute and solvent. (Text Example 11-5; Text Probs. 11-10, 11-14) (New Skills Example 6; Self Test 2, 6, 23)
    e) Molality, given the mass of solute and volume and density of solution. (Text Probs. 11-12, 11-13) (New Skills Example 7; Self Test 35)
    f) Percent by mass, given the mass of solute and solvent. (Text Example 11-6; Text Probs. 11-12, 11-13) (New Skills Example 8; Self Test 25)
3. Calculate the number of moles in a given volume of solution if the molarity is known. (Text Prob. 11-29) (New Skills Example 4)
4. Determine the concentration of ions given the concentration of solute. (Text Probs. 11-16, 11-17) (New Skills Examples 11, 12; Self Test 29)
5. Calculate the molarity of a solution made by diluting a stock solution of known molarity with a given quantity of water. (Text Probs. 11-19, 11-20, 11-45, 11-60) (New Skills Examples 9, 10; Self Test 11, 36)

6. Calculate the solubility (mole fraction) of a gas using Henry's law. (Text Probs. 11-22, 11-23, 11-47, 11-50) (New Skills Example 13; Self Test 4, 9, 18, 37)

11-4 Solubility

1. Explain why solute-solvent molecular attractions govern the solubility and dissociation of substances. (Text Probs. 11-46, 11-53) (Self Test 13, 22)
2. Use an example to explain the concept "like dissolves like." (Text Probs. 11-4, 11-24, 11-55) (Self Test 13, 17)
3. Explain why hydrogen bonding affects the solubility of some compounds and predict what types of compounds are likely to form hydrogen bonds. (Text Prob. 11-6) (Self Test 3)
4. Combine lattice energies and hydration energies to determine heats of solution. (Text Probs. 11-7, 11-26) (Self Test 7)
5. Predict the effect of temperature on the solubility of a solute if the algebraic sign of ΔH_{soln} is known. (Text Probs. 11-8, 11-21, 11-28) (Self Test 8, 18, 45)
6. Show the relationship of the size and charge density of an ion to its hydration energy and solubility. (Text Prob. 11-25)

11-5 Colligative properties

1. Explain why colligative properties are affected by the number but not the nature of particles in solution. (Self Test 24, 30)
2. Calculate the vapor pressure of a solution using Raoult's law. (Text Example 11-7; Text Prob. 11-31) (New Skills Example 14; Self Test 38)
3. Show why deviation from Raoult's law is a measure of nonideal behavior in real solutions. (Text Figure 11-12; Text Probs. 11-5, 11-51) (Self Test 10)
4. Calculate the partial pressure and mole fraction of each component of an ideal solution. (Text Probs. 11-37, 11-49, 11-58) (New Skills Example 15; Self Test 14)
5. Calculate the boiling-point elevation and the freezing-point depression of solutions. (Text Example 11-9; Text Probs. 11-30, 11-35, 11-54) (New Skills Example 16; Self Test 12, 19, 26, 39, 40)
6. Explain the processes of osmosis and reverse osmosis. (Text Figures 11-16 to 11-18; Text Prob. 11-52) (Self Test 15)
7. Calculate the osmotic pressure of a solution. (Text Prob. 11-31) (New Skills Example 17; Self Test 15, 41)
8. Calculate the molecular mass of a nonelectrolyte solute from its effect on a colligative property. (Text Examples 11-8, 11-10 to 11-12; Text Probs. 11-32 to 11-34, 11-36, 11-43, 11-56) (Self Test 42, 43)

11-6 Electrolytes

1. Explain the difference between strong electrolytes, weak electrolytes, and nonelectrolytes. (Text Prob. 11-39; Text Table 11-5) (Self Test 27)
2. Use Le Châtelier's principle to predict the amount of dissociation of weak electrolytes as a function of concentration. (Text Prob. 11-38)
3. Write an equation for a chemical reaction showing the formation of hydronium ions. (Self Test 28)
4. Make calculations relating the extent of dissociation of a weak electrolyte to the change of a colligative property. (Text Example 11-13; Text Probs. 11-41, 11-42) (New Skills Examples 18, 19; Self Test 44)
5. Write the Arrhenius definitions of acid, base, and salt, and write a chemical equation to show how a salt is formed in a neutralization reaction. (Text Prob. 11-57) (Self Test 20)
6. Cite some differences between the properties of hydrated and nonhydrated ions. (Text Prob 11-44)

7. Make a sketch showing the mechanism of hydration. (Text Probs. 11-6, 11-44)
8. Give examples showing how nonideal behavior of solutes can be determined from colligative property measurements.

NEW SKILLS

There are many important computational skills to be mastered in conjunction with Chapter 11. They will be used extensively in the following chapters, so now is the time to learn them.

11-3 Concentration units

It may seem that the quantitative expressions for concentration are just a lot of different ways of saying the same thing, and in a sense that is true. However, each expression has its own application and so all must be understood.

1. Mole fraction: (X_A) and mole percent

Mole fraction is used in Henry's law and Raoult's law. It is simply the moles of a component divided by the total moles in the mixture.

• EXAMPLE 1

Problem: Determine the mole fraction of each gas if 2 mol of SO_2, 4 mol of N_2, and 6 mol of H_2 are mixed together.

Solution:

$$x_{SO_2} = \frac{\text{mol } SO_2}{\text{total mol}} = \frac{\text{mol } SO_2}{\text{mol } SO_2 + \text{mol } N_2 + \text{mol } H_2}$$

$$= \frac{2 \text{ mol}}{2 \text{ mol} + 4 \text{ mol} + 6 \text{ mol}} = 0.17$$

Notice that mole units cancel so mole fraction is a unitless number.

$$x_{N_2} = \frac{\text{mol } N_2}{\text{total mol}} = \frac{4 \text{ mol}}{12 \text{ mol}} = 0.33$$

The total of mole fractions of all components must equal unity.

$$x_{SO_2} + x_{N_2} + x_{H_2} = 1$$

so we can find x_{H_2} by

$$x_{H_2} = 1 - (x_{SO_2} + x_{N_2})$$

$$= 1 - (0.17 + 0.33) = 0.50 \bullet$$

Parallel Problem: A solution contains 50 grams of water and 50 grams of ethanol (mol. mass = 46.0 g mol^{-1}). Determine the mole fraction of each component.

Ans: $X_{H_2O} = 0.72$ $X_{\text{ethanol}} = 0.18$

• EXAMPLE 2

Problem: What is the mole percent of each compound in Example 1?

Solution:

$$\begin{aligned}\text{Mol \%} &= \text{mole fraction}(100)\\ \text{Mol \% } SO_2 &= X_{SO_2}(100) = 0.17(100) = 17\%\\ \text{Mol \% } N_2 &= X_{N_2}(100) = 0.33(100) = 33\%\end{aligned}$$

The sum of the mole percents of all components must equal 100%.

$$\begin{aligned}\text{Mol \% } SO_2 + \text{mol \% } N_2 + \text{mol \% } H_2 &= 100\\ \text{Mol \% } H_2 = 100 - (\text{mol \% } SO_2 + \text{mol \% } N_2)&\\ = 100 - (17 + 33) = 50\% &\end{aligned}$$ •

Parallel Problem: What is the mole percent of each component in the previous Parallel Problem?
Ans: Mol % H_2O = 72%, Mol % ethanol = 18%

Now work Examples 11-1 and 11-2 in the text.

2. *Molarity*

Molarity is the most common concentration unit used for stoichiometric calculations. We will make extensive use of molarity in calculations throughout the rest of the course. Molarity is simply the moles of solute per liter of solution

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

• EXAMPLE 3

Problem: What is the molarity of the solution when 2.5 mol of substance are dissolved in enough water to make 6.0 liters of solution?

Solution:

$$M = \frac{\text{mol}}{\text{liter}} = \frac{2.5 \text{ mol}}{6.0 \text{ liters}} = 0.42\ M$$

The solution is 0.42 *M*. •

Parallel Problem: What is the molarity of the solution when 0.745 grams of KCl is dissolved in enough water to make 100 mL of solution?
Ans: 0.100 *M*

• EXAMPLE 4

Problem: How many moles of solute are needed to make 5.00 liters of 0.15 *M* solution?

Solution: Note that the problem does not specify the amount or type of solvent in the solution. It is slightly less than 5.00 liters because the solute occupies some volume. We do not need to know the specific amount of solvent to solve the problem. Solve the equation defining molarity for number of moles.

$$\text{Moles} = \text{molarity (volume)} = MV$$

$$\text{moles solute} = (0.15 \text{ mol liter}^{-1})(5.00 \text{ liters}) = 0.75 \text{ mol}$$

Notice that the number of moles in solution is not dependent on the formulas of the compounds. No matter what substances were used for solute and solvent, 0.75 mol of solute would be needed. •

Parallel Problem: How many grams of HCl are needed to make 500 mL of 3.00 M solution?
Ans: 54.6 g

Now work Example 11-3 in the text.

Molarity can also be calculated from the mass of the solute and solvent if the density of the solution is known.

• EXAMPLE 5

Problem: Dilute hydrochloric acid used in the laboratory can be prepared by dissolving 25.0 g HCl in 100 g H_2O. The resulting solution has a density of 1.10 g cm^{-3}. What is the molarity of the HCl?

Solution: The number of moles of HCl is

$$\text{Mol HCl} = 25.0 \text{ g HCl} \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 0.685 \text{ mol}$$

$$\text{Total mass of solution} = \text{g HCl} + \text{g } H_2O = 25.0 + 100 = 125 \text{ g}$$

$$\text{Volume of solution} = \frac{\text{g}}{\text{density}} = \frac{125 \text{ g}}{1.10 \text{ g cm}^{-3}} = 114 \text{ cm}^3 \quad \text{or} \quad 0.114 \text{ liter}$$

$$M = \frac{\text{mol}}{\text{volume}} = \frac{0.685 \text{ mol}}{0.114 \text{ liter}} = 6.01\,M \quad \bullet$$

Parallel Problem: What is the molarity of a solution containing 25 g of H_2SO_4 and 75 g H_2O? The density of the solution is 1.20 g mL^{-3}.
Ans: 3.1 *M*

Now work Example 11-4 in the text.

3. Molality

Molality (*m*) is used as a measure of concentration in boiling-point elevation and freezing-point depression equations and is defined as the moles of solute per kilogram of solvent.

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{\text{mol}}{\text{kg}}$$

• EXAMPLE 6

Problem: What is the molality of the solution when 1.2 mol of solute are dissolved in 600 g of solvent to make a solution.

Solution: In the case of molality, it is necessary to know the mass of solvent. (Remember: The volume of solution was used to determine molarity.)

$$m = \frac{1.2 \text{ mol solute}}{0.600 \text{ kg solvent}} = 2.00\ m$$

The solution is 2.00 *m*. As with molarity, the molality is independent of the kind of molecules used as solute or solvent. •

Parallel Problem: What is the molality of a solution made by dissolving 2.00×10^{-3} moles of solute in 1.50 mL of solvent?
Ans: 1.33 *m*

• EXAMPLE 7

Problem: An aqueous solution of NaCl contains 20 g of NaCl in 600 mL. What is the molality of the solution if its density is 1.04 g cm^{-3}?

Solution: We need to find the mass of water in the solution.

$$\begin{aligned}\text{Total mass of solution} &= \text{mass of solute} + \text{mass of solvent}\\ \text{Total mass of solution} &= (\text{volume})(\text{density})\\ &= (600 \text{ mL})(1.04 \text{ g cm}^{-3}) = 624 \text{ g}\end{aligned}$$

The mass of NaCl is 20 g.

$$\text{Mass of water} = \text{mass of solution} - \text{mass of NaCl}$$

$$= 624 - 20 = 604 \text{ g}$$

$$m = \frac{\text{mol NaCl}}{\text{kg } H_2O} = \frac{0.342 \text{ mol}}{0.604 \text{ kg}} = 0.566\ m \bullet$$

Parallel Problem: What is the molality of 300 mL of solution containing 40.0 g of K_2SO_4?
Ans: 0.738 *m*

Now work Example 11-5 in the text.

4. Percent by mass

Percent by mass or mass percent is commonly used in laboratories because it is easy to relate to the way a solution is prepared.

$$\text{mass \%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

• EXAMPLE 8

Problem: If 30 g of solution is evaporated by dryness and leaves 6.5 g of salt, what was the percent by mass of salt in the solution?

Solution:

$$\text{Mass \% salt} = \frac{\text{g salt}}{\text{g solution}} \times 100$$

$$= \frac{6.5\text{ g}}{30\text{g}} \times 100 = 22\% \quad \bullet$$

Parallel Problem: What mass of water and what mass of NaCl would you use to prepare 80.0 g of a 5.0% by mass salt solution?
Ans: 76 g of water and 4.0 g of NaCl

Work Example 11-6 in the text.

5. Change of molarity when diluting a solution

Solutions used in chemical laboratories are normally prepared from a fairly concentrated stock solution by adding solvent to obtain the desired concentration. It is easy to calculate the molarity of a dilute solution prepared from a concentrated solution.

• EXAMPLE 9

Problem: What is the molarity of a solution prepared by adding 1.00 liter of solvent to 100 mL of an 8.0 *M* concentrated solution?

Solution: We can develop a general formula for dilution problems as follows: The number of moles of solute does not change when the solvent is added.

$$(n_A)_{\text{conc}} = (n_A)_{\text{dil}}$$

If we solve the equation defining molarity for the moles of solute we have

$$n_A = MV$$

Substituting this into the equation for n_A gives

$$(MV)_{\text{conc}} = (MV)_{\text{dil}}$$

or

$$M_{\text{dil}} = M_{\text{conc}} \frac{V_{\text{conc}}}{V_{\text{dil}}}$$

Thus, the change in concentration on dilution is proportional to the ratio of the volumes of the concentrated and diluted solutions.

In the case of our solution

$$M_{\text{dil}} = 8.0\,M \frac{0.100\text{ L}}{1.00 + 0.100\text{ L}} = 0.73\,M \quad \bullet$$

Parallel Problem: What is the molarity of a solution prepared by adding 100 mL of concentrated sulfuric acid ($M = 18.0$) to 3.50 L of water?
Ans: 0.500 *M*

• EXAMPLE 10

Problem: How many milliliters of 15.0 *M* (concentrated) nitric acid, HNO_3, would you dilute to prepare 500 mL of 6.0 *M* (dilute) nitric acid?

Solution: The dilution equation of Example 9 can be solved for V_{conc}.

$$V_{conc} = V_{dil} \frac{M_{dil}}{M_{conc}}$$

$$= 500 \text{ mL} \frac{6.0\ M}{15.0\ M} = 200 \text{ mL}$$

The dilute solution is prepared by carefully adding 200 mL of concentrated nitric acid to 300 mL of water. •

Parallel Problem: What volume of water must be added to 50.0 mL of 0.30 *M* H_2SO_4 to convert it to 0.030 *M*?
Ans: 450 mL

6. *Relating molarity of ions to molarity of solute*

Before we leave concentration units we should investigate the relationship between the molarity of ions and the molarity of the parent salt.

• EXAMPLE 11

Problem: What is the molarity of NO_3^- ions in a 2.0-*M* solution of aluminum nitrate, $Al(NO_3)_3$?

Solution: The dissociation of $Al(NO_3)_3$ gives

$$Al(NO_3)_3 \rightarrow Al^{3+} + 3\ NO_3^-$$

Three moles of NO_3^- ions are produced from each mole of $Al(NO_3)_3$.

$$M_{NO_3^-} = \frac{2.0 \text{ mol } Al(NO_3)_3}{1 \text{ liter}} \times \frac{3 \text{ mol } NO_3^-}{1 \text{ mol } Al(NO_3)_3} = \frac{6 \text{ mol } NO_3^-}{1 \text{ liter}} = 6\ M$$ •

Parallel Problem: What is the molarity of Cl^- ions in a solution 1.0 *M* in $MgCl_2$ and 0.50 *M* in $AlCl_3$?
Ans: 3.5 *M*

• EXAMPLE 12

Problem: What is the molarity of Cl^- ions in a solution containing 0.5 mol NaCl, 1.5 mol $FeCl_3$, and 0.3 mol $CaCl_2$ in 1500 mL of solution?

Solution: We need to find the total number of moles of Cl^- ions.

$$\text{Mol } Cl^- \text{ from NaCl} = 0.5 \text{ mol NaCl} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol NaCl}} = 0.5 \text{ mol } Cl^-$$

$$\text{Mol } Cl^- \text{ from } FeCl_3 = 1.5 \text{ mol } FeCl_3 \times \frac{3 \text{ mol } Cl^-}{1 \text{ mol } FeCl_3} = 4.5 \text{ mol } Cl^-$$

$$\text{Mol } Cl^- \text{ from } CaCl_2 = 0.3 \text{ mol } CaCl_2 \times \frac{2 \text{ mol } Cl^-}{1 \text{ mol } CaCl_2} = 0.6 \text{ mol } Cl^-$$

$$\text{Total mol } Cl^- = 0.5 + 4.5 + 0.6 = 5.6 \text{ mol}$$

$$M_{Cl^-} = \frac{\text{mol } Cl^-}{\text{liters solution}} = \frac{5.6 \text{ mol}}{1.5 \text{ liters}} = 3.7\,M$$ •

Parallel Problem: What is the molarity of NO_3^- ions in a solution containing 0.30 moles of $Al(NO_3)_3$ and 0.45 moles of $Ca(NO_3)_2$ in 600 mL of solution?
Ans: 3.0 *M*

7. *Solubility of gases using Henry's law*

Henry's law states that the mole fraction of a dissolved gas is proportional to the partial pressure of the gas above the solution.

$$X = KP$$

where X = mole fraction of gas in solution
K = Henry's law constant (Table 11-2 in the text)
P = partial pressure of the gas above the solution

• EXAMPLE 13

Problem: Compare the composition of "air" dissolved in water at 20°C to that of the air above the water.

Solution: Air consists essentially of 21 percent oxygen and 79 percent nitrogen, so the partial pressures in air at 1 atm are

$$P_{O_2} = 0.21 \text{ atm} \qquad P_{N_2} = 0.79 \text{ atm}$$

and the mole fractions are

$$X_{O_2(\text{air})} = 0.21 \qquad X_{N_2(\text{air})} = 0.79$$

The ratio of O_2 to N_2 in air is 0.21:0.79 = 0.27. The mole fractions in solution are found from Henry's law. The constants at 20°C from Table 11-2 in the text have been multiplied by 10^5 so

$$K_{O_2} = 2.58 \times 10^{-5} \text{ atm}^{-1} \qquad K_{N_2} = 1.32 \times 10^{-5} \text{ atm}^{-1}$$

$$X_{O_2(\text{soln})} = K_{O_2}P_{O_2} = 2.58 \times 10^{-5} \text{ atm}^{-1} (0.21 \text{ atm}) = 5.4 \times 10^{-6}$$

$$X_{N_2(\text{soln})} = K_{N_2}P_{N_2} = 1.32 \times 10^{-5} \text{ atm}^{-1} (0.79 \text{ atm}) = 1.04 \times 10^{-5}$$

The ratio of O_2 to N_2 dissolved in water is

$$\frac{5.4 \times 10^{-6}}{1.04 \times 10^{-5}} = 0.52$$

Note that the ratio of O_2 to N_2 is nearly twice as high in solution as in the air. This shows that each gas behaves independently when dissolved and, strictly speaking, we should not refer to "air" dissolved in water. •

Parallel Problem: One reason trout prefer cold water to warm is the greater supply of oxygen in cold water. What is the ratio of solubility of O_2 in water at 20°C to that at 40°C?
Ans: 1.4

11-5 Colligative properties

Quantitative relationships between changes in colligative properties and concentration of solute can be calculated by the methods discussed in this section. We will consider each colligative property separately.

1. Vapor-pressure lowering (Raoult's law)

The relationship between the lowering of vapor pressure of a solvent by a solute to the solute concentration is given by Raoult's law (for ideal solutions).

$$P_1 = X_1 P^o{}_1$$

where P_1 = vapor pressure of the solution
$P^o{}_1$ = vapor pressure of pure solvent
X_1 = mole fraction of solvent

• EXAMPLE 14

Problem: The vapor pressure of water at 25°C is 23.79 mmHg. What is the vapor pressure of a 20.0 percent by mass solution of sucrose (table sugar; molar mass = 342) in water if Raoult's law is followed?

Solution: If we take 100 g of solution as a basis to determine mole fraction we have

$$\text{g sucrose} = 20\text{ g} \qquad \text{g } H_2O = 80\text{ g}$$

$$\text{Mol sucrose} = \frac{20.0\text{ g}}{342\text{ g mol}^{-1}} = 0.0585\text{ mol}$$

$$\text{Mol } H_2O = \frac{80.0\text{ g}}{18\text{ g mol}^{-1}} = 4.44\text{ mol}$$

$$X_{H_2} = \frac{\text{mol } H_2O}{\text{total mol}} = \frac{4.44\text{ mol}}{4.44\text{ mol} + 0.0585\text{ mol}} = 0.987$$

$$P_{soln} = X_{H_2O} P^o{}_{H_2O} = 0.987\ (23.79\text{ mmHg}) = 23.48\text{ mmHg}$$

It takes a lot of sugar in solution to lower the vapor pressure of water significantly! •

Parallel Problem: What is the vapor pressure of a 40.0 percent by mass solution of sucrose in water at 23°C?
Ans: 22.96 mmHg

Now work Example 11-7 in the text.

Raoult's law applies to both components in a solution of two volatile compounds, so the vapor pressure of each component can be determined and their sum will be the total vapor pressure of the solution.

• EXAMPLE 15

Problem: The vapor pressure of gasoline (average molar mass = 114) produced for summer consumption is 517 mmHg measured at 100°F. Gasohol is a mixture of alcohol and gasoline and its use has been proposed as a method of reducing our imports of petroleum products. What is the vapor pressure of a gasohol mixture made of 90 percent by mass gasoline and 10 percent methyl alcohol (CH_3OH)? The vapor pressure of pure methyl alcohol at 100°F is 230 mmHg.

Solution: We will apply Raoult's law to each component separately to determine their partial pressures and then find their sum to determine the total vapor pressure. First find the mole fractions using 100 g of solution as the basis of calculations.

$$\text{Mol gasoline} = \frac{90\ \text{g}}{114\ \text{g mol}^{-1}} = 0.79\ \text{mol}$$

$$\text{Mol } CH_3OH = \frac{10\ \text{g}}{32\ \text{g mol}^{-1}} = 0.31\ \text{mol}$$

$$X_{\text{gasoline}} = \frac{0.79\ \text{mol}}{1.10\ \text{mol}} = 0.72$$

$$X_{CH_3OH} = 1.00 - 0.72 = 0.28$$

Now use Raoult's law to find the partial pressures.

$$P_{\text{gasoline}} = X_{\text{gasoline}}P^{o}_{\text{gasoline}} = 0.72\ (517\ \text{mmHg}) = 372\ \text{mmHg}$$

$$P_{CH_3OH} = X_{CH_3OH}P_{CH_3OH} = 0.28\ (230\ \text{mmHg}) = 64.4\ \text{mmHg}$$

The vapor pressure of the gasohol is

$$P_{\text{gasoline}} = P_{CH_3OH} = 372\ \text{mmHg} + 64.4\ \text{mmHg} = 436\ \text{mmHg}\ \bullet$$

One of the criticisms of gasohol use is that it has a higher vapor pressure than gasoline and causes vapor-lock problems. That is, the formation of gas bubbles will interfere with the flow of the fluid. How do you feel about this criticism of gasohol? Ethyl alcohol has also been used in gasohol. Its vapor pressure at 100°F is 116 mmHg.

Parallel Problem: What is the vapor pressure of a gasohol mixture of 90 percent by weight gasoline and 10 percent ethyl alcohol? The vapor pressure of ethyl alcohol at 100°F is 116 torr.
Ans: 428 mmHg

2. *Boiling-point elevation*

The elevation of the boiling point of a solvent by a nonvolatile solute is proportional to the molality of the solute. The boiling-point elevation is the difference between the boiling points of the solution and the pure solvent.

$$\Delta T_b = T_{b(\text{soln})} - T_{b(\text{solv})}$$

The boiling-point elevation equation which holds for dilute solutions is

$$\Delta T_b = K_b m$$

where m is the molality of the solute and K_b is the molal boiling-point elevation constant. Each solvent has its own value of K_b. Values for some liquids are given in Table 11-4 in the text. Example 11-9 in the text illustrates the calculation of boiling-point elevation of a solution.

3. *Freezing-point lowering*

The freezing point of a solvent is lowered by the addition of a solute. The amount of lowering is again proportional to the molality of the solute

$$\Delta T_f = -K_f m$$

where ΔT_f = freezing-point lowering = $T_{f(\text{soln})} - T_{f(\text{solv})}$
K_f = molal freezing-point lowering constant
m = molality

Since $T_{f(\text{solv})}$ is greater than $T_{f(\text{soln})}$, ΔT_f is a negative quantity. Both K_f and m are positive, so the minus sign in front of K_f is necessary to preserve the sign conventions.

• EXAMPLE 16

Problem: Ethylene glycol, $C_2H_6O_2$, is used as a permanent antifreeze in automobile coolant systems. Calculate the number of grams of ethylene glycol per kilogram of water that will prevent freezing of the coolant down to 15.0°F.

Solution:

$$^\circ\text{C} = (15.0^\circ\text{F} - 32)\,\frac{5}{9} = -9.4^\circ\text{C}$$

$$\Delta T_f = T_{f(\text{soln})} - T_{f(\text{H}_2\text{O})} = -9.4 - 0 = -9.4^\circ\text{C}$$

The molality required is obtained from the freezing-point depression equation; K_f = 1.855°C m^{-1} is found form Table 11-4 in the text.

$$m = \frac{-\Delta T_f}{K_f} = \frac{-(-9.4^\circ\text{C})}{1.855^\circ\text{C}\ m^{-1}} = 5.07\ m$$

We can convert molality into grams of ethylene glycol per kilogram of water as follows:

$$\frac{5.07\ \text{mol}\ C_2H_6O_2}{1\ \text{kg}\ H_2O} \cdot \frac{62.0\ \text{g}\ C_2H_6O_2}{1\ \text{mol}} = 314\ \text{g}\ C_2H_6O_2\ (\text{kg}\ H_2O)^{-1}$$ •

Parallel Problem: Propylene glycol, $C_3H_8O_2$, is also used as an antifreeze. Calculate the number of grams of propylene glycol needed to give the same degrees of freezing protection as in Example 16.
Ans: 375 g propylene glycol

4. Osmotic pressure

Osmotic pressure is another colligative property that is directly proportional to the concentration of solute. Its value is calculated from the van't Hoff equation.

$$\Pi V = n_2RT$$

where Π = osmotic pressure
n_2 = moles of solute in V liters of solution
R = ideal-gas constant
T = temperature in kelvins

• EXAMPLE 17

Problem: Calculate the osmotic pressure of a solution of 30.0 g of sucrose (table sugar) in 1.00 liter of solution at 25°C. The molecular mass of sucrose is 342.

Solution: Solve the van't Hoff equation for Π and substitute the given values.

$$n_2 = \frac{30.0\text{g}}{342 \text{ g mol}^{-1}} = 0.0877 \text{ mol}$$

$$V = 1 \text{ liter}$$

$$R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$T = 25^\circ\text{C} + 273 = 298 \text{ K}$$

$$\Pi = \frac{n_2RT}{V} = \frac{0.0877 \text{ mol } (0.082 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.00 \text{ L}} = 2.14 \text{ atm}$$ •

Parallel Problem: Calculate the osmotic pressure of a 1.00×10^{-3} M aqueous solution at 25°C.
Ans: 0.0244 atm

5. *Calculation of molecular mass from measured colligative properties*

An important use of colligative properties is to calculate the molecular mass of a solute. Any of the colligative properties discussed in Chapter 11 can be used for this. The text gives an example of each type of calculation. Text Example 11-8 shows the use of Raoult's law to calculate the molecular mass of a solute from measurements of vapor pressure. Text Examples 11-10, 11-11, and 11-12 show how to calculate molecular mass from measurements of boiling-point elevation, freezing-point depression, and osmotic pressure, respectively.

11-6 Electrolytes

Determination of the number of particles produced by the dissociation of a strong electrolyte

Colligative properties measure the total number of particles in solution without regard to what kind of particles are present. Therefore, when a known number of molecules of a strong electrolyte is introduced into a solvent, the freezing-point lowering will tell how many particles have been produced by dissociation.

• EXAMPLE 18

Problem: A solution containing 1.25 g of a strong electrolyte (molar mass = 162.5) in 100 g of water freezes at -0.573°C. How many particles are formed from each molecule of solute?

Solution: The molality of the solute is calculated first.

$$m_{\text{solute}} = \frac{1.25\text{ g}}{0.100\text{ kg H}_2\text{O}} \bullet \frac{1\text{ mol solute}}{162.5\text{ g solute}} = 0.0769\ m$$

If no dissociation had occurred the freezing-point depression would have been the amount caused by a 0.0769 *m* solution. We can calculate the freezing-point depression for the undissociated solute.

$$\Delta T_{f(\text{undissociated solute})} = K_f m = -(1.855\text{°C } m^{-1})(0.0769\ m) = -0.143\text{°C}$$

The ratio of molality of dissociated particles to molality of undissociated solute is equal to the ratio of freezing-point depressions. If we divide the two freezing-point depression equations we get

$$\frac{\Delta T_{f(\text{dissociated particles})}}{\Delta T_{f(\text{undissociated solute})}} = \frac{-K_f m_{\text{diss}}}{-K_f m_{\text{undiss}}} = \frac{\text{mol dissociated/kg solvent}}{\text{mol undissociated/kg solvent}} = \frac{\text{mol dissociated}}{\text{mol undissociated}}$$

The observed freezing-point depression for the dissociated state was -0.573°C. Therefore, the ratio of moles of dissociated particles to moles of undissociated solute is

$$\frac{\text{mol dissociated}}{\text{mol undissociated}} = \frac{-0.573\text{°C}}{-0.143\text{°C}} = 4.01$$

Apparently, four particles are produced from each solute molecule that dissociates. •

Parallel Problem: A 0.15 molal aqueous solution of a compound freezes at -0.56°C. How many ions are produced from each molecule of the compound?
Ans: 2

The approach of Example 18 can be used to determine the percent dissociation of weak electrolytes as shown in the next example. Note that text Example 11-13 uses a very different approach to work this same problem.

• EXAMPLE 19

Problem: Hydrogen fluoride, HF, produces a solution of hydrofluoric acid when dissolved in water. HF is only partly dissociated in aqueous solutions. A $5.00 \times 10^{-2}\ m$ solution of HF in water has a freezing-point depression of -0.103°C. What is the percent dissociation of HF in the solution?

Solution: If no dissociation had taken place, the freezing-point depression would have been

$$\Delta T_{f(\text{undiss})} = -K_f m = -(1.86°\text{C } m^{-1})(5.00 \times 10^{-2}\ m) = -0.0930°\text{C}$$

The ratio of observed moles to undissociated moles (see previous example) is

$$\frac{\text{mol dissociated}}{\text{mol undissociated}} = \frac{\Delta T_{f(\text{diss})}}{\Delta T_{f(\text{undiss})}} = \frac{-0.103}{-0.0930} = 1.11$$

After dissociation, there is an increase of 0.11 mol of ions for each mole of HF. For the case of HF, the numbers of moles of positive ions and negative ions produced are equal, so the number of moles of HF dissociated is equal to the *increase* in moles of ions produced. The percent dissociation is

$$\%\ \text{dissociation} = \frac{\text{mol dissociated}}{\text{total mol}} = \frac{0.11}{1} \times 100 = 11\% \bullet$$

Parallel Problem: A 0.50 molal solution of acetic acid, $HC_2H_3O_2$, freezes at -0.95°C. What is the percent dissociation of the acetic acid?
Ans: 2.0%

KEY TERMS

11-1 General properties of solutions

Homogeneous mixture: A combination of substances characterized by a single phase of uniform composition.

Solution: A homogeneous mixture.

11-2 Types of solutions

Aqueous solution: A solution in which the major component is water.

Interstitial solid solution: A solution formed when impurities occupy the interstitial sites in a crystal lattice.

Substitutional solid solution: A solution formed when impurities occupy random lattice points of the crystal structure.

11-3 Concentration units

Concentrated: A general or qualitative term applied to a relatively high concentration of solute in a solution.

Dilute: A general or qualitative term applied to a low concentration of solute.

Molality: The number of moles of solute per kilogram of solvent.

Molarity: The number of moles of solute per liter of solution.

Mole fraction: The number of moles of one component in a solution divided by the total number of moles of all components.

Mole percent: Mole fraction multiplied by 100.

Percent by mass: The mass of one component divided by the total mass and expressed as a percentage, also known as mass percent.

Solute: A component of a solution present at a concentration which is low relative to that of the solvent. The dissolved substance.

Solvent: The major component in a solution. The dissolving medium.

11-4 Solubility

Dielectric constant: A measure of ability of molecules of a substance to allign themselves with or be polarized by an electric field.

Endothermic reaction: A reaction which absorbs heat.

Enthalpy of solution: The change in enthlapy when a substance dissolves. Same as heat of solution.

Exothermic reaction: A reaction which produces heat.

Heat of solution: Same as enthalpy of solution.

Henry's law: The solubility of a gas dissolved in a liquid is proportional to the partial pressure of the gas above the liquid.

Henry's law constant: The constant of proportionality in Henry's law.

Hydration: Clustering of water molecules around solute particles in solution.

Hydration energy: The amount of energy released when an ion becomes hydrated.

Hydrogen bond: Strong intermolecular forces between a molecule that contains hydrogen bonded to one electronegative atom with another electronegative atom such as N, O, or F on another molecule.

Insoluble: Compounds low in solubility, slightly soluble, or sparingly soluble.

Like-dissolves-like: A generalization that solvents will dissolve a solute if the solute has properties similar to the solvent.

Polarizability: The ability of a molecule to become distorted so that it partially neutralizes an electric field.

Saturated solution: A solution which is in equilibrium with excess solute and has dissolved the maximum amount of solute it can hold at equilibrium.

Solubility: The concentration of a solute in a saturated solution. The maximum amount of solute in a solution at equilibrium.

Soluble: A compound with high solubility.

Solute-solute forces: The forces between particles of the solute before it has dissolved.

Solute-solvent forces: The electrostatic forces between solute and solvent particles in a solution.

Solvation: The interaction of a solute with a solvent resulting in the clustering of solvent particles around the solute particles.

Solvent-solvent forces: The forces between solvent particles before a solution is formed.

Supersaturated solution: A solution in which the concentration of solute is greater than its concentration in a saturated solution.

Unsaturated solution: A solution in which the solute concentration is less than the concentration in a saturated solution.

11-5 Colligative properties

Boiling-point elevation: The increase in boiling point of a solvent as a result of the presence of a solute.

Boiling-point elevation constant: The proportionality constant between the boiling point elevation and the molality of the solute.

Colligative property: A property of a solution which depends upon the concentration of solute particles but not on their identities.

Escaping tendency: The tendency shown by a substance to escape from one phase to another.

Freezing-point depression: The lowering of the freezing point of a solvent as a result of the presence of a solute.

Freezing-point depression constant: The proportionality constant between the freezing point depression and the molality of the solute.

Ideal solution: A solution which obeys Raoult's law. A solution in which the interactions between all particles are equal.

Osmosis: The passing of solvent molecules through a semipermeable membrane from a solution of higher solvent concentration to one of lower solvent concentration.

Osmotic pressure: The pressure which must be applied to a solution phase on one side of a semipermeable membrane in order to stop osmosis.

Raoult's law: The partial pressure of a component in a liquid solution is proportional to the mole fraction of that component. The constant of proportionality is the vapor pressure of the pure component.

Reverse osmosis: Application of a pressure higher than the osmotic pressure to remove solvent from a solution of lower solvent concentration to one of higher solvent concentration.

Semipermeable membrane: A thin barrier that allows passage of solvent but not solute particles.

Vapor-pressure lowering: The decrease in solvent vapor pressure as a result of the presence of a solute.

11-6 Electrolytes

Acid: A compound that dissociates in water to give hydrogen ions. (Arrhenius definition)

Base: A compound that dissociates in water to give hydroxide ion. (Arrhenius definition)

Charge density: The electrostatic charge per unit volume of a particle.

Dissociation: The splitting apart of a molecule to form two fragments such as the reaction of an electrolyte with a solvent to form ions. Same as ionization.

Electrolyte: A substance which produces ions when dissolved in a solvent.

First hydration sphere: The water molecules bound most tightly and closest to an ion in an aqueous solution.

Hydration number: The number of water molecules in the first hydration sphere of an ion in an aqueous solution.

Hydronium ion: The hydrated hydrogen ion, represented by H_3O^+. Same as oxonium ion.

Ionic electrolyte: An electrolyte which exists as a combination of cations and anions before it is dissolved.

Ionization: Same as dissociation.

Molecular electrolyte: A polar molecule which is dissociated into ions by the action of water molecules during the dissolving process.

Neutralization reaction: An acid-base reaction.

Nonelectrolyte: A substance which does not dissociate when it dissolves in water.

Oxonium ion: Same as hydronium ion.

Salt: A compound formed from the positive ion of an Arrhenius base and the negative ion of an Arrhenius acid.

Strong electrolyte: A compound which completely ionizes in solution.

Weak electrolyte: A compound which only partially ionizes in solution.

SELF TEST

True or False

_____ 1. The properties of homogeneous mixtures are often not related to those of the pure components.

_____ 2. Aqueous solutions of equal molality can have different mole fractions of solute.

_____ 3. Hydrogen bonding increases the solubility of H_2.

_____ 4. The solubility of a gas is directly proportional to the partial pressure of the gas above the solution.

_____ 5. If a solution is made of 50 g of ethyl alcohol (molar mass = 46) and 50 g of water, the mole fraction of each is 0.50.

_____ 6. In dilute aqueous solutions molarity is essentially equal to molality.

_____ 7. Energy is released when a substance dissolves in water if the hydration energy is greater than the lattice energy.

_____ 8. The solubility of a substance will increase with increasing temperature if the heat of solution is negative.

_____ 9. Water saturated with oxygen at 25°C becomes supersaturated when cooled to 10°C.

_____ 10. A solution of two volatile components in which the attractions between solute and solvent molecules are stronger than solute-solute or solvent-solvent attractions will show negative deviation from Raoult's law.

_____ 11. When a solution of a strong electrolyte is diluted the number of moles of solute remains constant.

_____ 12. When 0.100 mol of $MgCl_2$ is dissolved in 100 mL of water the freezing point of the solution is -1.855°C.

_____ 13. A nonpolar solute is soluble in water.

_____ 14. Raoult's law can be used to calculate the vapor pressure of each component in a binary solution of liquids.

_____ 15. Osmotic pressure of a solution depends on atmospheric pressure.

completion

16. A solution is a ______________________ mixture.

17. Like dissolves ________________.

18. The solubility of gases in water usually ______________(increases, decreases) as temperature increases.

19. The molal freezing-point depression constant for water is _________________.

20. _____________________dissociate in water to give hydroxide ions.

21. _____________________ is the moles of solute divided by the total moles of solution.

22. If _______________ to ______________ interactions are stronger than ____________ to _______________ interactions or _______________ to ________________ interactions, the solute will be soluble.

23. Molality is defined as _______________ of solute per ______________ of solvent.

24. Four examples of colligative properties are _____________, ______________, ________________, and ________________.

25. A 30 percent by mass solution of NaCl in water contains 30 g of NaCl and _________ g of H_2O.

26. The normal boiling point of an aqueous solution containing 1 *m* nonelectrolyte solute will be _________°C if the solution is ideal.

27. Nearly all _______________ are completely dissociated in aqueous solutions.

28. The formula of the oxonium ion is __________________.

29. The molarity of chloride ions in a 0.45 *M* solution of $AlCl_3$ is ________________.

30. The characteristics of a solution that depend on the number but not the nature of solute particles present in solution are called __________________.

Multiple Choice

31. What is the mole fraction of MgF_2 in a solution of 50.0 g of MgF_2 dissolved in 200 g of water?
(a) 4.01 (b) 0.200 (c) 0.0722 (d) 0.0674

32. What is the mole percent of MgF_2 in the solution in Problem 31?
(a) 4.01% (b) 20.0% (c) 7.22% (d) 6.74%

33. What is the molality of the solution in Problem 31?
(a) 4.01 *m* (b) 0.200 *m* (c) 0.722 *m* (d) 0.0674 *m*

34. The density of the solution in Problem 31 is 1.070 g mL^{-1}. What is the molarity of the MgF_2?
(a) 4.01 *M* (b) 3.43 *M* (c) 0.200 *M* (d) 0.674 *M*

35. A solution is prepared by dissolving 26.0 g of NaCl in enough water to make 100 mL of a solution whose density is 1.10 g mL^{-1}. What is the molality of the solution?
(a) 0.445 *m* (b) 4.05 *m* (c) 4.45 *m* (d) 5.30 *m*

36. You are asked to prepare 1.00 liter of 0.250 M KCl from a stock solution which is 6.00 M. How many milliliters of stock solution should you use?
(a) 24.0 (b) 41.6 (c) 58.4 (d) 166

37. How many grams of oxygen can be dissolved in 2.00 liters of water at 20°C if the oxygen pressure is 2.00 atm? Henry's law constant for O_2 in water at 20°C is 2.58×10^{-5} atm^{-1}
(a) 5.16×10^{-5} g (b) 2.58×10^{-5} g
(c) 9.18×10^{-2} g (d) 0.198 g

38. The vapor pressure of pure water at 35°C is 42.18 mmHg. What is the vapor pressure of an aqueous solution which is 2.000 *m* in a nonvolatile nonelectrolyte at 35°C?
(a) 12.65 mmHg (b) 40.71 mmHg
(c) 84.36 mmHg (d) cannot be determined from the information given

39. The normal boiling point of a 0.200 *m* solution of NaCl in water would be
(a) 100.05°C (b) 100.10°C (c) 100.20°C (d) 100.31°C

40. What is the freezing point of a solution made of 5.00 g of toluene (C_7H_8) in 100 g of benzene (C_6H_6). The freezing point of pure benzene is 5.50°C and its molal freezing-point depression constant is 5.12°C cm^{-1}.
(a) -2.78°C (b) 2.78°C (c) 2.72°C (d) 0.38°C

41. The redwoods in California often grow to heights of 100 m. Assuming that osmotic pressure is responsible for carrying water from the roots to the upper leaves, what molarity of salts in the tree sap would be required to raise water 100 m at 25°C? (13.55 mm H_2O = 1 mmHg)
(a) 0.211 *M* (b) 0.244 *M* (c) 2.52 *M* (d) 0.397 *M*

42. An aqueous solution containing 2.50 g of a nonelectrolyte in 100 g of H_2O freezes at -0.415°C. What is the molar mass of the nonelectrolyte?
(a) 20.0 (b) 22.4 (c) 32.4 (d) 112

43. What is the molecular mass of a substance if an aqueous solution containing 5.00 g L^{-1} has an osmotic pressure of 0.0147 atm at 25°C?
(a) 698 (b) 1660 (c) 8320 (d) 8.42×10^5

44. Acetic acid, $HC_2H_3O_2$, is a weak electrolyte which partially dissociates in water to form H^+ and $C_2H_3O_2^-$ (acetate) ions. In a 0.150 *m* solution of acetic acid in water, the freezing point is –0.284°C. What is the percent dissociation of acetic acid in this solution?

(a) 1% (b) 2% (c) 8% (d) 10%

45. Potassium chloride absorbs heat as it dissolves in water. What will happen to the solubility of potassium chloride as the temperature is increased?

(a) remain the same (b) increase

(c) decrease (d) cannot tell from the information given

Chapter 12

AQUEOUS-SOLUTION REACTIONS

CHAPTER OVERVIEW

12-1 Acid-base reactions

Water is the most common solvent on earth yet it has unique properties that give it special significance in chemistry. In Chapter 11 we studied the effect of molecular solutes on the properties of water. In this chapter we will investigate water as a solvent for reactions of electrolytes.

Water is in equilibrium with H^+ and OH^- ions and these ions are responsible for much of the chemical activity of water. Acid-base reactions are very important in the chemistry of aqueous solutions. You should become familiar with the three different ways of defining acids and bases. The Arrhenius definition is probably most familiar, but it is also the most limited and applies only to aqueous solutions. The Brønsted-Lowry definition is more general and includes NH_3 as a base, an important advantage over the Arrhenius definition. The Lewis definition is very general; it is based on electron-pair transfer and includes many compounds omitted by the other two definitions.

12-2 Precipitation and complexation reactions

There are two keys to writing equations for precipitation reactions: (1) knowing how the reactants dissociate and then recombine into products and (2) knowing which products precipitate (come out of solution as an insoluble compound) or form weak electrolytes. Being successful in the first key step requires knowledge of formulas and charges of common ions. We studied this in Chapter 9 for simple ions. You should remember how to determine the charge on an ion from its position in the periodic table. You need to memorize the formulas and charges of common polyatomic ions such as NH_4^+, OH^-, NO_3^-, $C_2H_3O_2^-$, CO_3^{2-}, PO_4^{3-}, and any others your instructor may suggest. Some reactions involve two salts as reactants. To write an equation for these reactions you first write the ions which result from the dissociation of the salts and then pair each cation with a different anion, remembering to preserve electrical neutrality in the product compounds. If these products fall into the classification scheme for reactions in Section 12-3 of the text a chemical reaction will occur; otherwise, there will be no actual reaction for the equation.

Being successful at the second key requirement is straightforward. Simply learn to recognize which products are weak electrolytes and know the guidelines for soluble and insoluble compounds in Section 12-3 of the text. There are no shortcuts to learning this material. It takes hard work and memorization and must be done before you can be proficient at writing precipitation reactions. Learn the guidelines and then practice writing reactions.

Writing a reaction for the formation of a complex ion generally involves the combination of reactants into a single product or complex. Table 12-2 in the text shows the ligands and metal ions that commonly react to form complex ions. This concept will be discussed in detail in Chapter 22.

12-3 Net equations for aqueous-solution reactions

This section is really the application of the concepts presented in Section 12-2. Follow the examples closely and work as many problems as you can. In this chapter the adage "learn by doing" is of paramount importance. The net reaction eliminates all spectator ions and shows only the components that actually participate in the chemical reaction.

12-4 Electronic bookkeeping, part II: oxidation numbers

This section introduces a second method for dealing with the distribution of electrical charge in molecules. The first method (formal charges) was discussed in Section 8-4. Here we introduce the important concept of oxidation numbers. Oxidation numbers are used to organize and relate descriptive chemistry to the charge distribution of compounds, and to balance and interpret reactions involving electron transfer called oxidation-reduction reactions or redox reactions.

12-5 Electron-transfer reactions

There are two approaches to balancing electron transfer reactions: (1) oxidation number and (2) half-reaction method. Your course instructor will assign one or both methods for you to use. The half-reaction method will help you in understanding the concepts of Chapter 18. Becoming proficient at balancing redox equations is largely a matter of practice.

12-6 Solution stoichiometry

This section combines the concepts of concentration units from Chapter 11 and the stoichiometry of Chapter 2. As you can see, the possible types of problems are growing rapidly, but if you have learned the concepts presented so far, you should be able to work these problems. The concepts of equivalent mass and normality are widely used in stoichiometric calculations, so become familiar with them. Normality and equivalents are related in exactly the same way as molarity and moles.

$$M = \frac{\text{moles}}{\text{liter}} \qquad N = \frac{\text{equivalents}}{\text{liter}}$$

KEY EQUATIONS

12-6 Solution stoichiometry

1. Equivalents: acid-base

$$\text{Equivalent mass} = \frac{\text{formula mass}}{\text{no. of ionizable H}^+ \text{ or OH}^-}$$

$$\text{Number of equivalents} = \frac{\text{grams}}{\text{equivalent mass}}$$

$$\text{Normality} = N = \frac{\text{no. of equivalents of solute}}{\text{liters solution}}$$

$$= \text{molarity (no. of ionizable H}^+ \text{ or OH}^-)$$

For monoprotic acids or bases with one OH^-: $N = M$

For diprotic acids or bases with two OH^-: $N = 2M$

For triprotic acids or bases with three OH^-: $N = 3M$

For neutralization: $(NV)_{acid} = (NV)_{base}$

2. *Equivalents: redox*

$$\text{Equivalent mass} = \frac{\text{formula mass}}{\text{change in oxidation number}}$$

$$\text{Number of equivalents} = \frac{\text{grams}}{\text{equivalent mass}}$$

$$\text{Normality} = N = \frac{\text{number of equivalents of solute}}{\text{liters solution}}$$

$$= \text{molarity (change in oxidation number)}$$

For redox

$$(NV)_{oxidant} = (NV)_{reductant}$$

LEARNING OBJECTIVES

As a result of studying Chapter 12, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 212 of this *Study Guide*.

12-1 Acid-base reactions

1. Explain why water is the most important solvent for many chemical reactions and why reactions occur faster in aqueous solution.
2. Explain why the autodissociation of water plays an important part in acid-base chemistry. (Text Probs. 12-3, 12-7) (Self Test 17)
3. Write the Arrhenius definition of acids, bases, and salts and explain any limitations for each definition. (Text Probs. 12-1, 12-3, 12-11, 12-56) (Self Test 1, 16)
4. Show why neutralization is the combination of H^+ and OH^- ions no matter what the source of the H^+ and OH^- ions. (Self Test 4, 8)
5. Show how the solvent-system definition of acids and bases extends the Arrhenius concept to solvents other than water. (Text Probs. 12-7, 12-8) (Self Test 6)
6. Write the Brønsted-Lowry definition of acids and bases. (Text Probs. 12-1, 12-3, 12-4, 12-11) (Self Test 1)
7. Cite some examples of conjugate acid-base pairs. (Text Prob. 12-2) (Self Test 6, 7)
8. Explain what is meant by the strength of an acid and show how the leveling effect of water affects the strength of certain acids. (Text Probs. 12-5, 12-8, 12-9, 12-10) (Self Test 3, 30)
9. Write the Lewis definition of acids and bases and explain why this definition is more general than the Brønsted-Lowry or Arrhenius definitions. (Text Probs. 12-1, 12-6) (Self Test 2)

12-2 Precipitation and complexation reactions

1. Name all of the ions present in a solution of electrolytes. (Text Probs. 12-17, 12-18)
2. Give an example of a precipitation reaction and explain what causes a compound to precipitate. (Text Probs. 12-12, 12-13)
3. Write molecular, ionic, and net ionic equations given the reactants when an insoluble product or weak electrolyte is formed. (Text Examples 12-1 to 12-3; Text Probs. 12-19, 12-20, 12-22, 12-52, 12-53) (New Skills Examples 1 to 3; Self Test 11, 28)
4. Write the formula of a complex ion and explain how it is formed. (Text Probs. 12-14 to 12-16)

12-3 Net equations for aqueous-solution reactions

1. Know the guidelines given in the text for classifying aqueous-solution reactions.
2. Know the guidelines given in the text for classifying compounds as soluble or insoluble. (Text Probs. 12-12, 12-13) (Self Test 9, 12, 18, 19, 32, 33)
3. Know the guidelines given in the text for classifying electrolytes as strong or weak. (Self Test 31)
4. Use the guidelines to predict when a chemical reaction will occur in aqueous solutions and write an equation for the reaction. (Text Examples 12-4, 12-5; unworked examples 1 through 10 following Text Example 14-5; Text Probs. 12-21 to 12-23) (New Skills Examples 4, 5; Self Test 24, 32)

12-4 Electronic bookkeeping, part II: oxidation numbers

1. Use oxidation numbers to keep track of the distribution of valence electrons among atoms in a molecule.
2. Understand the limitations of oxidation numbers for describing the actual electrical charge on an ion.
3. Determine the oxidation number on each atom in a molecule or polyatomic ion using the rules given in the text. (Text Examples 12-6, 12-7; Text Probs. 12-25 to 12-29) (New Skills Example 6; Self Test 20 to 23, 38 to 40)

12-5 Electron-transfer reactions

1. Identify the components oxidized and those reduced in redox reactions. (Text Probs. 12-31, 12-32, 12-37, 12-65) (New Skills Examples 7 to 12; Self Test 22, 23, 34)
2. Use the oxidation-number method to balance redox reactions taking place in the absence of a solvent. (Text Examples 12-8, 12-9; Text Probs. 12-30, 12-37) (New Skills Examples 7, 8; Self Test 35)
3. Use the oxidation-number method to balance reactions in acidic or basic solutions. (Text Examples 12-10, 12-11; Text Probs. 12-33, 12-35, 12-59, 12-61) (New Skills Examples 9, 10; Self Test 36)
4. Use the half-reaction or ion-electron method to balance redox equations in aqueous solutions. (Text Examples 12-12, 12-13; Text Probs. 12-34, 12-36, 12-60, 12-62) (New Skills Examples 11, 12; Self Test 36, 37)

12-6 Solution stoichiometry

1. Determine the equivalent mass of a substance. (Text Example 12-18; Text Probs. 12-40, 12-55) (Self Test 15, 25, 44)
2. Calculate the number of equivalents in a given number of grams or moles of a substance. (Text Example 12-22; Text Prob 12-49) (New Skills Example 13; Self Test 14, 29, 42)

3. Perform calculations relating equivalent mass to molecular mass, equivalents to moles, and normality to molarity. (Text Example 12-19; Text Probs. 12-38, 12-39, 12-44, 12-47, 12-48, 12-50) (New Skills Examples 13 to 15; Self Test 5, 13, 26, 27, 29, 43)
4. Solve stoichiometric problems based on neutralization of acids and bases. (Text Examples 12-14 to 12-17, 12-20; Text Probs. 12-40 to 12-43, 12-45 to 12-48, 12-63, 12-64, 12-66) (New Skills Examples 16, 17; Self Test 10, 41)
5. Solve stoichiometric problems involving redox reactions. (Text Example 12-21, 12-23; Text Probs. 12-51 to 12-54, 12-68, 12-69) (New Skills Examples 18, 19; Self Test 45)
6. Solve stoichiometric problems involving precipitation reactions. (Text Example 12-24; Text Prob. 12-67)

NEW SKILLS

12-2 Precipitation and complexation reactions

You cannot write chemical equations until you can write chemical formulas and predict the ions that result when electrolytes are dissolved. If you have not yet learned the charges and formulas of common ions, you will find this chapter bewildering; if you have learned them, it should be understandable but will still require time to practice the skills.

Precipitation reactions

When two soluble electrolytes are mixed in solution a chemical reaction occurs if any combination of the mixed ions results in an insoluble compound. The insoluble compound will precipitate (come out of solution as a solid).

• EXAMPLE 1

Problem: A solution of sodium chloride is mixed with a solution of silver nitrate and an insoluble compound is formed. Write a molecular equation for the reaction.

Solution: The first step in writing a reaction is to find what ions are present when the solutions are mixed. Sodium chloride dissociates according to the reaction

$$NaCl \rightarrow Na^+ + Cl^-$$

and silver nitrate dissociates according to

$$AgNO_3 \rightarrow Ag^+ + NO_3^-$$

The ions present from dissociation of the reactants are Na^+, Ag^+, Cl^-, and NO_3^-. Only ions of opposite charge combine into products because the resulting molecules must be electrically neutral; therefore the *only* possible products, besides the reactant molecules, are $NaNO_3$ and AgCl. One of these must be insoluble. The molecular reaction is

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl$$

The positive and negative ions have simply traded partners. •

Parallel Problem: A solution of potassium hydroxide is mixed with a solution of copper(II) nitrate and an insoluble compound is formed. Write a molecular equation for the reaction.
Ans: $2\ KOH + Cu(NO_3)_2 \rightarrow 2\ KNO_3 + Cu(OH)_2$

• EXAMPLE 2

Problem: Write an ionic equation for the reaction in the previous example.

Solution: To write an ionic equation we need to know which product is the insoluble compound. The solubility guidelines in the text tell us that $NaNO_3$ is soluble but AgCl is insoluble. The ionic equation is

$$Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow Na^+ + NO_3^- + AgCl(s)$$

AgCl is not written in ionic form because it is insoluble and so does not form an appreciable concentration of ions. •

Parallel Problem: Write an ionic equation for the reaction in the previous Parallel Problem.
Ans: $2\,K^+ + 2\,OH^- + Cu^{2+} + 2\,NO_3^- \rightarrow Cu(OH)_2(s) + 2\,K^+ + 2\,NO_3^-$

• EXAMPLE 3

Problem: Write a net ionic equation for the reaction in Example 2.

Solution: To convert an ionic equation to a net ionic equation we simply eliminate the spectator ions. Spectator ions are those that stay in solution while the other ions participate in the reaction. They always occur on both sides of the equation in the same form. In this case, Na^+ and NO_3^- are spectator ions. Elimination of these from both sides of the equation gives the net ionic equation.

$$Cl^- + Ag^+ \rightarrow AgCl(s)$$ •

Parallel Problem: Write the net ionic equation for the reaction in the previous Parallel Problem.
Ans: $2\,OH^- + Cu^{2+} \rightarrow Cu(OH)_2(s)$

Now work through Example 12-1 in the text.

12-3 Net equations for aqueous-solution reactions

A real challenge in writing chemical equations is figuring out the products for a given set of reactants. You must know the classification schemes and guidelines in section 12-3 of the text to figure out reactions. The rest is a matter of "learning by doing."

• EXAMPLE 4

Problem: Will a reaction occur if solutions of sodium hydroxide and lead(II) chloride are mixed?

Solution: The ions produced by dissociation of the reactants are Na^+, OH^-, Pb^{2+}, and Cl^-. They can combine to form only two new compounds: NaCl and $Pb(OH)_2$. According to solubility guideline 8, $Pb(OH)_2$ is insoluble and a precipitation reaction will occur. •

Parallel Problem: Will a reaction occur if solutions of lithium phosphate and ammonium nitrate are mixed?
Ans: No. (No insoluble compounds or weak electrolytes are formed.)

• EXAMPLE 5

Problem: Hydrochloric acid is added to a sample of solid sodium carbonate. Give equations for the reactions that occur.

Solution: Sodium carbonate is soluble, but we should look for a chemical change which could result in different products. The hydrochloric acid furnishes H^+ and Cl^- ions. H^+ ions react with $CO_3{}^{2-}$ ions to form $HCO_3{}^-$, a weak acid; therefore, acids dissolve carbonate salts to give hydrogen carbonate products. The molecular reaction is

$$Na_2CO_3(s) + HCl \rightarrow NaCl + NaHCO_3$$

The ionic reaction is

$$Na_2CO_3(s) + H^+ + Cl^- \rightarrow 2\,Na^+ + Cl^- + HCO_3{}^-$$

and the net ionic reaction is

$$Na_2CO_3(s) + H^+ \rightarrow 2\,Na^+ + HCO_3{}^-$$

Check the last reaction to convince yourself that it is balanced atomically and with respect to charge.

If additional HCl is present the reaction can go further because $HCO_3{}^-$ and H^+ can combine to give the weak acid H_2CO_3. The net ionic equation for this reaction is

$$HCO_3{}^- + H^+ \rightarrow H_2CO_3$$

The Na^+ ions are in solution and become spectator ions. •

Parallel Problem: Solutions of HCN and NaOH are mixed. Write a net ionic equation for the chemical reaction.
Ans: $HCN + OH^- \rightarrow CN^- + H_2O$

Now work Examples 12-3 to 12-5 in the text and try to explain why reactions 1 through 10 following Example 12-5 take place.

12-4 Electronic bookkeeping, part II: oxidation numbers

The assignment of oxidation numbers to atoms in molecules is straightforward if the rules given in the text are followed. These rules may be summarized as follows:

1 Fluorine always has –1 oxidation number in compounds.

2 Oxygen has –2 oxidation number in compounds except for peroxides, superoxides, and with fluorine.

3 Hydrogen has +1 oxidation number when combined with nonmetals and –1 when combined with metals.

4 Groups IA, IIA, and IIIA metals have oxidation numbers equal to the charge on the ion.

5a The oxidation number of atoms unbonded, or in their elemental state, is zero.

5b For simple, monoatomic (one-atom) ions, the oxidation number is equal to the charge on the ion.

5c The sum of oxidation numbers of atoms in a molecule is 0.

5d The sum of oxidation numbers of all atoms in an ion is equal to the charge on the ion.

• EXAMPLE 6

Problem: Assign oxidation numbers to each atom in the following: Cl_2, Cl^-, NaCl, $CaSO_4$, CN^-, NH_4^+, $K_2Cr_2O_7$, and CH_2O.

Solution: We will apply the appropriate rules to each particle and write the oxidation number over each atom.

$\overset{\textcircled{0}}{Cl_2}$

Rule 5a: The oxidation number is zero in an uncombined element.

$\overset{\textcircled{-1}}{Cl^-}$

Rule 5b: The oxidation number is equal to the ionic charge for monoatomic ions.

$\overset{\textcircled{+1}}{Na}\ \overset{\textcircled{-1}}{Cl}$

Rule 5b: The oxidation number is equal to the charge on the ions for binary ionic compounds.

$\overset{\textcircled{+2}}{Ca}\ \overset{\textcircled{+6}}{S}\ \overset{\textcircled{-2}}{O_4}$

Rule 4: Gives oxidation number of Ca as +2

Rule 2: Gives oxidation number of O as –2

Rule 5c: Gives oxidation number of sulfur as +6 from the sum of oxidation numbers of the atoms.

$$\begin{aligned} Ca + S + 4(O) &= 0 \\ (+2) + x + 4(-2) &= 0 \\ x &= 6 \end{aligned}$$

$\overset{\textcircled{+2}}{C}\ \overset{\textcircled{-3}}{N^-}$

Rule 4: (extension) Gives N an oxidation number of -3 from its position in group VA in the periodic table.

Rule 5d: Gives C an oxidation number of +2 from the simple equation.

$$\begin{aligned} x - 3 &= -1 \\ x &= 2 \end{aligned}$$

$\overset{\textcircled{-3}}{N}\ \overset{\textcircled{+1}}{H_4^+}$

Rule 3: Gives H an oxidation number of +1.

Rule 5d: Gives N an oxidation number of –3 from the equation

$$\begin{aligned} x + 4(+1) &= +1 \\ x &= -3 \end{aligned}$$

Note that in a binary ion N takes the oxidation number predicted from its position in group VA (–3).

$\overset{+1}{K_2}\;\overset{+6}{Cr_2}\;\overset{-2}{O_7}$

Rule 2: Gives oxygen –2.
Rule 4: Gives potassium +1.
Rule 5c: Gives Cr +6 from the equation

$$\begin{aligned} 2x + 2(1) + 7(-2) &= 0 \\ x &= 6 \end{aligned}$$

The coefficient of 2 for x is required because there are two Cr atoms in the molecule.

$\overset{0}{C}\;\overset{+1}{H_2}\;\overset{-2}{O}$

Rule 2: Gives oxygen –2.

Rule 3: Gives hydrogen +1.

Rule 5c: Gives carbon an oxidation number of 0 from the equation

$$\begin{aligned} x + 2(1) - 2 &= 0 \\ x &= 0 \end{aligned}$$

●

Parallel Problem: Assign oxidation numbers to each atom in the following: NO_2^-, H_3PO_4, $NaClO_3$, $KMnO_4$, $MgTi(NO_3)_6$, $NaAl(OH)_4$, $NaHSO_3$, CrO_4^{2-}.

Ans:

+5–2 +1+5–2 +1+5–2 +1+7–2 +2+4 +5–2 +1+3 –2+1 +1+1+4–2 +6–2

NO_2^- H_3PO_4 $NaClO_3$ $KMnO_4$ $MgTi(NO_3)_6$ $NaAl(OH)_4$ $NaHSO_3$ CrO_4^{2-}

12-5 Electron-transfer reactions

Redox reactions are the basis of several important chemical changes. We will study their applications later in Chapter 18. Right now we are concerned with understanding the concepts involved and becoming familiar with them by learning two techniques used to balance redox equations. Each technique has its own advantages and the choice of one over the other is largely a matter of personal preference.

1. Oxidation-number method

There are often several possible products from a given set of reactants in redox reactions, so information about the product composition must be given before an equation can be written. Balancing the equation is a matter of following the steps as outlined in the text. We can illustrate this by example, starting with a simple one.

• EXAMPLE 7

Problem: Balance the following equation by the oxidation-number method.

$$Fe + O_2 \rightarrow Fe_2O_3$$

Solution: We will apply the steps outlined in the text.

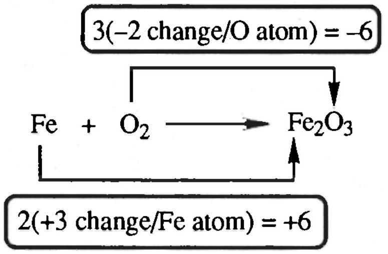
Step 1: Assign oxidation numbers

$$\overset{0}{Fe} + \overset{0}{O_2} \rightarrow \overset{+3}{Fe_2}\;\overset{-2}{O_3}$$

Step 2: Determine the number of electrons (oxidation numbers) gained and lost. The oxidation number of Fe increases from 0 to +3 so Fe is oxidized (hence it is the reducing agent because it reduces the oxygen). The oxidation number of O_2 decreases from 0 to –2 so O_2 is reduced (hence it is the oxidizing agent since it oxidizes Fe to Fe^{3+}).

Step 3: If a molecule has more than one atom that gains or loses electrons (changes in oxidation number), find the net gain or loss for that molecule. Step 3 does not apply in this example.

Step 4: Balance the electron transfer by inserting coefficients into the equation to make the number of electrons lost equal to the number of electrons gained. It is generally easiest to balance the left-hand side of the equation first, and our first consideration is to balance the changes in oxidation number (electrons transferred). Often arrows are used as a bookkeeping aid in this step.



The lowest common denominator for –2 and +3 is 6. Two Fe atoms have +6 change and three O atoms have –6 change; the gain in oxidation number (six electrons lost) equals the decrease in oxidation number (six electrons gained). The Fe and O_2 on the left-hand side can be balanced by taking two Fe atoms and three O atoms (or $\frac{3}{2}O_2$ molecules) and the partially balanced equation becomes

$$2\,Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3$$

Step 5: Complete the balancing. Now that we have balanced the electron transfer, we do not want to change the coefficients on the elements already balanced. Balance the rest of the equation using these coefficients as a guide. In this case, one molecule of Fe_2O_3 gives us the correct atomic balance. This equation could have been balanced by inspection quite easily, but it illustrates the steps involved in the oxidation-number method. The same approach will balance more difficult equations. •

Parallel Problem: Balance the following equation by the oxidation-reduction number method:

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$$

Ans: $3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$

• EXAMPLE 8

Problem: Balance the following equation by the oxidation-number method.

$$As_2S_5 + HNO_3 \rightarrow As_2O_5 + H_2SO_4 + NO + H_2O$$

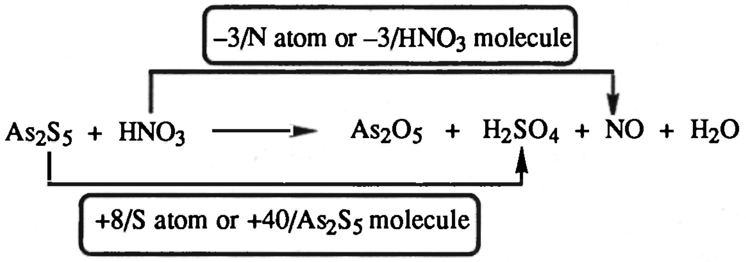
Solution: We apply the steps as outlined in the text.

Step 1: $\overset{+5}{As_2}\overset{-2}{S_5} + \overset{+5}{H}\ \overset{+5}{N}\ \overset{-2}{O_3} \rightarrow \overset{+5}{As_5}\overset{-2}{O_5} + \overset{+1}{H_2}\ \overset{+6}{S}\ \overset{-2}{O_4} + \overset{+2}{N}\ \overset{-2}{O} + \overset{+1}{H_2}\ \overset{-2}{O}$

Step 2: The oxidation number of sulfur changes from –2 to +6, a gain of 8. The oxidation number of nitrogen changes from +5 to +2, a loss of 3.

Step 3: Does not apply to this example.

Step 4: Using the arrow system to keep track of bookkeeping.



Since there are five sulfur atoms per As_2S_5 molecule and the oxidation number of each sulfur atom changes by +8, the total change for an As_2S_5 molecule is 5(+8) = +40. The lowest common denominator for balancing the electron transfer is 3 x 40 = 120. Three molecules of As_2S_5 have a total gain of 120 in oxidation number and 40 molecules of HNO_3 have a loss of 120 in oxidation number; therefore, we balance the electron transfer by

$$3\ As_2S_5 + 40\ HNO_3 \rightarrow As_2O_5 + H_2SO_4 + NO + H_2O$$

Step 5: The coefficients on the left-hand side balance the electron transfer so they must not be changed. We balance the rest of the equation using them as a guide. There are six atoms of As and 15 atoms of S on the left-hand side, so the same number must appear on the right-hand side. This requires the coefficient of As_2O_5 to be 3 and the coefficient of H_2SO_4 to be 15. The same reasoning requires 40 atoms of nitrogen on each side, so the coefficient of NO must be 40. The equation now becomes

$$3\ As_2S_5 + 40\ HNO_3 \rightarrow 3\ As_2O_5 + 15\ H_2SO_4 + 40\ NO + H_2O$$

Next we balance the oxygen atoms. There are 120 atoms of O on the left-hand side and this number must remain fixed. So far we have assigned 15 atoms of O to As_2O_5, 60 atoms to H_2SO_4, and 40 atoms to NO for a total of 15 + 60 + 40 = 115 atoms of O already assigned. The remaining five atoms (120 – 115 = 5 atoms left) require the coefficient of H_2O to be 5, and the balanced equation is

$$3\ As_2S_5 + 40\ HNO_3 \rightarrow 3\ As_2O_5 + 15\ H_2SO_4 + 40\ NO + 5\ H_2O$$

The hydrogen atoms are automatically balanced and can be used to check the coefficients. There are (2 x 15) + (5 x 2) = 40 H atoms on the right-hand side, which balances the 40 atoms on the left-hand side. Although this equation was more complex than Example 7, the balancing technique was the same. •

Parallel Problem: Balance the following equation by the oxidation-number method:

$$PbO_2 + MnSO_4 + H_2SO_4 \rightarrow PbSO_4 + HMnO_4 + H_2O$$

Ans: $5\ PbO_2 + 2\ MnSO_4 + 3\ H_2SO_4 \rightarrow 5\ PbSO_4 + 2\ HMnO_4 + 2\ H_2O$)

Now work Examples 12-8 and 12-9 in the text.

2. Balancing redox equations in aqueous solutions by the oxidation-number method

When a redox reaction occurs in acidic or basic solution, H^+, OH^-, and H_2O are often not included in the skeletal equation you are asked to balance. However, the amounts of these species are fixed by the reaction and are determined by applying the steps outlined in the text.

• EXAMPLE 9

Problem: The following reaction takes place in acidic solution. Complete and balance the equation by the oxidation-number method.

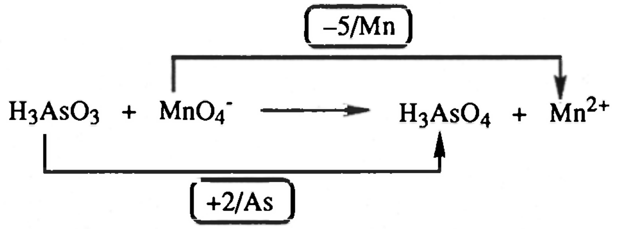
$$H_3AsO_3 + MnO_4^- \rightarrow H_3AsO_4 + Mn^{2+}$$

Solution: We will apply the steps outlined in the text for balancing redox equations in aqueous solution by the oxidation-number method.

Step 1:

$$\overset{\textcircled{+1}}{H_3}\ \overset{\textcircled{+3}}{As}\ \overset{\textcircled{-2}}{O_3} + \overset{\textcircled{+7}}{Mn}\ \overset{\textcircled{-2}}{O_4^-} \rightarrow \overset{\textcircled{+1}}{H_3}\ \overset{\textcircled{+5}}{As}\ \overset{\textcircled{-2}}{O_4} + \overset{\textcircled{+2}}{Mn^{2+}}$$

Step 2:



Step 4: $5\ H_3AsO_3 + 2\ MnO_4^- \rightarrow H_3AsO_4 + Mn^{2+}$

Step 5: $5\ H_3AsO_3 + 2\ MnO_4^- \rightarrow 5\ H_3AsO_4 + 2\ Mn^{2+}$

Step 7a: The net charge on the left-hand side is –2. The net charge on the right is +4. The left side is deficient +6 compared to the right. Since this is an acidic solution, we add 6 H^+ to the left to balance the charges.

$$6\ H^+ + 5\ H_3AsO_3 + 2\ MnO_4^- \rightarrow 5\ H_3AsO_4 + 2\ Mn^{2+}$$

Step 8: There are 15 + 8 = 23 O atoms on the left and 20 O atoms on the right. We need to add three H_2O molecules to the right-hand side to balance the oxygen.

$$6\ H^+ + 5\ H_3AsO_3 + 2\ MnO_4^- \rightarrow 5\ H_3AsO_4 + 2\ Mn^{2+} + 3\ H_2O$$

The hydrogen balance can be used as a check.

6 + (5 x 3) = 21 H on the left (5 x 3) + (2 x 3) = 21 H on the right •

Parallel Problem: The following reaction takes place in acidic solution. Complete and balance the equation by the oxidation-number method: $Mn_2^+ + MnO_4^- \rightarrow MnO_2$
Ans: $3\ Mn^{2+} + 2\ MnO_4^- + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+$

• EXAMPLE 10

Problem: Complete and balance the equation in Example 9 if it takes place in a basic solution.

Solution: Steps 1 through 6 are identical to those in Example 9 so we have

$$5\ H_3AsO_3 + 2\ MnO_4^- \rightarrow 5\ H_3AsO_4 + 2\ Mn^{2+}$$

Step 7b: The net charge on the left is –2 and on the right +4. The right-hand side is deficient by six negative charges. Since this is a basic solution we add 6 OH^- to the right to balance the charges.

$$5\ H_3AsO_3 + 2\ MnO_4^- \rightarrow 5\ H_3AsO_4 + 2\ Mn^{2+} + 6\ OH^-$$

Step 8: There are (3 x 5) + (2 x 4) = 23 O atoms on the left and (5 x 4) + 6 = 26 O atoms on the right. We add three molecules of H_2O to the left-hand side to balance oxygen.

$$5\ H_3AsO_3 + 2\ MnO_4^- + 3\ H_2O \rightarrow 5\ H_3AsO_4 + 2\ Mn^{2+} + 6\ OH^-$$

The hydrogen balance is used as a check.

(5 x 3) + (3 x 2) = 21 H on the left (5 x 3) + 6 = 12 H on the right •

Parallel Problem: Complete and balance the equation in the previous Parallel Problem if it takes place in a basic solution.
Ans: $3\ Mn_2^+ + 2\ MnO_4^- + 4\ OH^- \rightarrow 5\ MnO_2 + 2\ H_2O$

Now work through Examples 12-10 and 12-11 in the text.

3. *Balancing redox equations in aqueous solutions by the half-reaction or ion-electron method*

The second method of balancing redox equations does not use oxidation numbers as a balancing tool; rather, the overall reaction is divided into an oxidation half-reaction and a reduction half-reaction. These half-reactions are balanced separately and then added to get the overall equation, making sure the number of electrons lost in the oxidation half-reaction equals the number of electrons gained in the reduction half-reaction. The step-by-step procedure for this method is given in the text.

• EXAMPLE 11

Problem: The following reaction takes place in acidic solution. Complete and balance it by the half-reaction method.

$$Cr_2O_7^{2-} + 3\ H_2S \rightarrow Cr^{3+} + S$$

Solution: We will apply the steps for balancing redox reactions in aqueous solution by the half-reaction method.
Step 1: Step 1 requires that we recognize which species is oxidized and which is reduced. The easiest way to do this is to see which elements change in oxidation number. An increase in oxidation number is oxidation and a decrease is reduction. In our example, Cr is reduced from an oxidation number of +6 in $Cr_2O_7^{2-}$ to one of +3 in Cr^{3+}, while S

is oxidized from oxidation number –2 in H_2S to 0 in S. $Cr_2O_7^{2-}$ is the oxidizing agent or oxidant and H_2S is the reducing agent or reductant. The oxidation half-reaction includes the compounds containing sulfur in its different oxidation states.

$$H_2S \rightarrow S$$

and the reduction half-reaction shows Cr in its different oxidation states.

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Step 2: Now we balance each half-reaction according to the sequence of steps given in the text. First the reduction half-reaction. Balance the Cr atoms first. There are two Cr atoms on the left, so we need two on the right.

$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}$$

Now balance the oxygen by adding seven H_2O molecules to the right side to balance the seven oxygen atoms in $Cr_2O_7^{2-}$ on the left.

$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

The reaction occurs in acidic solution so we balance H by adding H^+ as needed to the left side. It takes 14 H^+ ions to balance the H_2O.

$$14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

Complete the balancing by adding e^- as needed to balance the charges. There is $+14 - 2 = +12$ net charge on the left and $2(+3) = +6$ net charge on the right. We are adding negative charges (electrons), so it takes $6e^-$ on the left to make the charges balance at +6 on the left and right.

$$14\,H^+ + Cr_2O_7^{2-} + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

Now we can balance the oxidation half-reaction. The sulfur atoms are already balanced and there are no oxygen atoms to balance so we proceed directly to Step 2c and add 2 H^+ ions to the right to balance H.

$$H_2S \rightarrow S + 2\,H^+$$

Now balance charges by adding 2 e^- to the right hand side.

$$H_2S \rightarrow S + 2\,H^+ + 2\,e^-$$

Step 3: Now we can combine the half-reactions. We must be sure the electron transfer is balanced; that is, the electrons lost in the oxidation half-reaction and the electrons gained in the reduction half-reaction must be equal. If we multiply the entire oxidation half-reaction by 3, there will be 6 e^- lost and 6 e^- gained. The two half-reactions can be added to give the overall reaction.

$$14\,H^+ + Cr_2O_7^{2-} + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

$$3\,H_2S \rightarrow 3\,S + 6\,H^+ + 6\,e^-$$

$$14\,H^+ + 3\,H_2S + Cr_2O_7^{2-} + 6\,e^- \rightarrow 3\,S + 6\,H^+ + 2\,Cr^{3+} + 7\,H_2O + 6\,e^-$$

Common species on both sides of the equation can be canceled just as in algebraic equations, so cancel 6 H^+ and 6 e^- from each side to leave the final equation.

$$8\,H^+ + 3\,H_2S + Cr_2O_7^{2-} \rightarrow 3\,S + 2\,Cr^{3+} + 7\,H_2O \;\bullet$$

Parallel Problem: The following reaction takes place in acidic solution. Complete and balance it by the half-reaction method. $H_2SO_3 + MnO_4^- \rightarrow SO_4^{2-} + Mn^{2+}$
Ans: $5\,H_2SO_3 + 2\,MnO_4^- \rightarrow 5\,SO_4^{2-} + 2\,Mn^{2+} + 4\,H^+ + 3\,H_2O$

• EXAMPLE 12

Problem: Use the half-reaction method to complete and balance the following reaction taking place in basic solution.

$$MnO_4^- + AsO_3^{3-} \rightarrow MnO_2 + AsO_4^{3-}$$

Solution: Apply the steps for the half-reaction method is given in the text.
Step 1: Mn is reduced from a +7 oxidation state to +4 and As is oxidized from +3 to +5. The reduction half-reaction is

$$MnO_4^- \rightarrow MnO_2$$

and the oxidation half-reaction is

$$AsO_3^{3-} \rightarrow AsO_4^{3-}$$

Step 2: Balance O, H, and charge for the reduction half-reaction first. To balance O add 2 H_2O to the right.

$$MnO_4^- \rightarrow MnO_2 + 2\,H_2O$$

The left side has four fewer H atoms. Since this is a basic solution we balance H by adding 4 H_2O to the left and 4 OH^- to the right.

$$MnO_4^- + 4\,H_2O \rightarrow MnO_2 + 2\,H_2O + 4\,OH^-$$

The duplicate H_2O molecules can be canceled. Now balance charges by adding 3 e^- to the left.

$$MnO_4^- + 2\,H_2O + 3\,e^- \rightarrow MnO_2 + 4\,OH^-$$

Now balance the oxidation half-reaction by the same steps. Balance O by adding 1 H_2O to the left.

$$AsO_3^{3-} + H_2O \rightarrow AsO_4^{3-}$$

Balance H by adding 2 H_2O to the right (it is deficient two H atoms) and 2 OH^- to the left.

$$AsO_3^{3-} + H_2O + 2\,OH^- \rightarrow AsO_4^{3-} + 2\,H_2O$$

Now cancel the duplicate H_2O and balance charges by adding 2 e^- to the right.

$$AsO_3^{3-} + 2\,OH^- \rightarrow AsO_4^{3-} + H_2O + 2\,e^-$$

Step 3: Balance the electron transfer by multiplying the entire reduction half-reaction by 2 and the oxidation half-reaction by 3 to get six electrons transferred. Add the half-reactions to get the overall equation.

Reduction: $2\,MnO_4^- + 4\,H_2O + 6\,e^- \rightarrow 2\,MnO_2 + 8\,OH^-$
Oxidation: $3\,AsO_3^{3-} + 6\,OH^- \rightarrow 3\,AsO_4^{3-} + 3\,H_2O + 6\,e^-$

$$2\,MnO_4^- + 3\,AsO_3^{3-} + H_2O \rightarrow 2\,MnO_2 + 3\,AsO_4^{3-} + 2\,OH^-$$

In the overall equation 6 e^-, 6 OH^-, and 3 H_2O have been canceled from both sides. •

Parallel Problem: Use the half-reaction method to complete and balance the following reaction taking place in basic solution: $HPO_3^- + H_2O_2 \rightarrow PO_4^{3-}$
Ans: $2\,HPO_3^- + H_2O_2 + 4\,OH^- \rightarrow 2\,PO_4^{3-} + 4\,H_2O$

Now work through Examples 12-12 and 12-13 in the text and try to balance some of the following equations. Answers are included after the Self Test answers for this chapter.

Balance redox reactions 1 to 10 by any method.

1 $As + HNO_3 \rightarrow As_2O_5 + NO + H_2O$
2 $H_2S + KMnO_4 + HCl \rightarrow S + KCl + MnCl_2 + H_2O$
3 $Fe_2(SO_4)_3 + KI \rightarrow FeSO_4 + K_2SO_4 + I_2$
4 $Sb_2S_3 + HNO_3 \rightarrow Sb_2O_5 + S + NO_2 + H_2O$
5 $C_2H_3OCl + Cr_2O_7^{2-} + H^+ \rightarrow Cr^{3+} + Cl_2 + CO_2 + H_2O$
6 $C_2O_4^{2-} + MnO_4^- + H^+ \rightarrow CO_2 + Mn^{2+} + H_2O$
7 $FeSO_4 + H_2SO_4 + KMnO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$
8 $Br_2 + NH_3 \rightarrow NH_4Br + N_2$
9 $F_2 + H_2O \rightarrow HF + O_3$
10 $Cu_2S + SO_4^{2-} + H^+ \rightarrow Cu^{2+} + H_2SO_3 + H_2O$

Reactions 11 to 17 occur in acidic solution. Complete and balance the equations by any method.

11 $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$
12 $MnO_2 + Cl^- \rightarrow Mn^{2+} + Cl_2$
13 $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$
14 $Ag^+ + AsH_3 \rightarrow H_3AsO_3 + Ag$
15 $C_2H_2 + MnO_4^- \rightarrow Mn^{2+} + CO_2$
16 $ClO_3^- + Br^- \rightarrow Cl^- + Br_2$
17 $MnO_4^- + H_2O_2 \rightarrow Mn^{2+} + O_2$

Reactions 18 to 22 occur in basic solution. Complete and balance the equations by any method.

18 $Br_2 \rightarrow Br^- + BrO_3^-$
19 $Cr(OH)_3 + Cl_2 \rightarrow Cl^- + CrO_4^{2-}$
20 $P_4 \rightarrow H_2PO_2^- + PH_3$
21 $CH_2O + Ag_2O \rightarrow Ag + HCO_2^-$
22 $Bi(OH)_3 + SnO_2^{2-} \rightarrow Bi + SnO_3^{2-}$

12-6 Solution stoichiometry

It is often necessary to know the relationship between the amounts of reactants and products in aqueous-solution reactions. An important example of the calculations involved in solution stoichiometry is the determination of the amounts of acid and base reacting in a neutralization reaction. These calculations are quite easy once you understand some basic relationships.

1. Acid-base stoichiometry by molarity

When the acid donates a single H^+ and the base donates a single OH^-, the stoichiometry is completely represented by the simple neutralization reaction:

$$H^+ + OH^- \rightarrow H_2O$$

An example of this type of reaction is

$$NaOH + HCl \rightarrow NaCl + H_2O$$

When a solution of either acid or base is completely neutralized, equal moles of acid and base are used in the reaction

$$\text{Moles acid} = \text{moles base}$$

Triprotic acids such as H_3PO_4 have three ionizable hydrogens. For this case the number of moles of base required for complete neutralization is three times the number of moles of acid present

$$\text{Moles base} = 3(\text{moles acid})$$

2. Determination of equivalent mass, equivalents, and normality

We could develop relationships for each different combination of acids and bases depending on how many hydrogens are donated by the acid and the number of hydroxides in the base, but we would have a different relationship for each type of problem using this approach. To get around this inconvenience the concepts of equivalents and normality were developed. Let us investigate the concepts of equivalents, equivalent mass, and normality and then apply them to neutralization reaction calculations.

An acid-base equivalent is defined as the mass in grams that supplies or reacts with one mole of H^+. An equivalent of base is one mole of available OH^-. Equivalents are related to moles as follows:

$$\underset{\text{(of acid or base)}}{\text{Equivalents}} = \underset{\text{(of acids or base)}}{\text{moles}} \times \underset{H^+ \text{ or } OH^- \text{ per molecule}}{\text{number of ionizable}}$$

Equivalents of acid or base = moles of acid or base x number of ionizable H^+ or OH^- per molecule.

If there is one ionizable H^+ (monoprotic acid), equivalents and moles are equal. If there are two ionizable H^+ per acid molecule (diprotic acid), there are two equivalents per mole; there are three equivalents per mole of triprotic acid. Similar relations hold for bases.

Equivalent mass is the mass in grams of one equivalent. It is related to molecular mass for acids and bases as follows:

$$\text{Equivalent mass} = \frac{\text{molecular mass}}{\text{number of ionizable } H^+ \text{ or } OH^-} = \frac{\text{g mol}^{-1}}{\text{equivalent mol}^{-1}} = \frac{\text{g}}{\text{equivalent}}$$

Normality is a concentration unit based on equivalents in the same way that molarity is based on moles

$$M = \text{molarity} = \frac{\text{moles}}{\text{liter}} \qquad N = \text{normality} = \frac{\text{equivalents}}{\text{liter}}$$

$$N = M(\text{equiv mol}^{-1})$$

In acid-base relationships the normality is the number of moles of available H^+ or OH^- per liter. The following examples will illustrate the use of these new terms.

• EXAMPLE 13

Problem: How many equivalents are there in (a) 1.00 mol of HCl? (b) 1.00 mol of H_2CO_3?
c) 1.00 mole of $La(OH)_3$?

Solution: We will work each part by a slightly different approach to illustrate the different relationships between moles and equivalents.
(a) HCl is a monoprotic acid, so there is one ionizable hydrogen per molecule or 1 equiv per mole

$$\text{Equivalents} = \text{mol of } H^+ = \text{mol HCl} \times \text{equiv mol}^{-1}$$

$$= 1.00 \text{ mol HCl} \times \frac{1 \text{ equiv}}{1 \text{ mol HCl}} = 1.00 \text{ equiv}$$

(b) H_2CO_3 is a diprotic acid, so there are two ionizable hydrogens per mole

$$\text{Equivalents} = \text{mol } H_2CO_3 \times \frac{\text{mol } H^+}{\text{mol } H_2CO_3}$$

$$= 1.00 \text{ mol } H_2CO_3 \times \frac{2 \text{ mol } H^+}{1 \text{ mol } H_2CO_3} - 2.00 \text{ equiv}$$

(c) $La(OH)_3$ has three ionizable hydroxide ions per mole, so there are 3 equiv per mole

$$\text{Equivalents} = \text{mol(No. of ionizable } OH^-) = 1.00 \text{ mol}(3 \text{ equiv mol}^{-1}) = 3.00 \text{ equiv} \quad \bullet$$

Parallel Problem: How many equivalents are there in (a) 2.00 mol of H_2SO_4 (b) 1.5 mol of $Al(OH)_3$ (c) 2.5 mol of KCl?
Ans: (a) 4 (b) 4.5 (c) 2.5

• EXAMPLE 14

Problem: What is the equivalent mass of $Mg(OH)_2$?

Solution: There are two ionizable OH^- per mol of $Mg(OH)_2$, so the equivalent mass is

$$\text{Equivalent mass} = \frac{\text{mol. wt.}}{\text{No. of ionizable OH}^-} = \frac{58.3 \text{ g mol}^{-1}}{2 \text{ equiv mol}^{-1}} = 29.2 \text{ g equiv}^{-1} \quad \bullet$$

Parallel Problem: What is the equivalent mass of $Al(OH)_3$?
Ans: 26 g equivalent^{-1}

• EXAMPLE 15

Problem: What is the normality of (a) 1.0 M HCl? (b) 2.0 M $Ca(OH)_2$?

Solution: (a) There is 1 equiv per mole for HCl so

$$N = M(\text{equiv mol}^{-1}) = 1.0\,M(1 \text{ equiv mol}^{-1}) = 1.0$$

Normality equals molarity for monoprotic acids or bases with one hydroxide.

(b) $Ca(OH)_2$ has 2 equiv of OH^- per mole

$$N = 2.0\,M(2 \text{ equiv mol}^{-1}) = 4.0\,N \quad \bullet$$

Parallel Problem: What is the normality of (a) 2.00 M H_2SO_4 (b) 1.5 M $Al(OH)_3$
Ans: (a) 4 N (b) 4.5 N

Now work through Examples 12-17 to 12-19 in the text.

3. *Use of normality in acid-base stoichiometry*

In all acid-base neutralization reactions the number of moles of H^+ equals the number of moles of OH^- at neutralization. Equivalents are the number of moles of available H^+ or OH^-, so the equivalents of acid always equal the equivalents of base at complete neutralization

$$\text{Number of equivalents of acid} = \text{Number of equivalents of base}$$

Since N = equiv liter^{-1}, the number of equivalents is

$$\text{Number of equivalents} = N \times \text{liters} = NV$$

where N is the normality of the solution and V is the volume in liters. Substituting NV for equivalents in the neutralization equation gives

$$(NV)_{\text{acid}} = (NV)_{\text{base}}$$

Since the equivalents of acid always equal the equivalents of base at complete neutralization, this equation is a general relationship and the single equation works for all acids and bases. Any one of the variables can be determined if the other three are known.

• EXAMPLE 16

Problem: How many milliliters of 0.200 *N* $Ca(OH)_2$ are needed to completely neutralize 40.0 mL of 0.150 *N* H_3PO_4?

Solution: The neutralization reaction in terms of normality works in all cases, so simply substitute the known values and solve for milliliters of $Ca(OH)_2$

$$(NV)_{Ca(OH)_2} = (NV)_{H_3PO_4}$$

$$V_{Ca(OH)_2} = V_{H_3PO_4} \frac{N_{H_3PO_4}}{N_{Ca(OH)_2}} = 40.0 \text{ mL} \frac{0.150\ N}{0.200\ N} = 30.0 \text{ mL} \quad \bullet$$

Parallel Problem: How many milliliters of 0.300 *N* NaOH are needed to completely neutralize 15.0 mL of 0.500 *N* H_2SO_4?
Ans: 25.0 mL

• EXAMPLE 17

Problem: How many milliliters of 0.200 *M* $Ca(OH)_2$ are needed to completely neutralize 40.0 mL of 0.150 *M* H_3PO_4?

Solution: We first convert the molarity values to normality

$$0.200\ M\ Ca(OH)_2 \frac{2 \text{ equiv } Ca(OH)_2}{1 \text{ mol}} = 0.400\ N$$

$$0.150\ M\ H_3PO_4 \frac{3 \text{ equiv } H_3PO_4}{1 \text{ mol}} = 0.450\ N$$

Now substitute these values into the neutralization equation as in the previous example

$$V_{Ca(OH)_2} = V_{H_3PO_4} \frac{N_{H_3PO_4}}{N_{Ca(OH)_2}} = 40.0 \text{ mL} \frac{0.450\ N}{0.400\ N} = 45.0 \text{ mL} \quad \bullet$$

Parallel Problem: How many milliliters of 0.350 *M* NaOH are needed to completely neutralize 25.0 mL of 0.250 *M* H_2SO_4?
Ans: 35.7 mL

Now work through Example 12-20 in the text.

4. *Use of equivalents and normality in stoichiometric calculations of electron-transfer reactions*

In the case of redox reactions an equivalent is defined as the mass in grams of a substance that accepts or donates one mole of electrons. It is related to moles by the equation

$$\text{Equivalents} = \text{moles (change in oxidation number of the compound)}$$

$$= \text{moles(electrons transferred)}$$

$$\text{Equivalent mass} = \frac{\text{molecular mass}}{\text{change in oxidation number}}$$

It should be apparent that since the change in oxidation number of an element can be different in different reactions, we need to specify the reaction to determine the equivalents of a compound in a redox reaction. The definition of normality is the same as for acid-base reactions and the equation

$$(NV)_{\text{oxidant}} = (NV)_{\text{reductant}}$$

holds for *all* redox reactions.

EXAMPLE 18

Problem: If 2.00 mol of ClO_3^- undergoes reaction to form Cl^-, how many equivalents of ClO_3^- reacted?

Solution: Cl changes from oxidation state +5 in ClO_3^- to –1 in Cl^-. The net change in oxidation number is –6. In calculating equivalents we use the numerical value of the change without regard to algebraic sign

$$\text{Equiv } ClO_3^- = 2 \text{ mol } ClO_3^- \frac{6\ e^- \text{ transferred}}{1 \text{ mol}} = 12 \text{ equiv}$$ •

Parallel Problem: If 3.00 mol of $Cr_2O_7^{2-}$ undergoes reaction to form Cr^{3+}, how many equivalents of $Cr_2O_7^{2-}$ reacted?
Ans: 18.0 equivalents

EXAMPLE 19

Problem: How many milliliters of 0.153 *M* $Cr_2O_7^{2-}$ are needed to react with 25.0 mL of 0.437 *M* H_2S if the $Cr_2O_7^{2-}$ is reduced to Cr^{3+} and the H_2S is oxidized to elemental sulfur?

Solution: If we change the molarity values to normality we can work the problem without having a balanced equation since one equivalent of oxidant reacts with one equivalent of reductant for all redox equations. The change in oxidation number of Cr is from +6 in $Cr_2O_7^{2-}$ to +3 in Cr^{3+} or –3 per Cr atom. Since there are two Cr atoms per $Cr_2O_7^{2-}$ the net change for $Cr_2O_7^{2-}$ is –6

$$N_{Cr_2O_7^{2-}} = 0.153\ M \frac{6 \text{ equiv}}{1 \text{ mol } Cr_2O_7^{2-}} = 0.918\ N$$

The change in oxidation state for S in H_2S is from –2 in H_2S to 0 in S, or +2 total change

$$N_{H_2S} = 0.437\ M \frac{2 \text{ equiv}}{1 \text{ mol } H_2S} = 0.874\ N$$

Now substitute into the equation

$$(NV)_{Cr_2O_7^{2-}} = (NV)_{H_2S}$$

and solve for $V_{Cr_2O_7{}^{2-}}$

$$V_{Cr_2O_7{}^{2-}} = V_{H_2S}\,\frac{N_{H_2S}}{N_{Cr_2O_7{}^{2-}}} = 25.0\text{ mL}\,\frac{0.874\,N}{0.918\,N} = 23.8\text{ mL} \quad \bullet$$

Parallel Problem: How many milliliters of 0.150 *M* $MnO_4{}^-$ are needed to react with 20.0 mL of 0.200 *M* $SO_3{}^{2-}$ if the $MnO_4{}^-$ is reduced to Mn^{2+} and the $SO_3{}^{2-}$ is oxidized to $SO_4{}^{2-}$?
Ans: 10.7 mL

Now work through Examples 12-21 to 12-23 in the text.

KEY TERMS

12-1 Acid-base reactions

Arrhenius acid: A substance which produces hydrogen ions in aqueous solution.

Arrhenius base: A substance which produces hydroxide ions in aqueous solution.

Autodissociation: Self-dissociation. The production of cations and anions by dissociation of solvent molecules without interaction with other chemical species.

Brønsted-Lowry acid: A proton donor.

Brønsted-Lowry base: A proton acceptor.

Complex ion: An ion consisting of a central atom surrounded by atoms or molecules called ligands bonded to it.

Complexation: The formation of a complex.

Conjugate acid: The acid formed by the addition of a proton to a base.

Conjugate base: The base formed by the removal of a proton from an acid.

Differentiating solvent: A solvent which discriminates among the strengths of acids or bases which are completely dissociated in water.

Leveling effect: The tendency for acids or bases stronger than the solvent to have the extent of dissociation controlled by the solvent so they all appear to have the same strength.

Lewis acid: An electron-pair acceptor.

Lewis base: An electron-pair donor.

Neutralization reaction: An Arrhenius acid-base reaction.

Precipitation reaction: A reaction which forms an insoluble compound.

Solvent-system definition: The extention of the Arrhenius concept of acids and bases to solvents besides water.

12-2 Precipitation and complexation reactions

Aqua complex: A complex with water molecules as ligands.

Coordination number: The number of bonds formed between the central ion and its ligands in a complex. Same as ligancy.

Ligancy: Same as coordination number.

Ligand: An atom, molecule, or ion bonded to the central atom in a complex.

12-3 Net equations for aqueous-solution reactions

Net ionic equation: An equation which shows only the chemical species undergoing a chemical change and not the spectator ions in a reaction.

Spectator ion: An ion present during a reaction which does not actually participate in the reaction.

12-4 Electronic bookkeeping, part II: oxidation numbers

Oxidation number: An approximation of the charge associated with valence-electron distribution in an atom based on a set of somewhat arbitrary but fixed rules.

Oxidation-reduction reaction: An electron transfer reaction. Same as redox reaction.

Redox reaction: Same as oxidation-reduction reaction.

12-5 Electron-transfer reactions

Half-reaction method: A method of balancing redox equations by combining the oxidation and reduction half-reactions. Same as ion-electron method.

Ion-electron method: Same as half-reaction method.

Oxidation: Loss of electrons.

Oxidizing agent: A chemical which gains electrons in a reaction.

Reducing agent: A chemical which loses electrons in a reaction.

Reduction: The gain of electrons.

12-6 Solution stoichiometry

Diprotic acid: An acid which can donate two protons.

Equivalent: The quantity of a substance which accepts or donates one mole of protons or one mole of electrons.

Equivalent mass: The mass in grams of one equivalent.

Normality: The number of equivalents per liter of solution.

Polyprotic acid: An acid which can donate more than one proton.

Triprotic acid: An acid which can donate three protons.

SELF TEST

True or False

_____ 1. All Arrhenius acids are also Brønsted acids.

_____ 2. According to the Lewis theory, an acid is an electron-pair donor.

_____ 3. In an aqueous solution of HCl, H_3O^+ is the strongest acid possible.

_____ 4. The reaction of an acid with an equivalent amount of base always gives a solution that is neutral.

_____ 5. There are always 2 equivalents per mole of $Ca(OH)_2$.

_____ 6. $NaNH_2$ is a base in liquid NH_3.

_____ 7. A weak acid forms a strong conjugate base.

_____ 8. In the neutralization of an acid and a base, the net ionic equation is always $H^+ + OH^- \rightarrow H_2O$.

_____ 9. Rb_2CO_3 is soluble.

_____ 10. In acid-base reactions, one equivalent of acid always reacts with one equivalent of base.

_____ 11. The net ionic equation for the reaction of $AgNO_3$ with $CaCl_2$ is: $Ag^{2+} + 2\,Cl^- \rightarrow AgCl_2$

_____ 12. According to the solubility guidelines, $NiCl_2$ is soluble in water.

_____ 13. Normality is equal to the equivalents of solute divided by the liters of solution.

_____ 14. The normality of a solution of MnO_4^- depends on the oxidation state of the manganese in the end products of the reaction.

_____ 15. Equivalent mass is equal to the molecular mass of a compound divided by the number of electrons or hydrogen or hydroxide ions exchanged per mole of the compound.

Completion

16. The Arrhenius concept of acids and bases is generally limited to ____________ solutions.

17. The reaction 2 $H_2O \rightarrow H_3O^+ + OH^-$ is an example of _______________.

18. $CaSO_4$ is _____________ (soluble, insoluble).

19. Most hydroxides are ________________ (soluble, insoluble).

20. The oxidation number of Cl in $HClO_2$ is ___________________.

21. The oxidation number of S in H_2SO_4 is ___________________.

22. Oxidation occurs when a substance ___________ (loses, gains) electrons or _________ (increases, decreases) in oxidation number.

23. $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$ is a(an) _______________(oxidation, reduction) reaction.

24. Mixing solutions of $Sr(NO_3)_2$ and Na_2CO_3 ___________ (will, will not) result in a chemical reaction.

25. There are ____________ equiv per mole of $La(OH)_3$.

26. A 0.400 *M* solution of H_2SO_4 would be _____________ *N*.

27. A 0.200 *M* solution of $FeCl_3$ reacts to form Fe. The normality of the $FeCl_3$ solution was _____________.

28. The net ionic equation for the reaction of K_2SO_4 with $Pb(NO_3)_2$ is ________.

29. The number of equivalents in 3.00 liters of 1.50 *M* H_2SO_4 is _____________.

30. According to the following reaction $H_2O + NH_2^- \rightarrow NH_3 + OH^-$ ___________ (OH^-, NH_2^-) is a stronger base than _______________ (OH^-, NH_2^-).

Multiple Choice

31. Which of the following is a weak electrolyte?
(a) $Ca(OH)_2$ (b) H_2SO_4 (c) Na_2CO_3 (d) H_2CO_3

32. When solutions of $Pb(NO_3)_2$ and Rb_2SO_4 are mixed, the precipitate that forms is:
(a) $RbNO_3$ (b) $PbSO_4$ (c) both $RbNO_3$ and $PbSO_4$
(d) no precipitate forms

33. Which of the following ions all form insoluble compounds with Ca^{2+}?
(a) NO_3 , $C_2H_3O_2^-$ (b) F^-, SO_4^{2-}, CO_3^{2-}
(c) Cl^-, PO_4^{3-}, OH^- (d) Br^-, SO_3^{2-}

34. In the redox reaction $Ca + 2\,H_2O \rightarrow Ca(OH)_2 + H_2$, the oxidant is
(a) Ca (b) H_2O (c) $Ca(OH)_2$ (d) H_2

35. What is the sum of the coefficients when the following redox equation is balanced?
$$AuCl_4^- + AsH_3 + H_2O \rightarrow H_3AsO_3 + H^+ + Au + Cl^-$$
(a) 10 (b) 14 (c) 19 (d) 23

36. How many molecules of water are required to balance the following redox equation in acidic solution?
$$HBr + MnO_4^- \rightarrow Br_2 + Mn^{2+}$$
(a) 2 (b) 3 (c) 5 (d) 8

37. Which set of coefficients will balance the following half-reaction?
$$H^+ + XeO_3 + e^- \rightarrow Xe + H_2O$$
(a) 4, 1, 4, 1, 2 (b) 12, 2, 2, 2, 6 (c) 6, 1, 6, 1, 3 (d) 2, 1, 2, 1, 1

38. The oxidation number of Cl in the compound $KClO_4$ is
(a) −1 (b) +3 (c) +5 (d) +7

39. The oxidation number of carbon in the compound CH_4 is
(a) 0 (b) +2 (c) +4 (d) −4

40. The oxidation number of lead in the compound Pb_3O_4 is
(a) $+\frac{4}{3}$ (b) +2 (c) $+2\frac{2}{3}$ (d) +4

41. How many milliliters of 0.200 *M* $Ca(OH)_2$ are required to neutralize 25.0 mL of 0.150 *M* HNO_3?
(a) 9.38 (b) 18.8 (c) 33.3 (d) 66.7

42. How many equivalents are in 3.00 mol of H_2SO_4?
(a) 1.00 (b) 2.00 (c) 3.00 (d) 6.00

43. HNO_3 is reduced to NO in a chemical reaction. If the HNO_3 was 2.00 *M*, what was its normality?
(a) 6.00 (b) 4.00 (c) 2.00 (d) 1.00

44. What is the equivalent mass of Na_2CO_3 in the reaction
$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl?$$
(a) 26.5 (b) 53.0 (c) 106.0 (d) 212.0

45. How many milliliters of 0.200 *N* $KMnO_4$ would be required to oxidize 30.0 mL of 0.250 *N* AsH_3?
(a) 37.5 (b) 16.0 (c) 1.50
(d) cannot tell without knowing the products of the reaction

Chapter 13

CHEMICAL KINETICS

CHAPTER OVERVIEW

13-1 Reaction rates and mechanisms: a preview

Chemical kinetics is the study of the rate or speed of chemical reactions and the step-by-step mechanism by which they proceed. Reaction rate is the speed of production of products or disappearance of reactants and is measured in units of concentration per time, usually moles per liter per second (mol L^{-1} s^{-1}). As reactant molecules are consumed in the reaction, their concentration decreases and the reaction gradually slows. The reaction rate depends mainly on the chemical properties and concentration of the reactants, and the temperature. Knowledge of the reaction rate allows calculation of the concentration of reactants at any time and of the length of time needed to reach a given concentration of reactants or products. It also helps us understand the mechanism of a reaction.

A knowledge of the Calculus will help in understanding the symbolism used in this section but is not essential to the concepts presents. If you have not yet had the Calculus, just read

$$\frac{\Delta[\mathrm{A}]}{\Delta t} \quad \text{or} \quad \frac{d[\mathrm{A}]}{dt}$$

as the rate of change of concentration of A with time.

$$\text{Rate} = -\frac{d[\mathrm{A}]}{dt}$$

simply says "the reaction rate is equal to the decrease in concentration of A per unit time." Note that the rate can be expressed as a function of the concentration of any reactant or product.

13-2 The rate law

A rate law is a mathematical equation that relates rate to the concentrations of reacting species, for example

$$\text{Rate} = -\frac{d[\mathrm{A}]}{dt} = k\,[\mathrm{A}]\,[\mathrm{B}]$$

The minus sign shows that [A] is decreasing as time increases. The term k is an important constant called the rate constant. Its magnitude reveals how fast the reaction proceeds at any given temperature. Its variation with temperature reveals much about the energy changes of a reaction, as we shall see later.

The concept of order of a reaction is simple, but make sure you understand it thoroughly. We will spend considerable time determining order of reactions. Knowledge of the order gives us basic clues about the reaction mechanism.

There are several techniques for finding values for reaction order and the rate constant depending on the type of data available. If you have rate data as a function of concentration (such as in Example 13-1 in the text) the method of initial rates works well. If you have concentration data as a function of time, a linear regression or graphical method is best. Reaction order can have any value from 0 to 3, but first-order reactions are most common.

13-3 Collision theory

Collision theory assumes that gas molecules must collide in order to react and only some of the collisions actually result in chemical reactions. According to this theory, the rate of reaction depends on the concentrations of the reactants; the frequency of collisions, Z; the fraction of molecules that have enough energy to react when they collide, $e^{-E_a/RT}$; and the probability that the molecules have the correct orientation, represented by the steric factor, p. Altogether this gives

$$\text{Rate} = pe^{-E_a/RT}Z_0[A][B]$$

from which $k = pe^{-E_a/RT}Z_0$ and can be calculated from theory. The collision theory works fairly well for very simple molecules, but there is no way to calculate p if the reacting molecules are complex and so use of the collision theory is limited.

The Arrhenius equation is very important because it allows determination of the energy of activation from measurements of the rate constant at different temperatures (Text Examples 13-3 and 13-4). The activation energy E_a is the energy the reactants must have in order for the reaction to occur. It is usually in the range of 40 to 200 kJ mol^{-1}.

13-4 The activated complex

The activated complex is an intermediate state between reactants and products. It occurs at the top of the energy hill in Figures 13-12 and 13-13. Those figures show the energy relationships during a chemical reaction in a graphical manner and help us visualize the energy changes during reactions.

13-5 Reaction mechanisms: an introduction

There is a saying "The only simple chemical reaction is one that hasn't been studied." Nearly all reactions take place through a series of steps or elementary reactions. Almost always, one of these steps is much slower than the others and limits the reaction rate. This rate-determining step is closely correlated with kinetic measurements. In fact, if the kinetics predicted by the mechanism through the rate-determining step do not agree with the kinetic rate law determined experimentally, the mechanism should be discarded. In this way kinetics is a guide to determining the correct mechanism and to better understanding (and hence controlling) of chemical reactions.

13-6 Catalysis

A catalyst is a substance that speeds a chemical reaction but can be recovered intact when the reaction is over. Catalysts act by lowering the E_a, thus allowing more molecules to react at lower temperatures. In the pharmaceutical industry drugs are produced that are very sensitive to heat. They would be destroyed by the temperatures needed to speed the reactions to the point at which the products could be manufactured at a commercially reasonable rate. Catalysts allow the production to proceed at a reasonable rate at temperatures low enough to preserve the product. Enzymes are very effective catalysts for biochemical reactions involving very large molecules that would have difficulty orienting themselves correctly for reaction without the enzyme.

Catalysts are generally highly specific to a particular reaction, so each new need for a catalyst is a new challenge to research. A homogeneous catalyst is present in the same phase as the reactant molecules and functions by forming a reactive intermediate with one reactant which, in turn, reacts with the other reactant to form products. A heterogeneous catalyst is in a different phase than the reactants and usually provides a surface on which the reactants can make contact. Inhibitors are substances that slow down a reaction. Promoters are substances that make a catalyst more effective.

KEY EQUATIONS

13-2 The rate law

Order	Rate law	Concentration vs. time relationship	$t_{1/2}$	Linear plot to test order
0	Rate $= \frac{-d[A]}{dt} = k_0$	$[A]_0 - [A] = k_0t$	$\frac{[A]_0}{2k_o}$	[A] vs. t
1	Rate $= \frac{-d[A]}{dt} = k_1[A]$	$\ln[A] = \frac{-k_1t}{2.303} + \ln[A]_0$	$\frac{0.693}{k_1}$	$\ln$[A] vs. t
2	Rate $= \frac{-d[A]}{dt} = k_2[A]^2$	$\frac{1}{[A]} = k_2t + \frac{1}{[A]_0}$	$\frac{1}{k_2[A]_0}$	$\frac{1}{[A]}$ vs. t

13-3 Collision theory

The rate of a biomolecular reaction according to collision theory is

$$\text{Rate} = pe^{-E_a/RT}Z_0[A][B]$$

from which it follows

$$k = pe^{-E_a/RT}Z_0$$

The Arrhenius equation is

$$k = Ae^{-E_a/RT}$$

The Arrhenius equation may be expressed in a useful form for calculating E_a from rate constant values at two different temperatures as

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note how closely this form of the equation resembles the Clausius-Clapeyron equation of Chapter 10.

LEARNING OBJECTIVES

As a result of studying Chapter 13, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 228 of this *Study Guide*.

13-1 Reaction rates and mechanisms: a preview

1. List the factors that determine the rate of a chemical reaction. (Text Probs. 13-2, 13-4) (Self Test 3, 18, 31)
2. Determine the average rate over a given time interval from a plot of concentration as a function of time. (Text Probs. 13-1, 13-8, 13-10) (Self Test 20, 39)
3. Determine the instantaneous rate from the slope of a tangent to a concentration versus time plot. (Text Probs. 13-1, 13-9) (Self Test 19)
4. Express the rate of reaction in terms of the change of concentration of any reactant or product with time. (Text Probs. 13-3, 13-5 to 13-7) (New Skills Example 1, 2; Self Test 1, 13, 32, 34)

13-2 The rate law

1. Write rate laws to show the relationship between concentration and reaction rate. (Text Probs. 13-12, 13-13) (Self Test 12, 16)
2. Identify the order of a reaction from the rate law. (Text Prob. 13-14) (Self Test 2, 5, 7, 17)
3. Write a rate law given the order of reaction of each reacting species. (Self Test 35)
4. Determine the initial rate of a reaction from a concentration versus time plot such as Figure 13-4 in the text.
5. Determine the order of reaction and rate constant using the method of initial rates. (Text Example 13-1; Text Probs. 13-15 to 13-17, 13-53, 13-54) (New Skills Examples 3, 4; Self Test 14, 22, 36)
6. Test reaction rate data for first- or second-order kinetics by a graphical method using concentration versus time data and determine the rate constant. (Text Example 13-2; Text Probs. 13-18 to 13-20, 13-55, 13-56) (New Skills Section 13-2:2; Self Test 8, 22, 24, 37, 38)
7. Calculate the half-life of first- and second-order reactions. (Text Probs. 13-21, 13-22) (New Skills Example 5; Self Test 23, 40)
8. Calculate the concentration of reactants remaining after a given time, and the time required for concentrations to change by a given amount for first- and second-order reactions. (Text Probs. 13-23, 13-24, 13-57, 13-58) (New Skills Example 6; Self Test 33, 41, 42)

13-3 Collision theory

1. Compare the relationship between molecularity and reaction order for general reactions and elementary processes. (Text Prob. 13-25) (Self Test 9)
2. List three factors that affect the efficiency with which collisions result in chemical reactions. (Text Probs. 13-27 to 13-30) (Self Test 25)
3. Show how collision theory is used to predict the correct form of rate laws for biomolecular gas reactions.
4. Show how reaction rate depends on activation energy. (Text Probs. 13-31, 13-35 to 13-37, 13-39) (Self Test 6)
5. Use the Arrhenius equation to calculate activation energy. (Text Examples 13-3, 13-4; Text Probs. 13-32, 13-38, 13-60) (Self Test 21, 43, 45)

6. Use the Arrhenius equation to calculate the rate constant when the activation energy and rate constant at a second temperature are known. (Text Probs. 13-33, 13-34) (New Skills Example 7; Self Test 15, 21, 44)

13-4 The activated complex

1. Make a sketch which shows the activated complex as an intermediate state between reactants and products. (Text Prob. 13-39) (Self Test 27)
2. Use a plot of change in potential energy during a reaction (such as Figure 13-12 in the text) to show the relationships among energy of activation, energy of reaction, and energy of the reactants and products. (Text Probs. 13-40 to 13-43, 13-51) (Self Test 28)

13-5 Reaction mechanisms: an introduction

1. Write rate laws for elementary processes. (Text Prob. 13-44)
2. Relate the kinetics of an overall reaction to the kinetics of the rate-determining step. (Text Prob. 13-45) (Self Test 10, 26)
3. Show how experimental kinetic data can be used to test the validity of a proposed reaction mechanism. (Text Prob. 13-48)

13-6 Catalysis

1. Give an example of a catalyst and explain how it functions. (Text Probs. 13-46, 13-47) (Self Test 30)
2. Illustrate the difference between a homogeneous and a heterogeneous catalyst. (Text Prob. 13-49) (Self Test 29)
3. Make a sketch showing how enzymes function as catalysts for biochemical reactions.

NEW SKILLS

13-1 Reaction rates and mechanisms: a preview

1. Determining rates from concentration-time data

You will be expected to understand the concepts of average rate and instantaneous rate and be able to determine both of them from data showing how concentration changes as a reaction proceeds (concentration versus time data). Figure 13-1 in the text shows how this is done graphically. Text Probs. 13-8 and 13-9 will give you practice in applying these techniques.

2. Expressing rates in terms of concentration changes

You can express the rate of reaction in terms of change of concentration of any reactant or product with time. For the general reaction

$$aA + bB \rightarrow cC + dD$$

the rates in terms of each species are related as follows

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

• EXAMPLE 1

Problem: Write an expression for the rate of the following reaction in terms of each chemical species in the reaction.

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$$

Solution: Using the relationship for rates of the general equation as a guide, we can write the required relations. The values of *a, b, c,* and *d* are the stoichiometric coefficients from the balanced chemical equation.

$$\text{Rate} = -\frac{d[C_3H_8]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{3}\frac{d[CO_2]}{dt} = \frac{1}{5}\frac{d[H_2O]}{dt} \quad \bullet$$

Parallel Problem: Write a rate expression for the following reaction in terms of each species in the reaction: $2\,NH_3 \rightleftarrows N_2 + 3\,H_2$

Ans: $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

• EXAMPLE 2

Problem: The rate in terms of O_2 in the previous example is

$$-\frac{d[O_2]}{dt} = 1.2 \times 10^{-4}\,M\,s^{-1}$$

What is the rate in terms of CO_2?

Solution: Using the rate relationships from the previous example we can see

$$-\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{3}\frac{d[CO_2]}{dt}$$

Solving for $d[CO_2]/dt$ and substituting the value given for O_2, we find

$$\frac{d[CO_2]}{dt} = -\frac{3}{5}(-1.2 \times 10^{-4}\,M\,s^{-1}) = 7.2 \times 10^{-5}\,M\,s^{-1} \quad \bullet$$

Parallel Problem: The rate in terms of H_2 in the previous Parallel Problem is

$$-\frac{d[H_2]}{dt} = 1.60 \times 10^{-3}\,M\,s^{-1}$$

What is the rate in terms of NH_3?

Ans: $\frac{d[NH_3]}{dt} = 1.07 \times 10^{-3}\,M\,s^{-1}$

Problems 13-3, 13-5, and 13-6 in the text are similar.

13-2 The rate law

1. Determining the order of a reaction by the method of initial rates

Experimentally, we measure how concentration changes with time. In Section 13-1 we used these experimental measurements to determine rates. In this section we will go one step further by using rates to find the order of a reaction. One technique for doing this is the method of initial rates. The initial rates of several experiments are determined as shown in Figure 13-2 in the text. If the experiments are arranged so the initial concentrations increase in a regular manner, the order can often be determined by inspection of the data.

• EXAMPLE 3

Problem: A set of experiments was run for the reaction A + B → C. Initial rates were determined for each experiment as follows:

Experiment	Initial [A], *M*	Initial [B], *M*	Initial rate, $M\ s^{-1}$
1	1.0	1.0	2.0×10^{-3}
2	2.0	1.0	4.0×10^{-3}
3	2.0	2.0	16.0×10^{-3}

Determine the order of reaction for each reactant and the overall order.

Solution: The rate law for the reaction must take the general form

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y$$

The experiments were designed so each reactant could be studied separately. In experiments 1 and 2, [B] is held constant so the change in rate is due only to [A]. As [A] doubles, the rate doubles. They are directly proportional so $x = 1$ and the reaction is first order with respect to A. In experiments 2 and 3, [A] is held constant so the change in rate is due only to [B]. As [B] doubles, the rate increases fourfold; since $4 = 2^y$ then $y = 2$, and the reaction is second order with respect to B and third order overall. •

Parallel Problem: The following rate data were obtained for the reaction $2\ \text{AB} + \text{C}_2 \rightarrow 2\ \text{ABC}$

Experiment	Initial [AB], *M*	Initial $[\text{C}_2]$, *M*	Initial rate $M\ s^{-1}$
1	0.01	0.01	1.0×10^{-2}
2	0.01	0.02	2.0×10^{-2}
3	0.02	0.01	4.0×10^{-2}

Determine the order of reaction for each reactant and calculate the value of the reaction rate constant. Write the rate law for the reaction.

Ans: $\text{Rate} = 1 \times 10^4[\text{AB}]^2[\text{C}_2]$

• EXAMPLE 4

Problem: Write the rate law for the reaction A + B → C from the following initial rate data:

Experiment	Initial [A], *M*	Initial [B], *M*	Initial rate, $M\ s^{-1}$
1	0.734	0.0171	1.23×10^{-3}
2	0.734	0.0233	1.44×10^{-3}
3	0.304	0.0233	3.84×10^{-4}

Solution: Simple proportionalities cannot be readily seen in these data so we will use a quantitative approach. The rate law is of the general form

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y$$

We need to determine numerical values of k, x, and y to write the rate law. There are three unknowns and we can write three equations from the experimental data to find values of k, x, and y. Substituting the experimental data into the general form of the rate law gives

Experiment 1: $\text{Rate}_1 = 1.23 \times 10^{-3} = k(0.734)^x(0.0170)^y$

Experiment 2: $\text{Rate}_2 = 1.44 \times 10^{-3} = k(0.734)^x(0.0233)^y$

Experiment 3: $\text{Rate}_3 = 3.84 \times 10^{-4} = k(0.304)^x(0.0233)^y$

Dividing the equation for experiment 1 by the equation for experiment 2 gives

$$\frac{1.23 \times 10^{-3}}{1.44 \times 10^{-3}} = \frac{k(0.0734)^x(0.0170)^y}{k(0.0734)^x(0.0233)^y}$$

This simplifies to

$$0.854 = (0.730)^y$$

Now take logarithms of both sides.

$$\ln 0.854 = y \ln 0.730$$

$$y = \frac{\ln 0.854}{\ln 0.730} = \frac{-0.158}{-0.315} = 0.502$$

So the reaction is 0.5 order in B. We can use experiments 2 and 3 in the same manner to find x. Divide the equation for experiment 2 by the equation for experiment 3.

$$\frac{1.44 \times 10^{-3}}{3.84 \times 10^{-4}} = \frac{k(0.734)^x(0.0233)^y}{k(0.304)^x(0.0233)^y}$$

This simplifies to

$$3.75 = (2.41)^x$$

Take logarithms of both sides.

$$\ln 3.75 = x \ln 2.41$$

$$x = \frac{\ln 3.75}{\ln 2.41} - \frac{1.32}{0.880} = 1.50$$

The reaction is 1.5 order in A. We can use the values of x and y in any of the rate equations to find k. Using the rate equation for experiment 3

$$3.84 \text{ x } 10^{-4}\, M \text{ s}^{-1} = k(0.304\, M)^{1.5}(0.0233\, M)^{0.5}$$

Solving for k

$$k = \frac{3.84 \text{ x } 10^{-4}\, M \text{ s}^{-1}}{(0.304\, M)^{1.5}\,(0.0233\, M)^{0.5}} = \frac{3.84 \text{ x } 10^{-4}\, M \text{ s}^{-1}}{0.168\, M^{1.5}(0.153\, M^{0.5})} = 0.0149\, M^{-1} \text{ s}^{-1}$$

The complete rate law is

$$\text{Rate} = 0.0149\, M^{-1} \text{ s}^{-1}\, [\text{A}]^{1.5}[\text{B}]^{0.5} \bullet$$

Parallel Problem: Write the rate law for the reaction A + 2 B → C using the following initial rate data:

Experiment	Initial [A], *M*	Initial [B], *M*	Initial rate, M s^{-1}
1	0.500	0.200	$1.67 \text{ x } 10^{-4}$
2	0.500	0.450	$5.65 \text{ x } 10^{-4}$
3	0.300	0.450	$4.39 \text{ x } 10^{-4}$

Ans: Rate = $1.06 \text{ x } 10^{-3}\, [\text{A}]^{1.5}[\text{B}]^{0.5}$

Now work through Example 13-1 in the text. For additional practice try Problems 13-15 to 13-17 in the text.

2. *Determination of order of a reaction by graphical methods*

When it is suspected that a reaction is zero, first, or second order, we can test the experimental data directly, without determining rates, by a graphical technique. A linear plot of concentration versus time shows the reaction is zero order. When the logarithm of concentration is plotted against time and a straight line is obtained, the reaction is first order. If a straight line is obtained by plotting 1/[A] versus time, the reaction must be second order. For any given reaction only one of these plots can result in a straight line; the others must be curved. Figure 13-5 in the text shows a straight-line plot of a first-order reaction, while Figure 13-6 is a linear plot of a second-order reaction. In each case the rate constant is found from the slope of the graph. Example 13-2 in the text illustrates this technique. Problem 13-18 in the text is designed to give further practice in using this method of determining order of reaction.

3. *Half-life*

The half-life of a reaction is the time it takes the concentration to decrease to half its initial values:

$$t_{1/2} = \frac{0.693}{k_1} \qquad \text{for a first-order reaction}$$

$$t_{1/2} = \frac{1}{k_2[\text{A}]_0} \qquad \text{for a second-order reaction}$$

$$t_{1/2} = \frac{[A]_0}{2k_0} \quad \text{for a zero-order reaction}$$

• EXAMPLE 5

Problem: The rate constant for the first-order reaction A → B + C is 0.0375 s^{-1} at 25°C. (a) What is the half-life of the reaction? (b) How long would it take the concentration of A to decrease from an initial value of 0.800 *M* to 0.100 *M*?

Solution: (a) The half-life of a first-order reaction is

$$t_{1/2} = \frac{0.693}{k_1}$$

Substituting the value for *k* gives

$$t_{1/2} = \frac{0.693}{0.0375\ s^{-1}} = 18.5\ s$$

(b) In going from 0.800 to 0.100 *M* the concentration is reduced by half three times, so the total time is three half-lives

$$t = 3t_{1/2} = 3(18.5\ s) = 55.5\ s \quad \bullet$$

Parallel Problem: The rate constant for the reaction A → 2 B is 3.73 x 10^{-3} s^{-1} at 35°C. (a) What is the half-life of the reaction? (b) The initial concentration of A is 1.000 *M*. What would be the concentration of A after four half-lives?
Ans: $t_{1/2}$ = 186 s [A] = .0625 *M*

Problems 13-21 to 13-23 in the text will give you practice using half lives.

4. *Calculation of concentration of a reactant at any time during a reaction*

Mathematical relationships permitting calculations of concentration of reactants at any time during a reaction are given in Table 13-1 in the text and summarized in the Key Equations section of this chapter in the *Study Guide*. These equations can be used to find the concentration of reactants remaining after a given time has passed if the concentration at time zero, $[A]_0$, and the rate constant are known for zero-, first-, or second-order reactions. Any of the variables in these equations can be determined if the others are known.

• EXAMPLE 6

Problem: The reaction A → B + C is first order with $k = 3.75 \times 10^{-4}\ s^{-1}$ at 25°C. (a) If the initial concentration of A is 0.500 *M*, what will be the concentration after 1 h? (b) How long will it take for the concentration of A to decrease from 0.500 to 0.00226 *M*?

Solution: The equation relating concentration and time for a first-order reaction is

$$\ln[A] = -k_1 t + \ln[A]_0$$

We can substitute the given values into this equation and solve for [A].

$$\ln[\mathrm{A}] = -3.75 \times 10^{-4}\ \mathrm{s}^{-1}(3600\ \mathrm{s}) + \ln 0.500$$

$$= 1.350 + (-0.693) = -2.043$$

$$[\mathrm{A}] = e^{-2.043} = 0.130\,M$$

(b) Solve the concentration-time equation for first-order reactions for *t*.

$$t = \frac{1}{k_1} \ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]}$$

Substitute the values given and solve for *t*.

$$t = \frac{1}{3.75 \times 10^{-4}\ \mathrm{s}^{-1}} \ln \frac{0.500}{0.00226}$$

$$= \frac{5.399}{3.75 \times 10^{-4}\ \mathrm{s}^{-1}} = 1.44 \times 10^{4}\ \mathrm{s} \quad \text{or} \quad 4.00\ \mathrm{h}$$ •

Parallel Problem: The reaction A → B is second order with $k = 3.54 \times 10^{-3}\ \mathrm{L\ mol^{-1}\ s^{-1}}$ at 25°C. (a) If the initial concentration of A is 0.300 *M*, what will be the concentration after 1 hour? (b) How long will it take the concentration of A to decrease from 0.300 *M* to 0.00740 *M*?
Ans: (a) 0.0628 *M* (b) 48.5 min

Problem 13-24 in the text is similar to this.

13-3 Collision theory

Determination of E_a and k using the Arrhenius equation

Probably the most useful form of the Arrhenius equation in calculations is

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

It can be used to find k_1, k_2, T_1, T_2, or E_a given values for the other four variables. The two most common uses are (1) calculating E_a when the rate constant is known at two temperatures and (2) calculating the rate constant at some desired temperature when it is given at a different temperature and E_a is known. Example 13-4 in the text uses two values of *k* in the Arrhenius equation to find E_a. Example 13-3 shows a graphical method for making this kind of calculation. Problems 13-38 and 13-60 in the text can be worked by either method.

• EXAMPLE 7

Problem: A certain reaction has $E_a = 90.0\ \mathrm{kJ\ mol^{-1}}$. The rate constant for this reaction is $4.17 \times 10^{-3}\ \mathrm{s}^{-1}$ at 35°C. What is the value of the rate constant at 75°C?

Solution: Using the Arrhenius equation we can substitute the given values and solve for k_2.

$$k_1 = 4.17 \times 10^{-3}\ \mathrm{s^{-1}}$$
$$T_1 = 35^\circ\mathrm{C} + 273 = 308\ \mathrm{K}$$
$$T_2 = 75^\circ\mathrm{C} + 273 = 348\ \mathrm{K}$$
$$E_a = 90{,}000\ \mathrm{J\ mol^{-1}}$$
$$R = 8.31\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$\ln \frac{k_2}{4.17 \times 10^{-3}} = \frac{90{,}000\ \mathrm{J\ mol^{-1}}}{(8.31\ \mathrm{J\ mol^{-1}\ K^{-1}})} \left(\frac{1}{308\ \mathrm{K}} - \frac{1}{348\ \mathrm{K}}\right) = 4.042$$

$$\frac{k_2}{4.17 \times 10^{-3}} = e^{4.042} = 56.9$$

$$k_2 = 56.9(4.17 \times 10^{-3}) = 0.237\ \mathrm{s^{-1}}\ \bullet$$

Parallel Problem: A certain reaction has $E_a = 75.0\ \mathrm{kJ\ mol^{-1}}$. The rate constant for this reaction is $5.86 \times 10^{-4}\ \mathrm{s^{-1}}$ at 30°C. What is the value of the rate constant at 80°C? *Ans:* $3.96 \times 10^{-2}\ \mathrm{s^{-1}}$

Problems 13-33 and 13-34 in the text involve similar calculations.

KEY TERMS

13-1 Reaction rates and mechanisms: a preview

Mechanism: A sequence of steps or elementary processes by which a chemical reaction takes place.

Reaction rate: The time rate of change of concentration of a reactant or product in a reaction.

13-2 The rate law

Half-life: The time necessary for the concentration of reactants to decrease to one-half the initial values.

Initial-rate method: A technique for determining the order of a reaction by using the relation between reactant concentrations and reaction rate at the start of the reaction.

Order of reaction: The exponent on a concentration term in the rate law. The overall order is the sum of all such exponents in the rate law.

Rate constant: The constant of proportionality in a rate law.

Rate law: The algebraic statement of the dependence of the rate of a reaction upon the concentration of chemical species in the reaction.

13-3 Collision theory

Activation energy: The kinetic energy which reactants must have in order to form the activated complex.

Arrhenius plot: A plot of the logarithm of the rate constant against reciprocal absolute temperature. Arrhenius plots are useful for determining the activation energy of the reaction.

Bimolecular process: An elementary process in which the activated complex is formed by the collision of two particles.

Collision frequency: The number of collisions between reactant particles per second, denoted by Z.

Collision theory: A theory of reaction rates based on the collision of molecules and the kinetic molecular theory of gases.

Diffusion-controlled reaction: A reaction in which the rate limiting step involves the diffusion of reactants.

Elementary process: A single step in a reaction mechanism.

Encounter: The time during which reactant molecules are trapped by a solvent-molecule cage in a liquid-phase reaction.

Frequency factor: The constant of proportionality between the rate constant and the exponential factor in the Arrhenius equation.

Maxwell-Boltzman distribution: The relation between kinetic energy and the fraction of molecules having a given kinetic energy.

Molecularity: The number of particles which collide simultaneously to form the activated complex.

Probability factor: The fraction of molecules colliding with the correct geometrical orientation to produce an activated complex. Same as steric factor.

Steric factor: Same as probability factor.

Unimolecular process: An elementary process in which the probability of an activated complex forming products is low in comparison to the probability that it will lose energy by collision.

13-4 The activated complex

Absolute-reaction-rate theory: The theory that reaction rate is determined by the formation and decomposition of the activated complex. Same as transition-state theory and activated-complex theory.

Activated complex: A short-lived combination formed by collision of reactant particles in an elementary process. Same as transition state.

Activated complex theory: Same as absolute-reaction-rate theory.

Transition state: Same as activated complex.

Transition state theory: Same as absolute-reaction-rate theory.

13-5 Reaction mechanisms: an introduction

Intermediate: A chemical species formed in one step in a reaction sequence and consumed in a subsequent step.

Rate-determining step: The slowest elementary process in a reaction mechanism. Same as rate-limiting step.

Rate-limiting step: Same as rate-determining step.

13-6 Catalysis

Active center: A location on the surface of a heterogeneous catalyst or enzyme at which reactant molecules can combine and react with low required activation energy. Same as active site.

Active site: Same as active center.

Adsorption: The process of a particle bonding to a surface.

Catalyst: A substance which increases the rate of reaction by lowering the required activation energy and is not consumed by the reaction.

Chemisorption: The formation of relatively strong bonds between surface and absorbed particles.

Enzyme: Protein molecules which act as catalysts in biochemical reactions.

Heterogeneous catalyst: A surface on which molecules can readily react.

Homoegeneous catalyst: A catalyst in the same phase as the reactants.

Inhibitor: A substance which reduces the rate of reaction

SELF TEST

True or False

_____ 1. Reaction rates can be expressed in terms of concentrations of reactants but not products.

_____ 2. The sum of powers of the concentrations in a rate law is the order of reaction.

_____ 3. The rate of a reaction is constant at any specific temperature.

_____ 4. The rate constant is the rate of reaction at a specific constant temperature.

_____ 5. A reaction with rate law: Rate = $k[\mathrm{A}][\mathrm{B}]$ is a second-order reaction.

_____ 6. The energy of activation is the minimum energy a substance must possess before a reaction can take place.

_____ 7. A reaction mechanism for which the rate law is rate = $k[\mathrm{A}][\mathrm{B}]^2$ is always first order in A.

_____ 8. If a plot of concentration versus time is linear, the reaction is first order.

_____ 9. The order of reaction is the same as the molecularity in a reaction mechanism.

_____10. In a chemical reaction the steps in a mechanism all proceed simultaneously even though one of them is the slow, rate-determining step.

_____11. According to the Arrhenius equation, a plot of ln k versus T should be linear.

_____12. First-order rate constants always have dimensions of reciprocal time.

_____13. In a first-order reaction the rate always doubles when the concentration of reactant doubles.

_____14. The method of initial rates can be used to determine the order and rate constant of a reaction.

_____15. The energy of activation of most reactions decreases as temperature increases.

Completion

16. In the equation rate = $k[A]$, k is called the ______________________.

17. For the rate law, rate = $k[A]^2[B]^{0.5}$, the overall order of reaction is ________________ and the reaction order with respect to A is ____________.

18. The four important factors or variables that affect reaction rate are ____________________, ____________________, ________________, and ____________________.

19. The slope of a tangent to a concentration-versus-time plot gives the ______________.

20. The units of rate are ________________.

21. The energy of activation can be determined from the slope of a(an) _________________ plot.

22. Two methods of determining the order of a reaction are __________________ and _________________.

23. The equation for half-life of a first-order reaction is __________________.

24. When the rate is independent of concentration the reaction is ______________ order.

25. The probability that molecules are oriented correctly for reaction when they collide is called the ________________.

26. The slow step in a mechanism is called the ____________________.

27. The unstable, short-lived particle at the top of the energy hill is called the _____________________.

28. The energy difference between reactants and the top of the energy hill is called the ____________________.

29. A catalyst in the same phase as the reactants is called a (an) ______________.

30. A catalyst ______________ (alters, does not affect) the mechanism of a reaction.

31. The value of the rate constant can be increased by
(a) increasing the temperature
(b) decreasing the temperature
(c) increasing the reactant concentration
(d) decreasing the reactant concentration

32. Which of the following statements is not true for the reaction A + B → 2 C?
(a) The rate of reaction can be expressed as the rate of increase of [C].
(b) The rate of reaction can be expressed as the rate of decrease of [A].
(c) The rate of decrease of [A] is equal to the rate of increase of [C].
(d) The rate of decrease of [A] is equal to the rate of decrease of [B].

33. For the reaction A + B → 2 C the rate law is rate = $k[A]^2[B]$. Doubling [A] and [B] at the same time increases the rate
(a) two-fold (b) three-fold (c) six-fold (d) eight-fold

34. For the homogeneous gas phase reaction $2\ H_2 + O_2 \rightarrow 2\ H_2O$, the rate of reaction can be expressed in which of the following ways?
(a) $\text{Rate} = -\frac{1}{2}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[H_2O]}{dt}$ (b) $\text{Rate} = 2\frac{d[H_2]}{dt} = \frac{d[O_2]}{dt}$
(c) $\text{Rate} = -\frac{1}{2}\frac{d[H_2]}{dt} = \frac{-d[O_2]}{dt}$ (d) $\text{Rate} = \frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O]}{dt}$

35. For the reaction A + B → 2 C, when [A] is doubled the rate doubles and when [B] is doubled the rate increases fourfold. The rate law is
(a) Rate = $k[A]^2[B]^4$ (b) Rate = $k[A][B]^2$
(c) Rate = $k[A]$ (d) Rate = $k[B]^2$

36. The following rate data for the reaction A + B → 2 C were obtained experimentally.

Initial [A], *M*	Initial [B], *M*	Initial rate, *M* s^{-1}
0.025	0.030	1.5×10^{-4}
0.025	0.090	9.0×10^{-4}
0.050	0.030	6.0×10^{-4}

The rate law for this reaction is
(a) Rate = $k[A][B]^2$ (b) Rate = $k[A]^2[B]$
(c) Rate = $k[A][B]$ (d) Rate = $k[A]^2[B]^2$

37. A reaction is known to be first order in A. One could obtain a straight line by plotting
(a) ln[A] versus time (b) ln[A] versus reciprocal time
(c) [A] versus time (d) 1/[A] versus time

38. If the reaction 2 A → B + C is second order, which of the following plots will give a straight line?
(a) $[A]^2$ versus time (b) ln[A] versus time
(c) 1/[A] versus time (d) [A] versus time

39. A certain reaction is second order in A. When [A] is 0.500 *M*, the rate is 4.00×10^{-3} *M*
s^{-1}. The rate when [A] is 0.250 *M* is:
(a) 4.00×10^{-4} *M* s^{-1} (b) 1.00×10^{-3} *M* s-1
(c) 2.00×10^{-3} *M* s^{-1} (d) 1.60×10^{-2} *M* s^{-1}

40. A certain reaction is first order in A. The rate constant is $1.74 \times 10^{-3}\ s^{-1}$. The half-life is
(a) 2.5×10^{-3} s (b) 39.8 s (c) 57.5 s (d) 398 s

41. A certain reaction is first order in [A]. In 30 min [A] decreases from 0.70 to 0.25 *M*. How many minutes will it take for [A] to decrease from 0.35 to 0.25 *M*?
(a) 6.7 (b) 9.8 (c) 15 (d) 22.6

42. For the reaction in Problem 41, if the initial concentration of A is 0.70 *M*, what will its concentration be after 1 h?
(a) 8.9×10^{-2} *M* (b) 0.10 *M*
(c) 0.35 *M* (d) 0.65 *M*

43. The activation energy of a reaction can be obtained from the slope of a plot of
(a) $\ln k$ versus $1/T$ (b) $\ln k$ versus T
(c) k versus $\ln T$ (d) k versus $\ln 1/T$

44. A certain reaction has $E_a = 90.0\ \text{kJ mol}^{-1}$. The rate constant is $5.44 \times 10^{-3}\ \text{s}^{-1}$ at 25°C. What is the value of the rate constant at 80°C?
(a) $1.56\ \text{s}^{-1}$ (b) $1.34 \times 10^{-2}\ \text{s}^{-1}$
(c) $7.33 \times 10^{-3}\ \text{s}^{-1}$ (d) $5.47 \times 10^{-3}\ \text{s}^{-1}$

45. A certain reaction has rate constant of $5.44 \times 10^{-3}\ \text{s}^{-1}$ at 25°C and $0.735\ \text{s}^{-1}$ at 80°C. What is the energy of activation in kilojoules per mole?
(a) 1.48 (b) 33.9 (c) 78 (d) 186

Chapter 14

CHEMICAL EQUILIBRIUM

CHAPTER OVERVIEW

14-1 Homogeneous chemical equilibria

The use of an arrow (→) in chemical equations discussed so far in the text may have given you the impression that chemical reactions proceed until all the reactants have been converted to products. This is not true. Actually, all chemical reactions proceed in the forward direction (reactants forming products) and also in the reverse direction (products decomposing into reactants). They are called reversible reactions and should be denoted by a double arrow (⇄) or an equal sign. When the rate of the forward reaction equals the rate of the reverse reaction there is no net change in concentration and the reaction is said to be at equilibrium. Figure 14-1 in the text illustrates how the concentrations of reactants and products approach equilibrium in a general case. Figure 14-2 in the text shows how equilibrium can be approached from either direction. If only a few molecules of reactants remain at equilibrium the reaction is said to "go to completion". Reactions which essentially go to completion include those in which an insoluble substance or a weak electrolyte is formed.

Note how Le Châtelier's principle predicts what will happen as a system at equilibrium is stressed by changing the concentration of reactants or products in Figure 14-3 in the text. Pay close attention to the concepts "shift to the right" and "shift to the left"; these are common terms used to describe changes in systems at equilibrium. "Stresses" on a system at equilibrium are changes in temperature, pressure, volume, or concentration of products or reactants. Changes in pressure or volume affect only gas-phase reactions in which the stoichiometric number of moles of reactants is different from the number of moles of products as indicated by the balanced chemical equation. An increase in pressure shifts the reaction toward the side of the equation having fewer moles of gaseous molecules because the increase in pressure is relieved by reducing the number of moles in a given volume. A decrease in volume has the same effect as an increase in pressure.

14-2 The law of chemical equilibrium

A very useful relation is the expression giving the equilibrium constant in terms of the concentration of reactants and products, often called the law of equilibrium. For the reaction $a\text{A} + b\text{B} \rightleftarrows c\text{C} + d\text{D}$, the equilibrium constant expression is

$$K = \frac{\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

where K is the equilibrium constant for the reaction.

Get used to the idea of products in the numerator of the equation and reactants in the denominator, usually called "products over reactants". We will see it often.

A quantity similar to the equilibrium constant expression is the mass-action expression

$$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

It is important to note that K and Q refer to different conditions. K applies only to equilibrium conditions while Q applies to all systems whatever the conditions might be, so Q is not a constant. It is *only* at equilibrium that $Q - K$. The difference in the numerical values of Q and K gives an indication of how far the system is from equilibrium. If Q is less than K, the reaction proceeds toward products to get to equilibrium. If Q is greater than K, more reactants are formed from products (reverse reaction) to get to equilibrium. Again we emphasize that only at equilibrium does $Q = K$.

In the next few chapters we apply equilibrium concepts to several types of reactions. Different names will be given to the equilibrium constant depending on the type of reaction considered, but the basic concepts involved are presented in this chapter. Getting a good understanding of equilibrium now will form a strong foundation for work ahead. K_c is the main equilibrium constant you will use, but be familiar with its close relative K_p. Notice that when the stoichiometric numbers of moles of gaseous products and reactants are equal, $\Delta n = 0$ and $K_c = K_p$.

14-3 Kinetics and equilibrium

The equilibrium constant expression can also be obtained by equating the forward and reverse rate equations, but no matter how you arrive at K, it has only one value at any given temperature. As the text explains, units on K are usually omitted. Notice how the magnitude of K tells how far the reaction has proceeded at equilibrium. If K is much greater than unity, the amount of products will be greater than the amount of reactants in the equilibrium mixture. If K is much less than unity, the amounts of reactants will be greater, so the magnitude of K gives us an idea of how far the reaction proceeds to "completion." The equilibrium constant of a reaction is closely related to the specific rate constants of the forward and reverse reactions, as the equation $K = k_f/k_r$ signifies.

14-4 Heterogeneous chemical equilibria

Concentrations of pure liquids and pure solids are *not* included in equilibrium constant expressions or in mass-action expressions.

14-5 The variation of K with temperature

It is important to remember that K depends on temperature so you should always give the temperature for any numerical value of K to avoid confusion. The van't Hoff equation is used to calculate K at any given temperature when the standard enthalpy of reaction and K at a different temperature are known.

14-6 Equilibrium calculations

There are several types of calculations that can be made in conjunction with equilibrium constants. We will consider them in detail in the New Skills section.

KEY EQUATIONS

14-2 The law of chemical equilibrium

For the general equation $a\mathrm{A} + b\mathrm{B} \rightleftarrows c\mathrm{C} + d\mathrm{D}$, the equilibrium constant expression is

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In terms of pressure units

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

The two constants are related by

$$K_p = K_c(RT)^{\Delta n}$$

14-5 The variation of *K* with temperature

The effect of temperature on K_p is given by the van't Hoff equation

$$\ln\frac{(K_p)_1}{(K_p)_2} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ΔH° is the standard enthalpy of reaction.

LEARNING OBJECTIVES

As a result of studying Chapter 14, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 246 of this *Study Guide*.

14-1 Homogeneous chemical equilibria

1. Understand that all chemical reactions are reversible. (Text Prob. 14-1) (Self Test 1, 2, 3)
2. Explain why the rate of the forward reaction decreases and the rate of the reverse reaction increases when reactants are converted to products as a reaction approaches equilibrium. (Text Figs. 14-1, 14-2; Text Prob. 14-3) (Self Test 4)
3. Apply Le Châtelier's principle to predict the response of a system at equilibrium to a change in temperature, pressure, or concentration. (Text Probs. 14-4, 14-6 to 14-11, 14-38) (New Skills Example 1; Self Test 5, 13, 16 to 19, 24, 26, 36 to 38)
4. List the factors that affect the value of K_c. (Self Test 12, 13, 15, 28)

14-2 The law of chemical equilibrium

1. Write expressions for the equilibrium constant and mass-action quotient for a reaction from the balanced chemical equation. (Text Probs. 14-13, 14-39) (New Skills Example 2; Self Test 6, 7, 21, 23, 27, 31 to 33)
2. Predict the direction a reaction will move to achieve equilibrium from the relative magnitudes of *Q* and *K*. (Text Example 14-2; Text Probs. 14-15 to 14-17, 14-40) (New Skills Example 3; Self Test 8, 14, 25, 35)
3. Calculate K_c from K_p or K_p from K_c. (Text Example 14-1; Text Probs. 14-20 to 14-22, 14-41, 14-47) (Self Test 20, 34)

14-3 Kinetics and equilibrium

1. Relate K_c to the rate constants of the forward and reverse reactions. (Text Prob. 14-5) (Self Test 9)
2. Write a net equation for a given reaction mechanism. (Text Prob. 14-18)
3. Express the rate of a reaction in terms of the kinetic rate constants and equilibrium constant for the steps in a multistep reaction mechanism. (Text Prob. 14-18)

14-4 Heterogeneous chemical equilibria

1. Write equilibrium constant expressions for reactions involving pure solids or pure liquids. (Text Prob. 14-14) (New Skills Example 4; Self Test 10, 11)

14-5 The variation of K with temperature

1. Calculate K_p at any temperature using the van't Hoff equation when K_p at one temperature and the standard heat of reaction are given. (Text Probs. 14-23, 14-24, 14-42) (New Skills Example 5; Self Test 22, 39)
2. Calculate ΔH° using the van't Hoff equation given K_p at two temperatures. (Text Example 14-3; Text Probs. 14-25, 14-43) (Self Test 15)

14-6 Equilibrium calculations

1. Calculate the value of K_c or K_p given equilibrium concentrations of all substances in a reaction. (Text Example 14-4) (New Skills Example 6; Self Test 29, 40)
2. Calculate the equilibrium concentration of a substance given the value of K_c and the concentration of other substances in the reaction at equilibrium. (Text Example 14-5; Text Probs. 14-26, 14-33, 14-45, 14-48, 14-50, 14-51) (New Skills Example 7; Self Test 30, 41, 42)
3. Calculate the equilibrium concentration of all substances in a chemical reaction given the value of K_c and the initial concentration of reacting substances. (Text Examples 14-6 to 14-8; Text Probs. 14-27, 14-29 to 14-32, 14-34 to 14-37, 14-44 to 14-46, 14-49, 14-52, 14-53) (New Skills Example 8; Self Test 43 to 45)

NEW SKILLS

14-1 Homogeneous chemical equilibria

Using Le Châtelier's principle to predict the effect of a change on a system at equilibrium

According to Le Châtelier's principle, when a system at equilibrium is subjected to a stress or change in temperature, volume, pressure, or concentration of one of the substances, the system will shift to relieve that stress. The text considers concentration stresses on the $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$ system in detail. Let us consider another example.

• EXAMPLE 1

Problem: The system

$$4\ NH_3(g) + 7\ O_2(g) \rightleftarrows 4\ NO_2(g) + 6\ H_2O(g)$$

is initial at equilibrium. Predict the effect, if any, of each of the following changes on the equilibrium, using Le Chatelier's principle. ΔH° for the reaction is negative. (a) Increasing the pressure. (b) Increasing the volume. (c) Adding 1 mol of NH_3. (d) Adding 1 mol of NO_2. (e) Increasing the temperature.

Solution: According to Le Chatelier's principle the system will shift to reduce the stress which is applied.
(a) Increasing the pressure puts a stress on the side of the reactants with the most gaseous molecules. In this case there are 11 mol of gaseous reactants and only 10 mol of gaseous products. The reaction moves to the side with fewer gaseous molecules to relieve the pressure increase. This is a shift to the right.
(b) Increasing the volume is the opposite of increasing the pressure, so following the reasoning in part (a) there would be a shift to the left.
(c) Adding reactants puts a stress on the reactant side. The system reacts to relieve this stress by converting some of the reactants to products, resulting in a shift to the right.
(d) Adding products puts a stress on the product side, resulting in a shift to the left.
(e) Since ΔH° is negative the reaction is exothermic and we can think of heat as a product. Increasing the temperature puts a stress on the product side which is generating heat. This is relieved by a shift to the left. •

Parallel Problem: The following reaction would eliminate two noxious pollutants from combustion gases if it could be carried out:

$$NO(g) + CO(g) \rightarrow 1/2\, N_2(g) + CO_2(g)$$

ΔH for the reaction is negative. Using Le Chatelier's principle predict the effect, if any, of each of the following changes on the position of equilibrium.
(a) Increase in pressure (b) increase in volume (c) adding CO (d) adding CO_2
(e) increase in temperature (f) adding a catalyst.
Ans. (a) shift to the right (b) shift to the left (c) shift to the right (d) shift to the left
(e) shift to the left (f) no effect. Catalysts affect the speed with which equilibrium is reached, but not the position of equilibrium.

14-2 The law of chemical equilibrium

1. Writing equilibrium expressions

You must be able to write and interpret chemical equilibrium expressions from a balanced chemical equation. It will be helpful if you understand the following guidelines:

1. The equilibrium expression is always the products over the reactants, with each term raised to the power indicated by its coefficient in the balanced overall equation.
2. If all the coefficients of a chemical equation are multiplied by 2, the equilibrium constant must be squared.
3. If a chemical equation is reversed, the equilibrium constant and equilibrium constant expression for the reversed reaction are the reciprocal of the original.
4. If two chemical equations are added, the equilibrium constant is the product of the *K*'s of the added reactions.

• EXAMPLE 2

Problem: Write the equilibrium condition or equilibrium expression for the Ostwald reaction given in Example 1.

Solution: Always be certain the equation is balanced before you write the equilibrium expression. The expression is always products over reactants, each to the power indicated by its coefficient in the chemical equation.

$$K_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7} \quad \bullet$$

Parallel Problem: Write the equilibrium expression for the reaction in the previous Parallel Problem.
Ans.

$$K_c = \frac{[N_2]^{1/2}[CO_2]}{[NO][CO]}$$

2. *Using the mass-action expression to predict changes in systems not at equilibrium*

The magnitude of the mass-action quotient can be compared to the value of K to determine which way a system will move to attain equilibrium.

1. If $Q < K$, more products will be formed until $Q = K$.
2. If $Q > K$, more reactants will be formed from products until $Q = K$.
3. If $Q = K$, the system is at equilibrium.

We can illustrate the use of Q to see how a system will react to attain equilibrium with an example.

• EXAMPLE 3

Problem: For a certain reaction at 25°C the mass-action quotient is 0.05. The equilibrium constant at this temperature is 125. Predict which direction the reaction will move to attain equilibrium.

Solution: For the reaction not at equilibrium

$$Q = \frac{[\text{products}]}{[\text{reactants}]} = 0.05$$

For the reaction at equilibrium

$$K = \frac{[\text{products}]}{[\text{reactants}]} = 125$$

Since Q is less than K, the reaction will move to increase Q by increasing products and reducing reactants. This is called a shift to the right or a shift to the products. This shift will continue until Q has increased enough to be equal to K. When $Q = K$ there will be no further reaction. •

Parallel Problem: If the mass-action quotient were 300 in Example 3, which way would the reaction move to attain equilibrium?
Ans: Shift to the left

Example 14-2 in the text illustrates how to calculate Q from given concentrations.

3. *The relationship between K_c and K_p*

Equilibrium conditions can be expressed in terms of molarity or, in the case of gases, of partial pressures of the gases. The text shows these equilibrium constants are related by equation.

$$K_p = K_c(RT)^{\Delta n}$$

where K_p = pressure equilibrium constant
K_c = concentration equilibrium constant
R = ideal-gas constant = 0.082 L atm mol^{-1} K^{-1}
T = temperature in kelvins
Δn = moles of gaseous products – moles of gaseous reactants and is determined from the balanced chemical equation

Example 14-1 in the text illustrates the calculation of K_p from K_c.

14-4 Heterogeneous chemical equilibria

Concentrations of pure liquids or solids such as $H_2O(l)$, $Hg(l)$, $Br_2(l)$, and $CaCO_3(s)$ are not included in equilibrium expressions.

• EXAMPLE 4

Problem: Write the equilibrium expression for the pressure equilibrium constant for the reaction

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

Solution:

$$Kp = P_{CO_2}$$

$CaCO_3$ and CaO are both solids so are not included in the equilibrium expression. For this reaction the equilibrium expression is just the partial pressure of CO_2 above the solids. •

Parallel Problem: Write the equilibrium expression for the concentration equilibrium constant for the reaction given in Example 4.
Ans: $K_c = [CO_2]$

14-5 The variation of K with temperature

The effect of temperature on K, the van't Hoff equation

The effect of temperature on the equilibrium constant of gas-phase reactions is given by the van't Hoff equation.

$$\ln \frac{(K_p)_1}{(K_p)_2} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This form of equation should be familiar by now (recall the Clausius-Clapeyron equation and the equation for E_a). As usual, any variable in the equation can be calculated if the others are known. The following example illustrates the calculation of K_p at the temperature different from the given value.

• EXAMPLE 5

Problem: The pressure equilibrium constant for a certain reaction at 25°C is 1.7×10^{-4} and its standard heat of reaction is 70 kJ mol^{-1}. What is the value of K_p at 100°C?

Solution: Substitute the given values into the van't Hoff equation and solve for $(K_p)_2$.

$$(K_p)_1 = 1.7 \times 10^{-4}$$
$$T_1 = 25^\circ\text{C} + 273 = 298 \text{ K}$$
$$T_2 = 100^\circ\text{C} + 273 = 373 \text{ K}$$
$$\Delta H^\circ = 70{,}000 \text{ J mol}^{-1}$$
$$R = 0.082 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\ln \frac{1.7 \times 10^{-4}}{(K_p)_2} - \frac{-70{,}000 \text{ J mol}^{-1}}{(8.31 \text{ J mol}^{-1} \text{ K}^{1})} \left(\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}} \right)$$

$$\ln \frac{1.7 \times 10^{-4}}{(K_p)_2} = -5.69$$

Taking antilogarithms and solving for $(K_p)_2$

$$\frac{1.7 \times 10^{-4}}{(K_p)_2} = e^{-5.69} = 3.39 \times 10^{-3}$$

$$(K_p)_2 = \frac{1.7 \times 10^{-4}}{3.39 \times 10^{-3}} = 0.050 \bullet$$

Parallel Problem: For a reaction with a standard heat of reaction of 100 kJ at 25°C, how much must the temperature be increased to double the equilibrium constant?
Ans: 5°C

14-6 Equilibrium calculations

1. General approach

Most equilibrium calculations can be approached in a general manner. The following guidelines will help you organize the data given to find the desired answer.

1. Write a balanced chemical equation for the reaction.
2. Write the equilibrium condition or expression for the reaction.
3. Prepare a table showing the given data and any changes from the initial conditions.
4. Calculate equilibrium concentrations in terms of the changes as far as possible.
5. Substitute equilibrium concentrations into the equilibrium expression and solve for the unknown quantity.
6. Be sure the unknown quantity is in the same units as requested by the problem.

We will illustrate the application of these guidelines to several types of equilibrium calculations.

2. Calculating K from equilibrium concentrations

• EXAMPLE 6

Problem: For the reaction

$$A(g) + 2\,B(g) \rightleftarrows 4\,C(g) + 3\,D(g)$$

it was found that an equilibrium mixture in a 2-liter vessel contained 0.50 mol of A, 1.70 mol of B, 1.90 mol of C, and 2.30 mol of D at 25°C. Calculate the value of the equilibrium constant at 25°C.

Solution: We will apply the calculation guidelines. The chemical equation is already balanced so the equilibrium expression is

$$K_c = \frac{[C]^4[D]^3}{[A][B]^2}$$

Since we are given equilibrium amounts we can omit guidelines (3) and (4) and proceed to (5). The equilibrium concentrations are

$[A] = 0.5 \text{ mol}/2 \text{ liters} = 0.25 \text{ mol liter}^{-1} = 0.25\ M$
$[B] = 1.70 \text{ mol}/2 \text{ liters} = 0.85 \text{ mol liter}^{-1} = 0.85\ M$
$[C] = 1.90 \text{ mol}/2 \text{ liters} = 0.95 \text{ mol liter}^{-1} = 0.95\ M$
$[D] = 2.30 \text{ mol}/2 \text{ liters} = 1.15 \text{ mol liter}^{-1} = 1.15\ M$

Substitute these values into the equilibrium expression and solve for K_c.

$$K_c = \frac{(0.95)^4(1.15)^3}{(0.25)(0.85)^2} = \frac{(0.81)(1.52)}{(0.25)(0.72)} = 6.8 \quad \bullet$$

Parallel Problem: The reversible reaction

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$

reaches equilibrium and the concentrations of SO_2, O_2, and SO_3 are found to be 1.4×10^{-2}, 1.0×10^{-2}, and 3.6×10^{-3} mol L^{-1} respectively. Calculate the value for K_c.
Ans: $K_c = 6.6$

Now work Example 14-4 in the text.

3. Calculating the equilibrium concentration of one substance when given the value of K and equilibrium concentrations of other substances in the reaction

• EXAMPLE 7

Problem: For the reaction $A + 2B \rightleftarrows 3C$ an equilibrium mixture in a 2.00-liter vessel at 25°C contained 0.750 mol of A and 0.350 mol of B. How many moles of C were in the vessel? K_c for the reaction is 9.00 at 25°C.

Solution: We will apply the guidelines for equilibrium calculations. The equilibrium expression for the reaction is

$$K_c = \frac{[C]^3}{[A][B]^2}$$

We can omit steps (3) and (4) because equilibrium concentrations are already given, so we proceed directly to step (5).

$$K_c = 9.0$$

$$[A] = 0.750 \text{ mol}/2.00 \text{ liters} = 0.375 \text{ mol liter}^{-1}$$
$$[B] = 0.350 \text{ mol}/2.00 \text{ liters} = 0.175 \text{ mol liter}^{-1}$$

Solve the equilibrium expression for [C] and substitute the required values.

$$[C]^3 = K_c[A][B]^2 = 9.00(0.375)(0.175)^2 = 0.103 \text{ mol}^3/\text{liter}^{-3}$$
$$[C] = (0.103)^{1/3} = 0.469 \text{ mol liter}^{-1}$$

Step (6) reminds us to check the problem to be sure we have answered the question asked. We calculated the concentration of C to be 0.469 mol liter^{-1}. The total number of moles of C in the reaction vessel is

$$\text{Mol C} = [C](\text{volume of vessel}) = (0.469 \text{ mol L}^{-1})(2.00 \text{ liters}) = 0.939 \text{ mol} \quad \bullet$$

Parallel Problem: $K_c = 3.5$ for the reaction

$$CO(g) + H_2O(g) = H_2(g) + CO_2(g)$$

An equilibrium mixture contains 1.5 mol CO_2, 1.7 mol H_2O, and 0.50 mol CO in a 4.00 L container. How many moles of H_2 are in the container?
Ans: 2.0 mol H_2

Example 14-5 in the text is a similar problem.

4. Calculating the equilibrium concentration of any substance given the value of K and the initial concentrations or amounts of substances reacting

In calculations of this type we need to use stoichiometric methods to determine equilibrium concentrations from initial concentrations. This can be done conveniently using a tabular method for calculations as illustrated in the following example.

• EXAMPLE 8

Problem: For the reaction A + B ⇄ 2 C the value of K_c at 35°C is 16.0. Calculate the equilibrium concentrations of A, B, and C at 35°C if 2 mol of A and 2 mol of B are mixed in a 1-liter container and allowed to reach equilibrium.

Solution: The equilibrium expression for the balanced chemical equation is

$$K = \frac{[C]^2}{[A][B]}$$

We will use the stoichiometry of the chemical equation to determine the changes in concentration that take place as the system reaches equilibrium. Let x equal the number of moles of C formed during the reaction. According to stoichiometry, the number of moles of A reacted is

$$x \text{ mol C} \left(\frac{1 \text{ mol A}}{2 \text{ mol C}}\right) = \frac{1}{2}x$$

and the number of moles of B reacted is

$$x \text{ mol C} \left(\frac{1 \text{ mol B}}{2 \text{ mol C}}\right) = \frac{1}{2}x$$

These facts can readily be shown in tabular form and can be used to calculate equilibrium concentrations using the law of conservation of mass

Amount present at equilibrium = amount present initially + change due to reaction

Substance	Initial amount, mol liter^{-1}	Change, mol liter^{-1}	Equilibrium amount, mol liter^{-1}
A	2	$-\frac{1}{2}x$	$2-\frac{1}{2}x$
B	2	$-\frac{1}{2}x$	$2-\frac{1}{2}x$
C	0	$+x$	x

The negative changes for A and B show that their concentrations were reduced during the reaction. Since [C] increases during reaction, its change is positive. Now we can apply guideline (5) by substituting the equilibrium concentrations in terms of the variable x into the equilibrium expression.

$$K_c = 16.0 = \frac{x^2}{\left(2-\frac{1}{2}x\right)\left(2-\frac{1}{2}x\right)}$$

We can take the square root of each side of the equation and solve for x.

$$4.0 = \frac{x}{\left(2-\frac{1}{2}x\right)}$$

$$x = 2.67 \text{ mol}$$

Therefore, the equilibrium concentrations are

$$[A] = 2 - \frac{1}{2}x = 2 - \frac{1}{2}(2.67) = 0.665 \text{ mol liter}^{-1}$$

$$[B] = 2 - \frac{1}{2}x = 2 - \frac{1}{2}(2.67) = 0.665 \text{ mol liter}^{-1}$$

$$[C] = x = 2.67 \text{ mol liter}^{-1}$$ •

Parallel Problem: For the reaction in the previous Parallel Problem calculate the moles of H_2 generated if 2.0 mol CO and 2.0 mol H_2O are mixed in a 4.0-L container and allowed to reach equilibrium.
Ans: 1.3 mol H_2

Example 14-6 in the text is a similar problem. If you have trouble following the reasoning involved in determining the concentration changes, try the tabular approach to calculations. Examples 14-7 and 14-8 in the text are very similar to Example 14-6 except that it is more difficult to solve the equations for x. Usually the simplifying assumptions used in Example 14-8 can be used to make the calculations easier.

KEY TERMS

14-4 Homogeneous chemical equilibria

Equilibrium: A state in which opposing processes or reactions take place at the same rate so no net change is observed.

14-2 The law of chemical equilibrium

Equilibrium condition: The condition that the mass-action expression equals the value of the equilibrium constant for a reaction, which is satisfied when the reacting system is at equilibrium.

Equilibrium constant: The value for the mass-action expression for a reaction at equilibrium.

Law of chemical equilibrium: At any given temperature the value of the mass-action expression for a given reaction at equilibrium is a constant.

Mass-action expression: Q. The product of the concentrations or partial pressures of the products in a reaction, divided by those of the reactants. Each term is raised to an exponential power corresponding to the coefficient of that term in the balanced chemical equation. Pure solids and liquids are omitted. Same as reaction quotient.

Reaction quotient: Same as mass-action expression.

14-4 Heterogeneous chemical equilibria

Heterogeneous reaction: A chemical reaction involving components in two or more phases.

14-5 The variation of *K* with temperature

van't Hoff equation: An algebraic equation relating the equilibrium constant to temperature.

SELF TEST

True or False

_____ 1. All chemical reactions tend to equilibrium.

_____ 2. A homogeneous equilibrium involves only one substance.

_____ 3. A reversible reaction is one in which the products are formed from reactants and reactants are formed from products.

_____ 4. When a system is at equilibrium the forward and reverse reaction rates have stopped.

_____ 5. When equilibrium systems are disturbed, they adjust to minimize the effect of the disturbance.

_____ 6. Equilibrium products appear in the numerator of the equilibrium expression.

_____ 7. At any given temperature the value for the mass-action expression for a given reaction at equilibrium is a constant.

_____ 8. If the mass-action quotient is smaller than the equilibrium constant, the reaction will shift to the left.

_____ 9. Equilibrium constants are related to specific rate constants only for elementary processes.

_____10. Equilibrium expressions do not apply to heterogeneous equilibria.

_____11. Pure liquids and solids are not included in equilibrium expressions.

_____12. Equilibrium constants are independent of concentrations of reactants.

_____13. The equilibrium state of a gaseous system is not affected by the addition of an inert gas.

_____14. If the equilibrium constant is greater than unity we are sure there are more products present at equilibrium than reactants.

_____15. If a reaction is exothermic K_c must increase as temperature is increased.

Completion

The reaction $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$ applies to questions 16 to 19.

16. Adding N_2 will shift an equilibrium mixture to the ____________ (right, left).

17. Removing H_2 will shift an equilibrium mixture to the __________(right, left).

18. Increasing the pressure will shift an equilibrium mixture to the ________ (right, left).

19. The reaction is exothermic so increasing the temperature will shift an equilibrium mixture to the __________ (right, left).

20. K_p is equal to K_c if Δn is equal to ____________________.

21. The products are included in the ____________________ (denominator, numerator) of the equilibrium expression.

22. The van't Hoff equation is used to determine K_p as a function of _______________.

23. The value of the mass-action quotient at equilibrium is called the ________________.

24. __________________ principle permits prediction of the effect a stress has on a system at equilibrium.

25. A reaction that goes to completion must have an equilibrium constant equal to ________________.

26. A reaction can be forced to go to completion by ________________ of one of the products.

27. An expression that takes the same form as an equilibrium expression, but describes a system that is not at equilibrium is called a ____________________.

28. Two factors that affect the value of the equilibrium constant of all reactions are ____________________ and _________________.

29. If the equilibrium concentrations for the reaction: $A + 2\ B \rightleftarrows 3\ C$ are $[A] = 3.0\ M$, $[B] = 3.0\ M$, and $[C] = 2.0\ M$, the value of the equilibrium constant is _________.

30. If the equilibrium constant for the reaction $A + B \rightleftarrows 2\ C$ is 8.0, the equilibrium concentration of A in equilibrium with $[B] = 3.0\ M$ and $[C] = 4.0\ M$ is ______________________.

31. The correct equilibrium expression for the reaction $2\ NO_2(g) \rightleftarrows N_2O_4(g)$ is

(a) $K_c = \frac{2\ [NO_2]}{[N_2O_4]}$ (b) $K_c = \frac{[N_2O_4]}{2\ [NO_2]}$

(c) $K_c = \frac{[N_2O_4]}{[NO_2]^2}$ (d) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$

32. The correct equilibrium expression for the reaction $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$ is

(a) $K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$ (b) $K_c = \frac{[CaCO_3]}{[CaO][CO_2]}$

(c) $K_c = \frac{1}{[CO_2]}$ (d) $K_c = \frac{[CaO]}{[CaCO_3]}$

33. The equilibrium constant for the reaction $2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g)$ is 4.8×10^{-3} at 700°C. What is the equilibrium constant at the same temperature for the reaction $2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$?

(a) 4.8×10^{-3} (b) 4.8×10^{3}

(c) 2.1×10^{2} (d) 9.6×10^{-3}

34. K_c for the reaction $A(g) + B(g) \rightleftarrows 2\ C(g)$ is 16.0 at 25°C. What is K_p at this temperature?

(a) 2.56×10^{-3} (b) 6.25×10^{-2}

(c) 16.0 (d) 391

35. A certain reaction $A(g) + B(g) \rightleftarrows 2\ C(g)$ has $K = 0.09$ at 35°C. If $[A] = 2\ M$, $[B] = 4\ M$, and $[C] = 1.5\ M$, which of the following is true for the mixture?

(a) it will shift to the left (b) it will shift to the right

(c) more C is needed to achieve equilibrium (d) the reaction is at equilibrium

Questions 36 to 38 refer to the equilibrium reaction

$$N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g) \qquad \Delta H^\circ = -92.2\ kJ$$

36. The concentration of NH_3 at equilibrium will increase if

(a) the temperature is increased (b) N_2 is added

(c) N_2 is removed (d) an inert gas is added

37. The concentration of H_2 at equilibrium will increase if

(a) the pressure is increased (b) N_2 is added

(c) NH_3 is removed (d) the temperature is increased

38. The reaction will go to completion if

(a) the temperature is increased (b) N_2 is removed

(c) NH_3 is removed (d) N_2 is added

39. A certain reaction $A(g) + B(g) \rightleftarrows C(g)$ has $K_p = 5.0$ at 25°C and $\Delta H^\circ = -125$ kJ. What is the value of K_p at 100°C?

(a) 1.96×10^{-4} (b) 5.05

(c) 7.85 (d) 20.0

40. For the gas-phase reaction $A + 2B \rightleftarrows 2C$, equilibrium measurements show [A] = 0.250 *M*, [B] = 0.300 *M*, and [C] = 0.210 *M*. What is the value of K_c under these conditions?
(a) 2.80
(b) 2.35
(c) 1.96
(d) 0.510

41. For the reaction $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$ at 700°C $K_p = 0.061$, what is the partial pressure of CO_2 in equilibrium with CaO and $CaCO_3$?
(a) 0.061 mmHg
(b) 16.4 mmHg
(c) 0.061 atm
(d) 16.4 atm

42. For the reaction $2C \rightleftarrows A + B$, $K_c = 8.50$ at 25°C, what are the concentrations of A and B in equilibrium with 0.020 *M* C if [A] = [B]?
(a) 0.17
(b) 5.80×10^{-2}
(c) 3.40×10^{-3}
(d) 6.85×10^{-3}

43. For the reaction $A(g) + B(g) \rightleftarrows C(s)$, $K_p = 3.00$ at 100°C, what is the partial pressure of A in equilibrium with a system in which the partial pressure of B is 0.750 atm?
(a) 2.25 atm
(b) 1.00 atm
(c) 0.444 atm
(d) cannot tell unless the partial pressure of C is given

44. For the reaction $A(g) + B(g) \rightleftarrows 2C(g)$, $K_c = 25$, what is the equilibrium concentration of C if 2.00 mol of it are placed in a one-liter vessel and allowed to reach equilibrium?
(a) 0.29 *M*
(b) 0.57 *M*
(c) 1.42 *M*
(d) 1.71 *M*

45. For the reaction $A(g) + B(g) \rightleftarrows 2C(g)$, what is the equilibrium concentration of C if we start with [A] = 1.00 *M*, [B] = 2.00 *M*, and no C present? $K_c = 3.00 \times 10^{-5}$
(a) 3.00×10^{-5} *M*
(b) 6.00×10^{-5} *M*
(c) 7.74 x 10-3 *M*
(d) 1.00 *M*

Chapter 15

AQUEOUS SOLUTIONS: ACID-BASE EQUILIBRIA

CHAPTER OVERVIEW

15-1 The dissociation of weak acids

A large part of this chapter is the application of equilibrium concepts from Chapter 14 to acids and bases. In Chapter 11 we calculated the degree of dissociation of weak acids. This section investigates the concept of dissociation of weak acids from an equilibrium viewpoint. The concepts are all familiar but some new terms are introduced. The equilibrium constant for the dissociation reaction of a weak acid in aqueous solution is called an acid dissociation constant, K_a, but it is no different from the equilibrium constants of Chapter 14. Since it applies to a special process it is given a special name.

The magnitude of K_a reveals the strength of the acid. Strong acids dissociate completely so the equilibrium is shifted far to the right in the chemical equation, making K_a very large. In weak acids the amount of dissociation is small, so the equilibrium is shifted to the left and K_a is also small. Table 15-1 in the text shows K_a values for a few weak acids. The favorite weak acid of most instructors is acetic acid, so you should become especially familiar with its dissociation reaction. Polyprotic acids are very similar to monoprotic acids except that their dissociation occurs in steps and so is a little more complex to analyze. Usually we neglect all but one dissociation step to simplify the calculations involved. The percent dissociation of weak acids increases as they become more dilute. However, the dilution reduces the concentration of H^+ so the more dilute solutions are less acidic even though the dissociation is higher.

15-2 The dissociation of weak bases

Strong bases are completely dissociated in water. All of the hydroxides of group IA and group IIA metals except beryllium are strong bases. Transition metal hydroxides, ammonium hydroxide (NH_4OH), and certain organic compounds are weak bases. Ammonium hydroxide is frequently used for illustrations and calculations involving weak bases, so become familiar with its dissociation. Ammonia, ammonia water, aqueous ammonia, and ammonium hydroxide are all names for the same substance: NH_3 dissolved in water. This is often a source of confusion to students in the classroom and laboratory because chemists are apt to use any or all of these names regularly. The dissociation constants of a few weak bases are listed in Table 15-3 in the text.

15-3 The dissociation of water

Since water is such an important compound and affects the dissociation of acids and bases dissolved in it, we consider its dissociation separately. Again, the equilibrium concepts are the same but there are some new terms. Get a feeling for these terms quickly and this section will not be difficult. pH is probably the chemical term used most often by nonchemists and has very widespread applications. Remember that a pH change of one unit means that the H^+ concentration has changed tenfold. Understanding Table 15-4 is basic to learning the language of acid-base chemistry.

15-4 Hydrolysis

Hydrolysis is another special name for a special reaction, a reaction with water. Anions of weak acids and cations of weak bases undergo hydrolysis. Note how the hydrolysis constant K_h is related to K_a or K_b and K_w. Instructors often assign a problem that is easily solved by the equilibrium expression of the hydrolysis reaction, but give K_a or K_b and expect the student to recognize that K_h must be calculated before the problem can be solved. Careful reading of problems will help you recognize such tricky situations.

Hydrolysis of salts usually results in a solution that is not neutral. Consequently, salts are classified as acidic or basic. The salt of a weak acid and a strong base is basic. The stronger acid or base always determines the acid-base character of the resulting salt.

15-5 Acid-base indicators and titration

Certain organic compounds are one color in basic solutions and a different color in acidic solutions. They are called indicators because their color indicates the acid-base character of the solution. Indicators that change colors at almost any given pH value are available. A universal indicator has several color changes through the range of pH. An important application of indicators is determining the equivalence point of a titration. Titration is a standard laboratory technique for determining the concentration of acid or base in solutions. Figures 15-3 and 15-4 in the text show how the pH changes during titration of a strong or weak acid. Care must be taken in selecting the correct indicator for titration of weak acids and weak bases because the pH change is gradual and the equivalence point is not at pH = 7.

15-6 Buffers

A buffer is a solution that resists changing its pH when H^+ or OH^- is added to it. It is always a combination of a weak acid or base and its salt (a conjugate acid-base pair). One compound of the buffer effectively removes H^+ as it is added; the other removes OH^-. Of course, the capacity of a buffer may be swamped by adding more acid or base than the buffer can remove. In the case of the acetic acid/acetate ion buffer, acetic acid neutralizes OH^- and the acetate ion reacts with H^+. The Henderson-Hasselbalch equation is a special form of the equilibrium expression for use with buffer solutions.

15-7 Simultaneous acid-base equilibria

Handling true simultaneous equilibria involves mathematical equations too complex to present in an introductory course. We will restrict ourselves to situations in which the dissociation constants of simultaneous equilibria are different enough in magnitude so that all but one can be neglected. In essence, we are making justified assumptions to simplify the problem to a single equilibrium expression.

KEY EQUATIONS

15-1 The dissociation of weak acids

The dissociation of weak acids can be represented by the general equation

$$HA \rightleftarrows H^+ + A^-$$

for which the equilibrium expression is

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

15-2 The dissociation of weak bases

The dissociation of weak bases can be represented by the general equation

$$BOH \rightleftarrows B^+ + OH^-$$

for which the equilibrium expression is

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

15-3 The dissociation of water

The equation for the dissociation of water is

$$H_2O \rightleftarrows H^+ + OH^-$$

for which the equilibrium expression is

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$[H^+]$ is measured by pH

$$pH = -\log[H^+]$$

The acid-base relationship in water is expressed by two equivalent relations

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

and

$$pH + pOH = 14$$

15-4 Hydrolysis

The hydrolysis of the anion of a weak acid is represented by the general equation

$$A^- + H_2O \rightleftarrows HA + OH^-$$

for which the equilibrium expression is

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

The hydrolysis of the cation of a weak acid is represented by the general equation

$$B^+ + H_2O \rightleftarrows BOH + H^+$$

for which the equilibrium expression is

$$K_h = \frac{[BOH][H^+]}{[B^+]}$$

K_h of an anion is related to K_a of the corresponding weak acid by

$$K_w = K_h K_a$$

K_h of a cation is related to K_b of the corresponding weak base by

$$K_w = K_h K_b$$

In general, K_a and K_b of a conjugate acid-base pair are related by

$$K_w = K_a K_b$$

15-6 Buffers

The Henderson-Hasselbalch equation relates the pH of a buffer to its composition.

$$\text{pH} = \text{p}K_a - \log\frac{[\text{weak acid}]}{[\text{salt of weak acid}]}$$

LEARNING OBJECTIVES

As a result of studying Chapter 15, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 268 of this *Study Guide*.

15-1 The dissociation of weak acids

1. Combine the concepts of weak electrolytes from Chapter 11 and equilibrium from Chapter 14 to understand the dissociation of weak acids and bases.
2. Write the dissociation reaction and its equilibrium expression for weak monoprotic and diprotic acids. (Self Test 11, 15)
3. Calculate K_a for weak acids given equilibrium concentrations of the dissociation species. (Text Probs. 15-18, 15-19, 15-42) (New Skills Example 1; Self Test 17)
4. Calculate the concentration of each chemical species and the pH of a solution of a weak acid. (Text Examples 15-1, 15-3, 15-5; Text Probs. 15-10 to 15-15, 15-17, 15-49, 15-52) (Self Test 1, 7, 17)
5. Calculate the percent dissociation of a weak acid. (Text Examples 15-2 to 15-4; Text Prob. 15-16) (Self Test 2)
6. Apply the common ion effect to calculate concentrations of ions of a weak acid. (Text Example 15-3; Test Probs. 15-12, 15-13, 15-19, 15-49) (Self Test 1, 16, 35)

15-2 The dissociation of weak bases

1. Write the dissociation reaction and its equilibrium expression for weak bases. (Self Test 27)
2. Calculate the concentration of each chemical species and the pH of a solution of a weak base. (Text Example 15-6; Text Probs. 15-20 to 15-23) (Self Test 34)
3. Know the different names for a solution of ammonia in water and write the dissociation reaction in terms of NH_3 or NH_4OH.

4. Apply the common-ion effect to calculate concentrations of ions of a weak base. (Text Example 15-7; Text Prob. 15-24)

15-3 The dissociation of water

1. Explain the dissociation of water in terms of chemical species obtained and their significance in chemistry. (Self Test 5, 26)
2. Memorize the numerical value of K_w and use it to calculate [H^+] or pH given [OH^-], and vice versa. (Test Examples 15-8, 15-9; Text Probs. 15-3, 15-7 to 15-9) (New Skills Example 2; Self Test 12, 37)
3. Explain what makes a solution acidic, basic, or neutral. (Self Test 28)
4. Know the definition of pH and solve for pH given [H^+], and vice versa. (Text Examples 15-10, 15-11; Text Probs. 15-1, 15-2) (New Skills Example 3; Self Test 3, 4, 18)
5. Calculate the pH of a solution given [OH^-], and vice versa. (Text Prob. 15-3) (New Skills Example 4; Self Test 4, 18, 19, 37 to 39)
6. Calculate the pH and pOH of strong acids and bases. (Text Examples 15-10, 15-12; Text Probs. 15-4 to 15-7, 15-51, 15-61) (New Skills Example 5; Self Test 4 to 6, 17 to 19, 24, 31, 38, 39)

15-4 Hydrolysis

1. Write chemical equations and equilibrium expressions for the hydrolysis of the anion of a weak acid and the cation of a weak base. (Text Prob. 15-25) (Self Test 10, 20, 32)
2. Predict whether or not anions and cations hydrolyze in solution. (Text Example 15-13; Text Probs. 15-25) (Self Test 8 to 10, 13)
3. Predict the acidic or basic character of a salt from the strengths of the acid and base from which it is derived. (Text Probs. 15-26) (Self Test 22)
4. Write an equation showing the relationship between K_h for an anion, K_a for its weak acid, and K_w. (Text Probs. 15-30, 15-31) (Self Test 21, 40)
5. Write an equation showing the relationship between K_h for a cation, K_b for its weak base, and K_w.
6. Write an equation showing the relationship between K_a, K_b and K_w for a conjugate acid-base pair. (Self Test 21)
7. Calculate the percent hydrolysis and concentration of chemical species in a solution of hydrolyzed salts. (Text Example 15-14; Text Probs. 15-29, 15-32, 15-53, 15-54) (Self Test 36, 42)
8. Calculate the pH of a salt whose ions hydrolyze. (Text Examples 15-14 to 15-16; Text Probs. 15-27, 15-28) (Self Test 25, 36, 42)
9. Calculate K_{diss} given the pH of a hydrolyzed salt. (New Skills Example 6)

15-5 Acid-base indicators and titration

1. Explain how titration is used to determine the concentration of solutions of acids and bases.
2. Understand how indicators are used to determine the equivalence point of a titration and what factors must be considered in choosing an indicator for a given titration. (Text Prob. 15-43) (Self Test 29)
3. Explain why the equivalence point of the titration of a weak acid or weak base is not necessarily at pH 7. (Self Test 23)
4. Calculate the pH at the equivalence point for an acid-base titration. (Text Examples 15-17, 15-18; Text Probs. 15-33 to 15-37) (New Skills Example 7; Self Test 23)
5. Calculate the pH at any point on the titration curve of an acid-base titration. (Text Example 15-19; Text Probs. 15-38 to 15-40) (New Skills Examples 8, 9; Self Test 23, 41)
6. Construct a titration curve. (Text Figs. 15-3 to 15-5; Text Prob. 15-41)

15-6 Buffers

1. Write chemical equations to show how buffers resist change in pH when acid or base is added. (Text Prob. 15-45) (Self Test 14, 33, 43)
2. Use the Henderson-Hasselbalch equation to calculate the pH of a buffer solution or the composition of a buffer of known pH. (Text Example 15-21; Text Probs. 15-44, 15-46, 15-50, 15-59) (New Skills Examples 10, 11; Self Test 30, 42, 44, 45)
3. Use the Henderson-Hasselbalch equation to determine the change in pH of a buffer solution after the addition of a given quantity of acid or base. (Text Example 15-20; Text Probs. 15-47, 15-48) (New Skills Example 12; Self Test 43)

15-7 Simultaneous acid-base equilibria

1. Make justified assumptions about which dissociation steps can be neglected in calculations involving simultaneous equilibria. (Text Example 15-22) (Self Test 11)
2. Calculate the total ion concentration of a species involved in simultaneous equilibria. (Text Example 15-23; Text Probs. 15-55 to 15-58, 15-60)

NEW SKILLS

This chapter emphasizes solving equilibrium problems in acid-base reactions. Understanding the examples in the text is basic to solving the problems at the end of the chapter. In most equilibrium problems it is possible to make a justified assumption that will greatly simplify the mathematics and yet not affect the answer. Learn how to recognize when and where to make these assumptions by paying close attention to how they are made in the worked examples. As in previous chapters, we will work problems presenting new concepts in considerable detail the first time, then reduce the detail and discussion as we repeat similar calculations.

15-1 The dissociation of weak acids

It should become quickly apparent that all equilibrium problems involving weak acids and weak bases are centered around setting up and solving the appropriate equilibrium expression. You should have learned the basic steps in solving equilibrium problems in Chapter 14.

1. Calculation of concentration of species in dissociation of a pure weak acid

To calculate the concentration of all species in a solution, you first need to know what species are involved. Get in the habit of writing the dissociation reaction and corresponding equilibrium expression so the chemistry of the reaction is well defined and understood before you set up the calculation. Notice how this is done in Example 15-1 in the text.

2. Calculation of concentration of species in the dissociation of a weak acid when other sources of ions are present (common-ion effect)

There is often another source of ions in the solution in addition to the dissociating acid. This source must also be considered in the equilibrium expression. In the case of acetic acid, $HC_2H_3O_2$, H^+ could also come from a strong acid present in solution and acetate ion could come from a dissolved salt present in addition to the acetic acid. Example 15-3 in the text illustrates the calculation of all species in a solution of acetic acid in the presence of sodium acetate. Acetate ions are common to both substances, so the compounds exhibit a common-ion effect.

Note that in Example 15-1, x represents the concentration of both H^+ and acetate ion at equilibrium, while in Example 15-3, x is only part of the equilibrium concentration of acetate ion but represents all of the H^+. It is important to fully understand the meaning of x in each problem to be able to relate its numerical value to the concentration desired.

When the value of the equilibrium constant is small it is usually valid to assume that x can be neglected when it is subtracted from a concentration. The validity of the assumption can be tested by comparing the calculated value of x with the concentration from which it would have been subtracted. If x is small in comparison with the concentration you are justified in neglecting it when calculating the val of x. It generally is.

3. *Calculation of K_{diss} given the concentration of the weak acid and of the ions formed by its dissociation*

Another variation on the equilibrium calculations involving weak acids is solving the equilibrium expression for K_{diss} when the concentration of all species is given or can be determined from the data given.

• EXAMPLE 1

Problem: In a 0.500 *M* solution of hydrofluoric acid, HF, it was found that the equilibrium concentration of H^+ was 5.5 x 10^{-3} *M* at 25°C. What is the acid dissociation constant for HF?

Solution: As is the case in all equilibrium calculations, first we need the chemical reaction and corresponding equilibrium expression.

$$HF \rightleftarrows H^+ + F^-$$

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

According to the chemical equation, the $[F^-]$ must equal the $[H^+]$. [HF] has been reduced by the amount of H^+ produced.

$$[H^+] = 5.6 \text{ x } 10^{-3}\ M$$
$$[F^-] = 5.6 \text{ x } 10^{-3}\ M$$
$$[HF] = 0.050 - (5.6 \text{ x } 10^{-3}) = 0.044\ M$$

Neglecting the amount of HF dissociated would not really simplify the calculations and it is not negligible with respect to the 0.050 *M* initial concentration. Since we have equilibrium concentrations we can substitute directly into the equilibrium expression and solve for K_a.

$$K_a = \frac{(5.6 \text{ x } 10^{-3})^2}{0.044} = 7.1 \text{ x } 10^{-4} \ \bullet$$

Parallel Problem: A solution of hydrocyanic acid, HCN, is 0.300 *M* and has H^+ concentration of 1.1 x 10^{-5} *M* at 25°C. What is the acid dissociation constant for HCN?
Ans: 4.0 x 10^{-1}

4. *Calculation of percent dissociation of a weak acid*

We must be given the concentration of weak acid and its dissociation constant (Table 15-1 in the text) to make this calculation. Examples 15-2 and 15-4 in the text show this calculation and illustrate how the percent dissociation changes with concentration of the weak acid.

15-2 The dissociation of weak bases

Calculations concerning the dissociation of weak bases are approached in exactly the same manner as those for weak acids. The same types of calculations are possible. NH_3 in aqueous solution is by far the most common weak base, and most calculations you make involving weak bases are likely to involve it. Example 15-6 in the text illustrates the method of calculating concentrations of dissolved species and Example 15-7 illustrates the common-ion effect when additional OH^- is present.

15-3 The dissociation of water

1. Using the ion-product constant of water, K_w, in calculations

The dissociation constant, or ion-product constant, of water is a simple but powerful tool for calculating acid-base concentrations in water solutions.

$$H_2O \rightleftarrows H^+ + OH^-$$

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

The product of $[H^+]$ and $[OH^-]$ is always 1×10^{-14} at 25°C regardless of what other chemical reactions are taking place in the solution. If $[H^+]$ is known, $[OH^-]$ can be calculated from K_w, and if $[OH^-]$ is known, $[H^+]$ can be determined.

• EXAMPLE 2

Problem: Calculate $[H^+]$ in a 0.030 *M* solution of $Sr(OH)_2$.

Solution: $Sr(OH)_2$ is a strong base and completely dissociates in aqueous solution.

$$Sr(OH)_2 \rightarrow Sr^{2+} + 2\,OH^-$$

Since 2 mol of OH^- are obtained for each mole of $Sr(OH)_2$

$$[OH^-] = 2[Sr(OH)_2] = 2(0.030\,M) = 0.060\,M$$

Using K_w to find $[H^+]$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.060} = 1.7 \times 10^{-13}\,M$$

Parallel Problem: Find $[H^+]$ in a 0.0025 *M* solution of $Mg(OH)_2$.
Ans: $[H^+] = 2 \times 10^{-12}\,M$

Example 15-8 in the text illustrates the calculation of $[OH^-]$ in an acid solution.

2. pH calculations

pH is a measure of $[H^+]$ defined as $pH = -\log[H^+]$. $[H^+]$ can commonly vary from 10^{-14} to 1 *M*. The pH scale varies from 0 to 14 over this range and is a more convenient measurement to use. Its use is so common that you must memorize the definition. Also become familiar with Table 15-4 in the text so you understand the pH scale. First we will work some simple problems to become familiar with pH. Example 15-10 in the text illustrates the basic calculation. If you are rusty on using logarithms refer to Appendix D-3 in the text or to any algebra text.

• EXAMPLE 3

Problem: What is the $[H^+]$ of a solution of pH 5.62?

Solution: Solve the definition of pH for $[H^+]$. Since $pH = -\log [H^+]$

$$\begin{aligned} \log [H^+] &= -pH \\ [H^+] &= 10^{-pH} \\ [H^+] &= 10^{-5.62} = 2.40 \times 10^{-6}\, M \end{aligned}$$ •

Parallel Problem: Find $[H^+]$ for a solution of pH 9.14.
Ans: 7.24×10^{-9}

• EXAMPLE 4

Problem: Calculate $[OH^-]$ of a solution of pH 8.54.

Solution: First find the $[H^+]$ as in Example 3; then use K_w to find $[OH^-]$.

$$[H^+] = 10^{-pH} = 10^{-8.54} = 2.88 \times 10^{-9}\, M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.88 \times 10^{-9}} = 3.47 \times 10^{-6}\, M$$

Alternate solution: Determine the pOH and find $[OH^-]$ from pOH.

$$pH + pOH = 14$$

$$pOH = 14 - pH = 14 - 8.54 = 5.46$$

$$[OH^-] = 10^{-pOH} = 10^{-5.46} = 3.47 \times 10^{-6}\, M$$ •

Parallel Problem: Find $[OH^-]$ for the solution in the previous Parallel Problem.
Ans: 1.38×10^{-6}

• EXAMPLE 5

Problem: What is the pOH of a $4.45 \times 10^{-4}\, M$ solution of HBr?

Solution: HBr is a strong acid so

$$[H^+] = [HBr] = 4.45 \times 10^{-4}\, M$$

$$pH = -\log [H^+] = -\log (4.45 \times 10^{-4}) = 3.35$$

$$pOH = 14 - pH = 14 - 3.35 = 10.65$$

Alternate Solution: First determine $[OH^-]$ from $[H^+]$ using K_w; then find pOH

$$[H^+] = [HBr] = 4.45\ 10^{-4}\ M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{4.45 \times 10^{-4}} = 2.25 \times 10^{-11}\ M$$

$$pOH = -\log [OH^-] = -\log (2.25 \times 10^{-11}) = 10.65$$ •

Parallel Problem: What is the pOH of the solution in the previous Parallel Problem?
Ans: 4.86

Examples 15-8 to 15-12 in the text are problems similar to these.

15-4 Hydrolysis

1. *The pH of hydrolyzed salts*

Salts ionize when they dissolve and certain cations and anions undergo hydrolysis in solution. Anions may hydrolyze to form weak acids while cations hydrolyze to weak bases. Either of these situations will affect the pH of the solution.

NaCN is the salt of a strong base, NaOH, and a weak acid, HCN. We expect its solution to be basic, so the pH will be greater than 7. The dissociation reaction is

$$NaCN \rightarrow Na^+ + CN^-$$

We must examine each ion formed to see if it hydrolyzes. There is no tendency for Na^+ to react with water to form NaOH + H^+ because NaOH is a strong base. However, the hydrolysis $H_2O + CN^- \rightleftarrows HCN + OH^-$ occurs because HCN is a weak acid (see Table 15-1 in the text). Examples 15-14 and 15-15 in the text illustrate the calculation of the pH of a basic salt and an acidic salt which undergo hydrolysis.

2. *Determination of dissociation constants from hydrolysis data*

Since the dissociation constant of a weak acid or base is related to the hydrolysis constant of its salt through K_w, we can determine dissociation constants by measuring the pH of hydrolyzed salts.

• EXAMPLE 6

Problem: The pH of 0.100 *M* sodium hypochlorite, NaOCl, is 10.25. Calculate K_a for hypochloric acid, HClO.

Solution: First we will determine K_h for the hypochlorite ion and then find K_a for HClO. The dissociation reaction for the salt is

$$NaClO \rightarrow Na^+ + OCl^-$$

The hypochlorite ion hydrolyzes according to the reaction

$$OCl^- + H_2O \rightleftarrows HOCl + OH^-$$

The hydrolysis expression for OCl^- is

$$K_h = \frac{[HOCl][OH^-]}{[OCl^{-1}]}$$

We can find the equilibrium concentration of OH^- from the given pH

$$[H^+] = 10^{-pH} = 10^{-10.25} = 5.62 \times 10^{-11}\,M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{5.62 \times 10^{-11}} = 1.78 \times 10^{-4}\,M$$

The hydrolysis reaction for OCl^- tells us that equal numbers of moles of HOCl and OH^- are generated during hydrolysis. It also says that the original OCl^- concentration decreases by an amount equal to the OH^- generated.

$$[OH^-] = 1.78 \times 10^{-4}\,M$$

$$[HOCl] = 1.78 \times 10^{-4}\,M$$

$$[OCl^-] = 0.100 - 1.78 \times 10^{-4} = 0.100\,M$$

Substituting these values into the hydrolysis expression gives the value of K_h.

$$K_h = \frac{(1.78 \times 10^{-4})^2}{0.100} = 3.17 \times 10^{-7}$$

Now we can use the relationship between K_h, K_a, and K_w to find K_a.

$$K_a = \frac{K_w}{K_h} = \frac{1.0 \times 10^{-14}}{3.17 \times 10^{-7}} = 3.15 \times 10^{-8}$$

This calculated value compares well with the value tabulated in Table 15-1 in the text. •

Parallel Problem: The pH of 0.100 M potassium acetate, $KC_2H_3O_2$, is 8.87. Calculate K_a for acetic acid, $HC_2H_3O_2$.
Ans: 1.8×10^{-5}

15-5 Acid-base indicators and titration

In a titration procedure we want the indicator to change color at the equivalence point. Since different indicators change color at different pH values, we must predict the pH at the equivalence point before we can choose an appropriate indicator.

1. *pH at the equivalence point in a titration of a strong acid with a strong base*

Any neutralization of a strong acid with a strong base can be represented by the reaction

$$H^+ + OH^- \rightleftarrows H_2O$$

The equivalence point is defined as the point during titration when equal numbers of moles of H^+ and OH^- have been added. The resulting solution must be neutral, so the pH is 7. See Example 15-17 in the text.

2. *pH at the equivalence point of titration involving weak acids or weak bases*

• EXAMPLE 7

Problem: What is the pH at the equivalence point for the titration of 30.0 mL of 0.10 *M* NH_3 solution with 0.30 *M* HCl?

Solution: The reaction for the neutralization of the weak base and the strong acid is

$$NH_3 + HCl \rightleftarrows NH_4^+ + Cl^-$$

At the equivalence point equal numbers of moles of NH_3 and HCl have been added so the solution contains NH_4^+ and Cl^- ions. NH_4^+ is the cation of a weak base so it hydrolyzes according to the reaction

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

The presence of H_3O^+ will make the solution acidic at the equivalence point. The pH will be the pH of the NH_4Cl solution.

Let us first find the concentration of NH_4Cl. The titration involved adding 0.30 *M* HCl to 30.0 mL of 0.10 *M* NH_3 until the moles of each were equal. The volume of HCl is found using the titration equation.

$$(NV)_{NH_3} = (NV)_{HCl}$$

Molarity equals normality for both HCl and NH_3, so the volume of HCl is

$$V_{HCl} = \frac{N_{NH_3}}{N_{HCl}} V_{NH_3} = \frac{0.10\,N}{0.30\,N}(30.0\text{ mL}) = 10.0\text{ mL}$$

The total volume after titration is 30.0 mL + 10.0 mL = 40.0 mL. There was (0.10 mol L^{-1}) (0.030 L) = 3.0×10^{-3} mol of NH_3 originally present, and the neutralization reaction says that the number of moles of NH_4^+ produced must be equal to the number of moles of NH_3 reacted. The concentration of NH_4^+ before hydrolysis is

$$[NH_4^+]_o = \frac{3.0 \times 10^{-3}\text{ mol}}{0.040\text{ L}} = 0.075\,M$$

The only sources of H^+ at the equivalence point are the hydrolysis of NH_4^+ and water dissociation. Normally we can neglect the $[H^+]$ from water dissociation. The pH of 0.075 *M* NH_4Cl can be calculated by the procedure of Example 15-15 in the text.

$$K_h = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

The value of K_b is given in Table 15-3 in the text. The hydrolysis expression for NH_4^+ is

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

Let x = the amount of NH_4^+ that hydrolyzes, in moles per liter. From the hydrolysis reaction we can see that $x = [NH_3] = [H_3O^+]$, and since x is very small

$$[NH_4^+] = 0.075 - x = 0.075\ M$$

The criteria for neglecting x with respect to 0.075 are met, so we can substitute concentrations into the hydrolysis expression and solve directly for x.

$$5.6 \times 10^{-10} = \frac{x^2}{0.075}$$

$$x^2 = 4.2 \times 10^{-11}$$

$$x = [H_3O^+] = 6.5 \times 10^{-6}\ M$$

Now the pH can be found.

$$\text{pH} = -\log[H_3O^+] = -\log(6.5 \times 10^{-6}) = 5.2$$

As was predicted, the pH at the equivalence point is acidic rather than neutral. Example 15-18 in the text illustrates a similar calculation for the titration of a weak acid with a strong base. There the equivalence point pH is basic. •

Parallel Problem: What is the pH at the equivalence point for the titration of 25 mL of 0.20 M methyl amine with 0.10 M HNO_3? Refer to Text Table 15-3 for necessary constants.
Ans: pH = 5.9

3. *Construction of titration curves for strong acids with strong bases*

The change of pH in a solution being titrated can be plotted against the amount of titrant added to give a titration curve. Figures 15-13 to 15-5 in the text show examples of titration curves. If we calculate the pH of the solution being titrated at several points during the titration we could construct a titration curve for any given titration. We will investigate the method of calculation for a strong acid-base titration first.

• EXAMPLE 8

Problem: A titration is performed in which 25.0 mL of 0.150 M NaOH is titrated with 0.150 M HCl. What is the pH of the solution after 10.0 mL of HCl have been added?

Solution: Titration of a strong acid with a strong base does not produce ions that hydrolyze so the neutralization is completely described by the reaction

$$NaOH + HCl \rightleftarrows NaCl + H_2O$$

or the net ionic equation

$$H^+ + OH^- \rightleftarrows H_2O$$

The number of moles of NaOH neutralized equals the number of moles of HCl added.

Moles of NaOH in initial solution = 0.150 mol L^{-1} (0.0250 L) = 3.75×10^{-3} mol
Moles of HCl added = 0.150 mol L^{-1} (0.0100 L) = 1.50×10^{-3} mol
Moles of NaOH remaining after HCl addition = $3.75 \times 10^{-3} - 1.50 \times 10^{-3} = 2.25 \times 10^{-3}$ mol

After 10.0 mL of HCl is added the total volume of solution is 0.0250 L + 0.0100 L = 0.0350 L.

$$[\text{NaOH}] \text{ after } 10.0 \text{ mL HCl } = \frac{2.25 \times 10^{-3} \text{ mol}}{0.0350 \text{ L}} = 0.0643\ M$$

Since NaOH is a strong base it is completely dissociated so

$$[\text{OH}^-] = [\text{NaOH}] = 0.0643\ M$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0643} = 1.56 \times 10^{-13}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.56 \times 10^{-13}) = 12.81 \bullet$$

Similar calculations could be done using several different volumes of added HCl and the results plotted to give a graph similar to Fig 15-3 in the text.

Parallel Problem: If 35.0 mL of 0.250 *M* HNO_3 is titrated with 0.400 *M* KOH, what is the pH of the solution after 20.0 mL of KOH have been added?
Ans: pH = 1.86

4. *Construction of a titration curve for titrations involving weak acids or weak bases*

Since the salts of weak acids and weak bases give ions that hydrolyze in solution, the pH of the solution is affected by the concentrations of weak acid or weak base remaining to be titrated and of the salt formed during titration. To calculate the pH of these solutions we need to consider both the neutralization and hydrolysis reactions and their effect on the OH^- and H^+ concentrations.

• EXAMPLE 9

Problem: If 25.0 mL of 0.150 *M* NH_3 solution is titrated with 0.200 *M* HBr, what is the pH of the NH_3 solution after adding 10.0 mL of HBr?

Solution: First we will investigate the stoichiometry of the neutralization process to determine the amount of NH_3 remaining after 10.0 mL of HBr is added. The neutralization reaction is

$$NH_3 + HBr \rightleftarrows NH_4^+ + Br^-$$

Initial moles of NH_3 = 0.150 mol L^{-1} (0.0250 L) = 3.75×10^{-3} mol
Moles HBr added = 0.200 mol L^{-1} (0.0100 L) = 2.00×10^{-3} mol
Moles NH_3 remaining after HBr addition = $3.75 \times 10^{-3} - 2.00 \times 10^{-3} = 1.75 \times 10^{-3}$ mol

After the HBr addition the total volume of solution is 25.0 mL + 10.0 mL = 35.0 mL.

$$[NH_3] = \frac{1.75 \times 10^{-3} \text{ mol}}{0.0350 \text{ L}} = 0.0500\ M$$

The number of moles of NH_4^+ formed is equal to the number of moles of NH_3 neutralized, 2.00×10^{-3} mol.

$$[NH_4^+]_o = \frac{2.00 \times 10^{-3} \text{ mol}}{0.0350 \text{ L}} = 0.0571\ M$$

The NH_4^+ hydrolyzes according to the reaction

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

and the hydrolysis expression is

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

We can find the concentrations after hydrolysis by a typical equilibrium calculation. Let x = the amount of NH_4^+ hydrolyzed in moles per liter.

	Concentration after neutralization, mol liter^{-1}	Concentration change from hydrolysis	Equilibrium concentration after hydrolysis, mol liter^{-1}
NH_4^+	0.0571	$-x$	$0.0571 - x$
NH_3	0.0500	$+x$	$0.0500 + x$
H_3O^+	0	$+x$	x

The criteria to neglect x with respect to 0.0571 and 0.0500 are met, so the hydrolysis expression becomes

$$K_h = 5.6 \times 10^{-10} = \frac{0.0500x}{0.0571}$$

$$x = [H_3O^+] = 6.4 \times 10^{-10}\,M$$

$$pH = -\log[H^+] = -\log(6.4 \times 10^{-10}) = 9.19 \quad \bullet$$

Parallel Problem: If 20.0 mL of 0.300 M acetic acid solution is titrated with 0.200 M KOH, what is the pH of the acetic acid solution after adding 10.0 mL of KOH?
Ans: pH = 4.45

Values of pH could be calculated using other volumes of added HBr and the results plotted to give a titration curve similar to Fig 15-14 in the text. Example 15-19 in the text illustrates a similar calculation for titration of a weak acid with a strong base.

15-6 Buffers

1. *Calculation of the pH of a buffer of known composition*

The Henderson-Hasselbalch equation is used to calculate the pH of a buffer if the concentration of weak acid or weak base and the corresponding salt are known.

• EXAMPLE 10

Problem: What is the pH of a buffer solution made of 0.50 M $HC_2H_3O_2$ and 0.30 M $NaC_2H_3O_2$?

Solution: The Henderson-Hasselbalch equation can be written as

$$pH = pK_a - \log\frac{[\text{weak acid}]}{[\text{salt}]}$$

For this system

$$[HC_2H_3O_2] = 0.50\,M$$

$$[NaC_2H_3O_2] = 0.30\,M$$

$$K_a = 1.8 \times 10^{-5} \quad \text{from Text Table 15-1}$$

$$pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Substituting these values into the Henderson-Hasselbalch equation gives

$$\text{pH} = 4.74 - \log\frac{0.50}{0.30} = 4.74 - 0.22 = 4.52 \bullet$$

Parallel Problem: What is the pH of a buffer solution made of 0.010 M HCN and 0.10 M NaCN?
Ans: pH = 10.4

2. *Calculation of the composition of a buffer to provide a given pH*

The Henderson-Hasselbalch equation can also be used to determine the amounts of weak acid, base, or salt necessary to make a buffer of a certain pH.

• EXAMPLE 11

Problem: How many moles of NH_4Cl must be added to 500 mL of 0.500 M NH_3 to make a buffer of pH 9.50?

Solution: The Henderson-Hasselbalch equation for basic buffers is

$$\text{pOH} = pK_b - \log\frac{[\text{weak base}]}{[\text{salt}]}$$

For this buffer

$$[\text{Weak base}] = [NH_3] = 0.500\,M$$

$$K_b = 1.8 \times 10^{-5} \quad \text{from Text Table 15-3}$$

$$pK_b = -\log K_b = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pOH} = 14 - \text{pH} = 14 - 9.50 = 4.50$$

Now we can substitute these values into the Henderson-Hasselbalch equation and solve for [salt].

$$4.50 = 4.74 - \log\frac{0.500}{[\text{salt}]}$$

$$\log\frac{0.500}{[\text{salt}]} = 0.24$$

$$\frac{0.500}{[\text{salt}]} = 10^{0.24} = 1.74$$

$$[\text{salt}] = [NH_4Cl] = \frac{0.500}{1.74} = 0.288\ M$$

The number of moles of NH_4Cl needed is

$$\text{Moles } NH_4Cl = 0.288 \text{ mol L}^{-1} \times 0.500 \text{ L} = 0.144 \text{ mol} \quad \bullet$$

Parallel Problem: How many moles of NaCN must be added to 1.00 liter of 0.300 *M* HCN to make a buffer of pH = 9.0?
Ans: 0.075 mol NaCN

3. *Comparison of the effect of adding H^+ or OH^- to a buffer or to pure water*

• EXAMPLE 12

Problem: Compare the change in pH upon adding 0.100 mol of H^+ to one liter of the buffer in Example 11 to the pH change when the same amount of H^+ is added to one liter of pure water.

Solution: The change for the buffer system can be determined by the Henderson-Hasselbalch equation. We can determine the concentrations by the usual methods of equilibrium calculations. The 0.100 mol of H^+ converts 0.100 mol of NH_3 to 0.100 mol of NH_4^+, so the $[NH_3]$ decreases by 0.100 mol L^{-1} and the $[NH_4^+]$ increases by 0.100 mol L^{-1}. Substituting these values into the Henderson-Hasselbalch equation gives

$$pOH = 4.74 - \log\frac{0.500 - 0.100}{0.288 + 0.100}$$

$$= 4\ 74 - \log\frac{0.400}{0.388} = 4.73$$

$$pH = 14.00 - 4.73 = 9.27$$

The initial pH of the buffer (Example 11) was 9.50, so the pH change is

$$pH = 9.50 - 9.27 = 0.23$$

The pH change for pure water is found as follows: The $[H^+]$ is 0.10 mol liter^{-1}, so the pH is

$$pH = -\log[H^+] = -\log(0.10) = 1.00$$

The pH of pure water is 7.00, so the change in pH is

$$pH = 7.00 - 1.00 = 6.00$$

The pH of the pure water changed by 6.00 pH units while that of buffer changed by only 0.23 units. •

Parallel Problem: Compare the change in pH upon adding 0.10 mol of OH^- to one liter of the buffer in the previous Parallel Problem to the pH change when the same amount of OH^- is added to one liter of pure water.
Ans: Change in pH for the buffer is 0.16 pH units. Change in pH for the pure water is 6.00 pH units.

Example 15-20 in the text is a similar calculation for a weak acid buffer.

KEY TERMS

15-1 The dissociation of weak acids

Activity: A measure of the effective concentration or partial pressure of a chemical species which takes into account intermolecular interactions which produce nonideal behavior. Same as chemical activity.

Common ion effect: The shifting of an ionic equilibrium due to the addition of an ion involved in the equilibrium.

Dissociation constant: The equilibrium constant for a dissociation equilibrium. Same as ionization constant.

Ionization constant: The same as dissociation constant.

15-3 The dissociation of water

Acidic solution: An aqueous solution in which the concentration of hydrogen ions exceeds that of hydroxide ions.

Autodissociation: The production of ions by dissociation of solvent molecules without interaction with solute particles. Same as self-dissociation.

Basic solution: An aqueous solution in which the concentration of hydroxide ions exceeds that of hydrogen ions.

Chemical activity: Same as activity.

Dissociation constant for water: The equilibrium constant for the autodissociation of water. $K_w = 1.0 \times 10^{-14}$ at 25°C. Same as ion product for water,.

Ion product for water: Same as dissociation constant for water.

Neutral solution: An aqueous solution in which the concentrations of hydrogen and hydroxide ions are equal. A solution with pH = 7.0 at 25°C.

pH: The negative common logarithm of the hydrogen ion concentration in an aqueous solution.

pOH: The negative common logarithm of the hydroxide ion concentration in an aqueous solution.

Self-dissociation: Same as autodissociation.

15-4 Hydrolysis

Hydrolysis: The reaction of an ion with water to form a weak acid plus OH^- or a weak base plus H^+.

Hydrolysis constant: The equilibrium constant for a hydrolysis reaction. Same as hydrolytic constant.

Hydrolytic constant: Same as hydrolysis constant.

15-5 Acid-base indicators and titration

End point: The point at which an indicator signals the end of a titration.

Equivalence point: The point in a titration when equivalent amounts of both reactants have been mixed.

Indicator: A conjugate acid-base pair in which at least one of the pair is colored.

Titrant: The substance added during a titration.

Titration: The slow addition of one reactant to a second reactant until the equivalence point is reached as signaled by an indicator or other method.

Titration curve: A graph of the pH of a solution being titrated as a function of the amount of titrant added.

15-6 Buffers

Buffer: A solution containing a Brønsted-Lowry conjugate acid-base pair. A solution which resists change in pH when acid or base is added.

Henderson-Hasselbalch equation: A relation between the pH of a buffer and the dissociation constant and concentrations of the conjugate acid-base pair comprising the buffer solution.

pK: The negative common logarithm of an equilibrium constant.

15-7 Simultaneous acid-base equilibria

Acid salt: A salt containing an anion formed by removal of one or more protons from a polyprotic acid.

SELF TEST

True or False

_____ 1. The presence of acetate ions in a solution of acetic acid shifts the acid dissociation to the left.

_____ 2. The percent dissociation of a weak acid increases as the solution is concentrated.

_____ 3. A pH change of 3 means the [H^+] has changed by 300.

_____ 4. A 1×10^{-3} *M* solution of KOH has a pH of 3.

_____ 5. A water solution of a strong acid contains hydroxide ions as well as hydrogen ions.

_____ 6. In a pure solution of a strong acid, HA, if the concentration of acid is x molar, then [H^+] is x molar.

_____ 7. In a dilute solution of a pure weak acid, HA, if the concentration of weak acid is x molar, then [H^+] is usually $\sqrt{(x)\,(K_a)}$.

_____ 8. A salt of a strong acid and a strong base does not undergo hydrolysis.

_____ 9. Anions of very weak acids tend to hydrolyze strongly.

_____10. Anions of weak bases hydrolyze in solution to form the weak base plus OH^-.

_____11. K_{a2} is always smaller than K_{a1} for polyprotic acids.

_____12. The product of [H^+] and [OH^-] in water solutions is a constant no matter what other ions are present.

_____13. Anions of very weak acids tend to hydrolyze strongly.

_____14. A buffer has no change in pH when H^+ or OH^- are added.

_____15. The equilibrium expression for the Arrhenius equation for the dissociation of a weak acid is different from the equilibrium expression based on the Brønsted-Lowry definition.

Completion

16. Repression of dissociation of HCN molecules by the presence of ________________ is called the ________________ effect.

17. The $[H^+]$ of strong acids is always equal to the original concentration of ________________, but the concentration of H^+ of weak acids must be calculated using the ________________.

18. The pH of a 1 x 10^{-3} M HCl solution is ________________.

19. The pH of a 1 x 10^{-3} M NaOH solution is ________________.

20. Hydrolysis is the reaction of the ________________ of a ________________ with water.

21. The relationship between K_h, K_a, and K_w may be expressed mathematically as ________________.

22. The salt of a ________________ plus a ________________ is basic.

23. The pH at the equivalence point for the titration of a strong base and a weak acid is ________________ (greater than, less than, equal to) 7.

24. A solution of pH = 12 is strongly ________________ (acidic, basic, neutral).

25. An aqueous solution of potassium fluoride will have a pH ________________ (greater than, less than, equal to) 7.

26. The concentration of water in aqueous solutions is about ________________.

27. The ________________ (Brønsted-Lowry, Arrhenius) perspective is used to describe weak base dissociation.

28. The pH of a basic solutions is ________________ (less than, greater than, equal to) 7.

29. A conjugate acid-base pair where the acid has one color and the base another can be used as a (an) ________________ in ________________.

30. The Henderson-Hasselbalch equation may be used to calculate the ________________ or ________________ of a buffer.

Multiple Choice

31. The pOH of 5.0×10^{-5} *M* HBr is
(a) 4.3 (b) 9.0 (c) 9.7 (d) 11.9

32. Which of the following is the equilibrium expression for the hydrolysis constant for NaCN?
(a) $\frac{[Na^+][CN^-]}{[NaCN]}$ (b) $\frac{[Na^+][OH^-]}{[CN^-]}$ (c) $\frac{[CN^-][H^+]}{[HCN]}$ (d) $\frac{[HCN][OH^-]}{[CN^-]}$

33. Which of the following make a buffer?
(a) HBr, NH_4Br (b) NaOH, HCl (c) NaCN, HCN (d) NaOH, HCN

34. Adding NaOH to a solution of acetic acid
(a) increases $[H^+]$
(b) increases $[HC_2H_3O_2]$
(c) decreases $[C_2H_3O_2^-]$
(d) increases $[C_2H_3O_2^-]$

35. Which of the following will have the lowest $[H^+]$?
(a) 1.0 *M* $HC_2H_3O_2$ in 1.0 *M* $NaC_2H_3O_2$
(b) 1.0 *M* $HC_2H_3O_2$ in 1.0 *M* HCl
(c) 1.0 *M* $HC_2H_3O_2$ in 1.0 *M* KCl
(d) 1.0 *M* $HC_2H_3O_2$ in 1.0 *M* HCN

36. Given $K_h = 5.6 \times 10^{-10}$ for NH_4^+, the pH of 0.100 *M* NH_4Cl is
(a) 2.9 (b) 5.1 (c) 8.9 (d) 10.2

37. The $[OH^-]$ in 0.10 *M* HCl is
(a) 0.10 *M*
(b) 1.0×10^{-13} *M*
(c) HCl is a strong acid and does not contain OH^-
(d) cannot be calculated unless K_a for HCl is known

38. The pH of 0.010 *M* $Ba(OH)_2$ is
(a) 13.0 (b) 12.6 (c) 12.3 (d) 12.0

39. If the pH of a solution of $Sr(OH)_2$ = 10.0 at 25°C, then the $[OH^-]$ is
(a) 1.0×10^{-10} *M*
(b) 5.0×10^{-5} *M*
(c) 2.0×10^{-4} *M*
(d) 1.0×10^{-4} *M*

40. K_{a2} for sulfurous acid is 6.30×10^{-8}. The hydrolysis constant for the sulfite ion, SO_3^{2-}, is
(a) 3.15×10^{-8} (b) 1.60×10^{-7} (c) 6.30×10^{-6} (d) 2.51×10^{-4}

41. When 40.0 mL of 0.100 *M* HCl reacts with 25.0 mL of 0.150 *M* NaOH, the final $[H^+]$ is
(a) 4.54×10^{-3} *M*
(b) 2.50×10^{-4} *M*
(c) 1.00×10^{-7} *M*
(d) 2.60×10^{-12} *M*

42. What is the $[OH^-]$ in a solution containing 0.100 mol NH_4Cl and 0.050 mol NH_3 per liter? ($K_b = 1.8 \times 10^{-5}$)
(a) 3.10×10^{-3} *M*
(b) 3.60×10^{-5} *M*
(c) 9.00×10^{-6} *M*
(d) 1.04×10^{-9} *M*

43. When a small amount of NaOH is added to a buffer made of $HC_2H_3O_2$ and $NaC_2H_3O_2$, the pH changes very little because
(a) the $HC_2H_3O_2$ dissociates to compensate for the NaOH
(b) $NaC_2H_3O_2$ hydrolyzes to form NaOH and $HC_2H_3O_2$
(c) $C_2H_3O_2^-$ react with NaOH to form $HC_2H_3O_2$
(d) $HC_2H_3O_2$ dissociates to give H^+, which reacts with OH^- to form H_2O

44. Given $K_a = 1.8 \times 10^{-5}$, a buffer made of an equal number of moles of acetic acid and sodium acetate has a pH of
(a) 1.8 (b) 3.74 (c) 4.74 (d) 9.26

45. How many moles of NaF should be added to 0.100 *M* HF to prepare one liter of a buffer with pH 4.00? ($K_a = 6.7 \times 10^{-4}$)
(a) 0.0100 (b) 0.0148 (c) 4.00 (d) 6.76

Chapter 16

AQUEOUS SOLUTIONS: SOLUBILITY AND COMPLEX-ION EQUILIBRIA

CHAPTER OVERVIEW

Chapter 16 is a continuation of the application of equilibrium concepts. We will apply these concepts to saturated solutions of slightly soluble electrolytes in water to study and predict the solubility of salts and to determine when precipitates are expected to form. We will also apply equilibrium concepts to complex ions and multicomponent systems.

16-1 The solubility of ionic solids

The equilibrium constant describing the solubility of an electrolyte is called the solubility product constant or solubility product and is designated K_{sp}. Equilibrium conditions for solutions of any salt are obtained by writing the equilibrium expression for the dissociation reaction of the salt. Note that the salt itself does not appear in the expression because it is a pure substance. The dissociation reaction for the salt M_2A_3 is:

$$M_2A_3 \rightleftarrows 2\,M^{3+} + 3\,A^{2-}$$

The solubility product expression is

$$K_{sp} = [M^{3+}]^2[A^{2-}]^3$$

Numerical values of K_{sp} are tabulated for many salts. See Table 16-1 and Appendix H-3 in the text (or any chemical handbook) for a more extensive list.

There are no new *concepts* presented in this section, only new applications of familiar equilibrium concepts. Note how the common-ion effect has a dramatic effect on the solubility of salts. Le Châtelier's principle is used to predict the results of the common-ion effect. Equilibrium calculations in this section are very similar to those of Chapters 14 and 15.

16-2 Precipitation reactions

When the value of the ion-product or mass-action expression is less than K_{sp}, the solution is unsaturated; when it is equal to K_{sp}, the solution is saturated; when it is greater than K_{sp}, the solution is supersaturated and precipitation will generally occur unless care is taken to preserve a supersaturated solution and prevent precipitation. Comparing numerical values of the mass-action quotient (or calculated ion product) with K_{sp} allows us to predict whether or not a precipitation will occur and what compound will precipitate from solution.

16-3 Complex-ion equilibria

The basic terms used in complex-ion chemistry were introduced in Section 12-2. You may want to review some of the definitions in Chapter 12 to be sure you do not hinder your study in this section by a lack of understanding of the terms. Equilibrium concepts used in this chapter are the same as the ones you have already used, but the terms are specific for the kinds of reactions involved.

16-4 Simultaneous equilibria

When a given substance is involved in several different equilibria at the same time, calculating concentrations can be very difficult and may require a computer. Often, however, simplifying assumptions can be made because one equilibrium condition dominates the system, making the calculation much simpler. Note how the equilibria in Examples 16-10 and 16-11 in the text are treated independently even though they occur simultaneously. Watch for these simplifying techniques when you work simultaneous equilibria problems.

LEARNING OBJECTIVES

As a result of studying Chapter 16, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 283 of this *Study Guide*.

16-1 The solubility of ionic solids

1. Write an expression for the equilibrium condition for solution of an electrolyte. (New Skills Sec. 16-1; Self Test 9, 16 to 18, 30, 32)
2. Calculate K_{sp} for an electrolyte given its solubility. (Text Examples 16-1, 16-2; Text Probs. 16-1 to 16-7) (News Skills Example 1; Self Test 1 to 3, 31, 34)
3. Calculate the solubility of an electrolyte given K_{sp}. (Text Examples 16-3, 16-4; Text Probs. 16-8, 16-10, 16-11, 16-22, 16-24) (Self Test 5, 7, 35)
4. Calculate the solubility of an electrolyte in solution containing additional sources of ion common to the electrolyte (common-ion effect). (Text Examples 16-5, 16-6; Text Probs. 16-9, 16-23) (New Skills Example 2; Self Test 10, 19, 37, 38)

16-2 Precipitation reactions

1. Calculate the minimum concentration of ions necessary to cause precipitation of a salt. (Text Probs. 16-12, 16-25, 16-28) (New Skills Example 3; Self Test 4, 37)
2. Predict whether or not a precipitate will form by comparing the calculated ion product with K_{sp}. (Text Example 16-7; Text Probs. 16-13, 16-26, 16-29) (New Skills Example 4; Self Test 2, 8, 21)
3. Predict what salt will precipitate first from a solution containing several ions when a common ion is added. (Text Example 16-8; Text Prob. 16-27) (Self Test 10)

16-3 Complex-ion equilibria

1. Write dissociation reactions and equilibrium expressions for complex ions. (New Skills Example 5; Self Test 11, 22, 25, 26, 39)
2. Relate the relative stabilities of complex ions to the numerical values of their cumulative dissociation constants. (Self Test 12, 13, 23)

3. Calculate the concentration of metal ion in equilibrium with a complex ion. (Text Example 16-9; Text Probs. 16-14 to 16-16, 16-30) (New Skills Example 5; Self Test 28, 40)
4. Write chemical equations showing amphoteric behavior of a metal hydroxide. (Self Test 14, 24, 27, 41)
5. Write chemical equations showing amphiprotic behavior of a complex ion containing water and hydroxide as ligands. (Self Test 43)

16-4 Simultaneous equilibria

1. Determine the order of precipitation of different salts as an electrolyte is added to a solution containing several ions. (Text Example 16-10; Text Probs. 16-17, 16-18, 16-31)
2. Calculate the amount of substance necessary to give a common-ion effect sufficient to cause or to prevent the precipitation of a salt. (Text Example 16-11; Text Probs. 16-19, 16-20, 16-32, 16-33) (New Skills Examples 6, 7; Self Test 6, 10, 15, 20, 29, 33, 36, 42)
3. Calculate the amount of common ion necessary to separate substances by selective precipitation. (Text Example 16-12; Text Prob. 16-21) (Self Test 29, 43 to 45)

NEW SKILLS

16-1 The solubility of ionic solids

In this section we use a special equilibrium constant called the solubility product constant. It is equal to the product of the concentrations of ions in solution, each raised to the power indicated by the stoichiometric coefficient of the dissociation equation. For example, silver phosphate, Ag_3PO_4, is a slightly soluble salt. It dissolves in water according to the reaction

$$Ag_3PO_4(s) \rightleftarrows 3\ Ag^+ + PO_4^{3-}$$

The equilibrium for a saturated solution is described by the expression

$$K_{sp} = [Ag^+]^3[PO_4^{3-}]$$

Since Ag_3PO_4 is a pure solid, it is not included in the equilibrium expression. A saturated solution contains all the Ag^+ and PO_4^{3-} ions it can hold in equilibrium with solid Ag_3PO_4. Adding more solid Ag_3PO_4 does not change the concentration of ions in solution. As long as the solution remains saturated, the product $[Ag^+]^3[PO_4^{3-}]$ must be constant. If additional Ag^+ is added, $[PO_4^{3-}]$ will decrease; if more PO_4^{3-} is added, $[Ag^+]$ decreases so that their product always equals K_{sp} for a saturated solution.

1. Calculation of K_{sp} from solubility data

Problems in this chapter can be solved by the general approach to equilibrium problems used in Chapters 14 and 15. It is always a good idea to begin by writing a balanced chemical equation for the process and analyzing the stoichiometry involved.

$$Ag_3PO_4 \rightleftarrows 3\ Ag^+ + PO_4^{3-}$$

Stoichiometry tells us that for every mole of Ag_3PO_4 that dissolves, 3 mol of Ag^+ and 1 mol of PO_4^{3-} are produced.

• EXAMPLE 1

Problem: A saturated solution of silver phosphate at 25°C is $1.6 \times 10^{-5}\ M$. Calculate K_{sp} at 25°C for Ag_3PO_4.

Solution: The balanced equation representing the solution reaction is

$$Ag_3PO_4(s) \rightleftarrows 3\ Ag^+ + PO_4^{3-}$$

and the equilibrium expression is

$$K_{sp} = [Ag^+]^3[PO_4^{3-}]$$

The concentration tells us that there is 1.6×10^{-5} mol liter^{-1} of Ag_3PO_4, so

$$[Ag^+] = 3(1.6 \times 10^{-5}) = 4.8 \times 10^{-5}\ M$$
$$[PO_4^{3-}] = 1.6 \times 10^{-5}\ M$$

Substituting these concentrations into the equilibrium expression gives the value of K_{sp}.

$$K_{sp} = [Ag^+]^3[PO_4^{3-}] = (4.8 \times 10^{-5})^3(1.6 \times 10^{-5}) = 1.8 \times 10^{-18} \ \bullet$$

Parallel Problem: A saturated solution of lead fluoride at 25°C is $2.1 \times 10^{-3}\ M$. Calculate K_{sp} at 25°C for PbF_2.
Ans: 3.7×10^{-8}

Now work through Examples 16-1 and 16-2 in the text.

2. *Calculation of solubility from K_{sp}*

Since values of K_{sp} are available in tables, a common problem is to calculate the concentration of ions in a saturated solution using the value of K_{sp}. Examples 16-3 and 16-4 in the text illustrate this calculation.

3. *The common-ion effect on solubility*

Since the product of the concentrations of ions in a saturated solution must equal K_{sp}, the presence of two salts containing a common ion in the same solution will affect the solubility of the system. Generally, the net result is to decrease the solubility of the less soluble salt.

• EXAMPLE 2

Problem: Compare the solubility of AgI in pure water and in 0.10 M $AgNO_3$ at 25°C. K_{sp} for AgI is 8.5×10^{-17} at 25°C.

Solution: AgI dissolves in pure water or in 0.10 M $AgNO_3$ according to the reaction

$$AgI(s) \rightarrow Ag^+ + I^-$$

and the equilibrium is represented by

$$K_{sp} = 8.5 \times 10^{-17} = [Ag^+][I^-]$$

In pure water $[Ag^+] = [I^-]$. Let $x = [Ag^+] = [I^-]$. Then

$$x^2 = 8.5 \times 10^{-17}$$

$$x = \text{solubility} = 9.2 \times 10^{-9}\ M$$

In 0.10 M $AgNO_3$ the concentration of Ag^+ is 0.10 M. Adding AgI will increase this by about 9.2×10^{-9} M, which is negligible compared to 0.10. Let $x = [I^-]$. Then

$$[Ag^+] = 0.10 \qquad [I^-] = x$$

Substitute these values into the K_{sp} expression.

$$K_{sp} = 8.5 \times 10^{17} = [Ag^+][I^-] = 0.10(x)$$

$$x = [I^-] = \frac{8.5 \times 10^{-17}}{0.10} = 8.5 \times 10^{-16}\ M$$

Even though $[Ag^+] = 0.01$ M, the solubility of AgI is limited to the $[I^-]$. Therefore

$$[I^-] = \text{solubility} = 8.5 \times 10^{-16}\ M$$

in 0.10 M $AgNO_3$, or about 10^7 times less than the solubility in pure water. •

Parallel Problem: Calculate the solubility of AgCl in 0.10 M $AgNO_3$ at 25°C. K_{sp} for AgCl is 1.7×10^{-10} at 25°C.
Ans: 1.7×10^{-9} M

Example 16-5 in the text shows how the presence of I^- from a second source also dramatically affects the solubility of AgI. Example 16-6 in the text shows how pH has a large effect on the solubility of slightly soluble bases.

16-2 Precipitation reactions

1. Predicting when precipitation will occur

A comparison of the numerical value of the ion product or mass-action coefficient with K_{sp} will show if a solution is unsaturated, saturated, or supersaturated. A supersaturated solution can result in precipitation of the compound until its concentration is reduced to the saturated level. If Q represents the ion product:

$Q < K_{sp}$	means the solution is unsaturated
$Q = K_{sp}$	means the solution is saturated
$Q > K_{sp}$	means precipitation can occur because the solution is supersaturated

• EXAMPLE 3

Problem: Calculate the [Ag+] necessary to initiate precipitation of AgI from a solution that is 0.0030 M in iodide ions at 25°C. K_{sp} for AgI at 25°C is 8.5×10^{-17}.

Solution: Precipitation of AgI will occur as soon as the ion product, $[Ag^+][I^-]$, exceeds K_{sp}.

$$K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17}$$

For a solution with $[I^-] = 0.0030$

$$Ag^+ = \frac{K_{sp}}{[I^-]} = \frac{8.5 \times 10^{-17}}{3.0 \times 10^{-3}} = 2.8 \times 10^{-14}\,M$$

As soon as $[Ag^+]$ exceeds $2.8 \times 10^{-14}\,M$, precipitation of AgI will occur. •

Parallel Problem: Calculate the $[Ag^+]$ necessary to initiate precipitation of AgCl from a solution $3.00 \times 10^{-5}\,M$ in chloride ion at 25°C. K_{sp} for AgCl is 1.7×10^{-10} at 25°C.
Ans: $5.7 \times 10^{-6}\,M$

• EXAMPLE 4

Problem: If 300 mL of 0.100 M HCl and 300 mL of $5.0 \times 10^{-3}\,M$ $Pb(NO_3)_2$ are mixed, will $PbCl_2$ precipitate? K_{sp} for $PbCl_2$ is 1.6×10^{-5}.

Solution: Precipitation will occur if the ion product for $PbCl_2$ exceeds K_{sp}.

$$PbCl_2(s) \rightleftarrows Pb^{2+} + 2\,Cl^-$$

For a saturated solution

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$$

When the two solutions are mixed, the total volume will be 600 mL, or twice the original volumes; therefore, the ion concentrations will be one-half the original values.

$$[Cl^-] = 0.100\left(\frac{300}{600}\right) = 0.0500\,M$$

$$[Pb^{2+}] = 5.00 \times 10^{-3}\left(\frac{300}{600}\right) = 2.50 \times 10^{-3}\,M$$

The ion-product quotient is

$$Q = [Pb^{2+}][Cl^-]^2 = (2.50 \times 10^{-3})(0.0500)^2 = 6.3 \times 10^{-6}$$

Since $Q < K_{sp}$, precipitation will not occur. •

Parallel problem: If 100 mL of $1.0 \times 10^{-4}\,M$ HCl and 1.00 mL of $1.0 \times 10^{-5}\,M$ $AgNO_3$ are mixed, will AgCl precipitate? K_{sp} for AgCl is 1.7×10^{-10} at 25°C.
Ans: No.

Example 16-7 in the text illustrates a case where precipitation will occur.

2. *Predicting which compound will be the first to precipitate*

When the concentration of a mixture of ions is increased, the compound whose ion product exceeds K_{sp} first will precipitate first. Example 16-8 in the text illustrates this calculation.

16-3 Complex-ion equilibria

Complex ions are often used to regulate the concentration of metal ions in solution during electroplating processes. A very small, but constant, concentration of metal ion gives a uniform layer of metal deposited during electroplating.

• EXAMPLE 5

Problem: Silver plating is done from a solution containing the complex ion $Ag(CN)_2^-$. What is the concentration of silver ions in a solution which is 0.100 M in $Ag(CN)_2^-$?
$K_{formation}$ for $Ag(CN)_2^-$ is 3.0×10^{20}.

Solution: The formation reaction for $Ag(CN)_2^-$ is

$$Ag^+ + 2\,CN \rightleftarrows Ag(CN)_2^-$$

$$K_{form} = 3.0 \times 10^{20} = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2}$$

Let $x = [Ag^+]$. Then

$$2x = [CN^-]$$

$$[Ag(CN)_2^-] = 0.10 - x \cong 0.100$$

The large value of K_{form} shows that x is very small and can be neglected with respect to 0.100. Substituting these values into the expression for K_{form} gives

$$3.0 \times 10^{20} = \frac{0.100}{x(2x)^2}$$

$$x^3 = \frac{0.100}{4(3.0 \times 10^{20})} = 8.3 \times 10^{-23}$$

$$x = [Ag^+] = 4.4 \times 10^{-8}\,M \quad \bullet$$

Parallel Problem: What is the concentration of silver ions in a solution which is 1.00×10^{-6} M in $Ag(CN)_2^-$? $K_{formation}$ for $Ag(CN)_2^-$ is 3.0×10^{20}.
Ans: $9.4 \times 10^{-10}\,M$

Example 16-9 in the text shows the calculation of metal-ion concentration in equilibrium with a complex ion using the cumulative dissociation constant. The formation and dissociation constants are related by

$$K_{diss} = \frac{1}{K_{form}}$$

16-4 Simultaneous equilibria

Sometimes the solubility of a compound is affected by other ions in solution. When this happens it is necessary to consider the interacting equilibria simultaneously.

• EXAMPLE 6

Problem: Will MnS precipitate if 1.0×10^{-3} *M* $Mn(NO_3)_2$ is saturated with H_2S? A saturated H_2S solution is 0.10 *M*. K_{sp} for MnS is 1.0×10^{-16}.

Solution: The MnS and H_2S equilibria must be considered simultaneously. First let us find the concentration of S^{2-} in a saturated H_2S solution. The two-step dissociation is represented by

$$H_2S \rightleftarrows H^+ + HS^- \qquad K_1 = 1.1 \times 10^{-7}$$
$$HS^- \rightleftarrows H^+ + S^{2-} \qquad K_2 = 1.0 \times 10^{-14}$$

Since K_1 is much larger than K_2, nearly all the H^+ will be produced from the first dissociation step, and $[H^+]$ will be approximately equal to $[HS^-]$. We can find $[H^+]$ as follows: Let $x = [H^+] = [HS^-]$. Then

$$[H_2S] = 0.10 - x \cong 0.10$$
$$K_1 = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10 - x} \cong \frac{x^2}{0.10}$$
$$x^2 = 0.10(1.1 \times 10^{-7}) = 1.1 \times 10^{-8}$$
$$x = [H^+] = [HS^-] = 1.05 \times 10^{-4}$$

Now we can use K_2 to find $[S^{2-}]$.

$$K_2 = 1.0 \times 10^{-14} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{1.05 \times 10^{-4}[S^{2-}]}{1.05 \times 10^{-4}}$$

$$[S^{2-}] = K_2 = 1.0 \times 10^{-14}$$

We can use this value for $[S^{2-}]$ to see if the ion product $[Mn^{2+}][S^{2-}]$ is greater than K_{sp}.

$$[Mn^{2+}] = 1.0 \times 10^{-3} \qquad [S^{2-}] = 1.0 \times 10^{-14}$$

$$[Mn^{2+}][S^{2-}] = 1.0 \times 10^{-3}(1.0 \times 10^{-14}) = 1.0 \times 10^{-17}$$

Since the ion product is smaller than K_{sp}, MnS will not precipitate from a saturated H_2S solution. Note, however, that if the pH were increased, the $[H^+]$ would be less, the dissociations would shift to the right to increase $[S^{2-}]$, and MnS would precipitate. •

Parallel Problem: Will NiS precipitate if 1.0×10^{-3} *M* $Ni(NO_3)_2$ is saturated with H_2S? K_{sp} for NiS is 1.0×10^{-19}.
Ans: Yes

• EXAMPLE 7

Problem: A 1.0×10^{-3} *M* solution of MnS is buffered at pH 7 and saturated with H_2S (0.10 *M*). Will MnS precipitate? (See Example 6 for equilibrium constants.)

Solution: Since $[H^+]$ is known, we can use the overall equilibrium for H_2S dissociation to find $[S^{2-}]$.

$$H_2S \rightleftarrows 2\,H^+ + S^{2-}$$

$$K = K_1K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = 1.1 \times 10^{-7}\,(1.0 \times 10^{-14}) = 1.1 \times 10^{-21}$$

$$[H^+] = 10^{-pH} = 10^{-7}$$

$$[H_2S] = 0.10$$

Substituting these values in the equilibrium expression and solving for $[S^{2-}]$ gives

$$[S^{2-}] = \frac{[H_2S]K}{[H^+]^2} = \frac{0.10(1.1 \times 10^{-21})}{(10^{-7})^2} = 1.1 \times 10^{-8}$$

Now determine the ion product $[Mn^{2+}][S^{2-}]$ using this value for $[S^{2-}]$.

$$[Mn^{2+}] = 1.0 \times 10^{-3} \qquad [S^{2-}] = 1.1 \times 10^{-8}$$

$$[Mn^{2+}][S^{2-}] = 1.0 \times 10^{-3}(1.1 \times 10^{-8}) = 1.1 \times 10^{-11}$$

which is considerably larger than the value for K_{sp} , 1.0×10^{-16}. Therefore, MnS will precipitate from a saturated H_2S solution at pH 7. •

Parallel Problem: A 1.0×10^{-3} *M* solution of NiS is buffered at pH 7.0 and saturated with H_2S (0.10 *M*). Will NiS precipitate? (See the previous Parallel Problem and Example 6 for equilibrium constants.)
Ans: Yes. Note that Ni^{2+} could be separated from Mn^{2+} by adding H_2S, but the solution must be acidic to get quantitative separation.

Text Examples 16-10 to 16-12 give additional illustrations of simultaneous equilibria.

KEY TERMS

16-1 The solubility of ionic solids

Solubility equilibrium: A two-phase system in which a solid is in equilibrium with its ions in solution.

Solubility product constant: K_{sp}. The equilibrium constant for an ionic solubility equilibrium.

16-3 Complex-ion equilibria

Amphiprotic: A chemical species which can either gain or lose a proton during reaction.

Amphoteric: A chemical species which can react as either an acid or a base.

Cumulative dissociation constant: The product of the dissociation constants for the steps in the stepwise dissociation of a complex.

Dissociation constant: K_{diss}. The equilibrium constant for a dissociation equilibrium.

Exchange reaction: A reaction involving an exchange of ligands on the central atom of a complex.

Formation constant: The equilibrium constant for the formation reaction of a complex. Same as stability constant. The reciprocal of an instability constant.

Instability constant: The equilibrium constant for the dissociation reaction of a complex. The reciprocal of the stability or formation constant.

Stability constant: Same as formation constant.

SELF TEST

True or False

_____ 1. K_{sp} is the solubility of a compound.

_____ 2. The ion product and solubility product are different names for K_{sp}.

_____ 3. Solubility products can be calculated from solubilities.

_____ 4. K_{sp} values apply only to saturated solutions of slightly soluble compounds.

_____ 5. K_{sp} for AgCl is 1.7×10^{-10} and K_{sp} for $CaSO_4$ is 2.4×10^{-5}; therefore, $CaSO_4$ is more soluble than AgCl.

_____ 6. The presence of HCl in a solution increases the solubility of AgCl.

_____ 7. If K_{sp} of two compounds are equal they will have equal solubilities.

_____ 8. A salt, MA, will precipitate if $[M^+][A^-]$ is greater than K_{sp}.

_____ 9. Supersaturated solutions are not at equilibrium.

_____10. Mixing solutions of $AgNO_3$ and NaCl will always result in a precipitate of AgCl.

_____11. A complex ion is a charged particle composed of a central metal ion and surrounding ligands.

_____12. The ligands of many complex ions can be exchanged for different molecules or ions.

_____13. Cumulative dissociation constants are a measure of the stability of complex ions.

_____14. Amphoteric substances can behave as either acids or bases.

_____15. Most insoluble metal sulfides can be dissolved in acidic solutions.

Completion

16. The ion product for CaF_2 can be expressed as ________________________.

17. The solubility product expression for $Ca(OH)_2$ is ________________________________.

18. The chemical equation for the solubility equilibrium of $Al(OH)_3$ is ________________

19. The presence of NaCl in a solution of Ag^+ will ________________ (increase, decrease) $[Ag^+]$.

20. The presence of H^+ will _____________ (increase, decrease) the solubility of $Mg(OH)_2$.

21. A precipitate will form if the ______________________ is ___________________ (greater, less) than K_{sp} for the compound.

22. The metal ion in a complex ion is surrounded by ______________________.

23. The reciprocal of the dissociation constant of a complex ion is called the ______________________.

24. A ___________________________ compound is soluble in either acid or base.

25. The algebraic expression for the formation constant of the complex ion $Co(NH_3)_6{}^{3+}$ is ______________________.

26. The cumulative dissociation reaction for the complex ion $Cu(NH_3)_4{}^{2+}$ is __________________________.

27. Insoluble metal hydroxides can be dissolved by adding ______________________.

28. AgCl can be dissolved by adding ______________________.

29. Metal sulfides can be separated by selective precipitation from a saturated H_2S solution by controlling the ___________________ of the solution.

30. The equation $H_2S \rightleftarrows 2\,H^+ + S^{2-}$ ___________________ (does, does not) represent an equilibrium.

Multiple Choice

31. The solubility of silver carbonate, Ag_2CO_3, is 0.032 g/L at 20°C. K_{sp} for Ag_2CO_3 at 20°C is
(a) 6.2×10^{-12} (b) 1.6×10^{-12} (c) 2.7×10^{-8} (d) 1.3×10^{-4}

32. The expression for the solubility product constant for $Fe(OH)_3$ is $K_{sp} =$
(a) $[Fe^{+3}][OH^-]$ (b) $\frac{[Fe^{+3}][OH^-]}{[Fe(OH)_3]}$
(c) $[Fe^{+3}]^3[OH^-]$ (d) $[Fe^{+3}][OH^-]^3$

33. In a saturated solution of $Fe(OH)_3$ the pH was found to be 5.13. What is the solubility of $Fe(OH)_3$?
(a) 2.47×10^{-6} (b) 1.35×10^{-9} (c) 4.50×10^{-10}
(d) insufficient information to determine

34. The solubility of BaF_2 is 7.5×10^{-3} *M*. K_{sp} for BaF_2 is
(a) 7.5×10^{-3} (b) 5.6×10^{-5} (c) 1.7×10^{-6} (d) 4.2×10^{-7}

35. The solubility, *M*, of $Pb(IO_3)_2$ is related to K_{sp} by
(a) $K_{sp} = 4\,M^3$ (b) $K_{sp} = M$ (c) $K_{sp} = 2\,M^3$ (d) $K_{sp} = 2\,M^2$

36. K_{sp} for $Ca(OH)_2$ is 1.3×10^{-6}. In which of the following is $Ca(OH)_2$ most soluble?
(a) 1 *M* HCl (b) 1 *M* NaOH (c) 1 *M* $CaCl_2$ (d) pure water

37. Addition of $AgNO_3$ to a saturated solution of AgI will
(a) lower K_{sp} for AgI
(b) lower $[Ag^+]$
(c) lower the ion product of AgI
(d) lower $[I^-]$

38. K_{sp} for AgI is 8.5×10^{-17}. The solubility of AgI in 0.028 *M* NaI is
(a) 1.1×10^{-13} *M* (b) 1.5×10^{-15} *M*
(c) 3.0×10^{-15} *M* (d) 2.4×10^{-18} *M*

39. The equilibrium expression for the formation of the complex ion $Ag(NH_3)_2^+$ is
(a) $K_f = [Ag^+][NH_3]$ (b) $K_f = [Ag^+][NH_3]^2$
(c) $K_f = \frac{[Ag^+][(NH_3)]^2}{[Ag(NH_3)_2^+]}$ (d) $K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

40. K_{diss} for $Ag(NH_3)_2^+$ is 5.9×10^{-8}. The concentration of Ag^+ ion in 1.0 L of solution containing 0.10 mol of $AgNO_3$ and 0.50 mol of NH_3 is
(a) 1.2×10^{-8} (b) 2.4×10^{-8} (c) 6.6×10^{-8} (d) 1.2×10^{-9}

41. An amphoteric substance
(a) forms a complex ion when it dissolves
(b) is soluble in acid or base but not in pure water
(c) acts as either an Arrhenius acid or an Arrhenius base
(d) all of the above

42. What is the minimum concentration of chloride ions necessary to precipitate $PbCl_2$ from a solution which is 0.010 *M* in $Pb(NO_3)_2$? K_{sp} for $PbCl_2$ is 1.6×10^{-5}.
(a) 1.6×10^{-2} *M* (b) 4.0×10^{-2} *M*
(c) 8.0×10^{-2} *M* (d) 1.6×10^{-3} *M*

43. What is the lowest pH at which $Fe(OH)_3$ can be precipitated from a 0.020 M solution of Fe^{3+}? K_{sp} for $Fe(OH)_3$ is 1.1×10^{-36}.
(a) 5.1 (b) 5.4 (c) 8.9 (d) 9.4

44. What concentration of NH_4^+ is necessary to prevent the precipitation of $Fe(OH)_2$ in a solution that is 0.020 M in Fe^{2+} and 0.050 M in NH_3? K_{sp} for $Fe(OH)_2$ is 2×10^{-15}.
(a) 2.9 M (b) 2.5 M (c) 8.9×10^{-4} M
(d) 3.2×10^{-7} M

45. A solution that is 5×10^{-3} M in Sn^{2+} and 0.050 M in H^+ is saturated with H_2S (0.10 M). What concentration of Sn^{2+} remains in solution after SnS has precipitated?
K_{sp} for SnS is 1×10^{-26}. $K_1 = 1.1 \times 10^{-7}$; $K_2 = 1.0 \times 10^{-14}$ for H_2S.
(a) 9.1×10^{-5} M (b) 4.5×10^{-6} M
(c) 2.3×10^{-7} M (d) 1.0×10^{-13} M

Chapter 17

CHEMICAL THERMODYNAMICS

CHAPTER OVERVIEW

One of the most powerful tools for understanding why and how chemical reactions occur is through the analysis of energy changes accompanying chemical and physical changes. The study of energy and work changes was introduced in Chapter 3 through our study of the first law of thermodynamics. In Chapter 17 you will study two additional fundamental laws of thermodynamics and use them to help you better understand chemistry. Writing and balancing chemical reactions was covered in Chapters 2 and 12, but simply having a balanced chemical equation does not tell whether the reaction will actually take place. An understanding of thermodynamics will allow you to predict, with confidence, when a reaction can take place, or better, when it is thermodynamically allowed. Chapter 17 will show you how to apply the laws of thermodynamics to determine whether a chemical reaction is spontaneous or nonspontaneous.

17-1 The first law: a reconsideration

A reaction that is allowed in a thermodynamic sense is called a spontaneous reaction. In a nonscientific sense a spontaneous reaction is one that starts or ignites by itself. To a chemist, however, a spontaneous change is one capable of doing work. A thermodynamically spontaneous reaction may not be self-starting, and energy may even be consumed, but the capability of doing work is present and that is the necessary condition for spontaneity. The reverse of a change capable of doing work is a change requiring an input of work. Likewise, the reverse of a spontaneous change, a nonspontaneous change, can be accomplished only by the input of work into the system by some external source. This is an important concept to understand about spontaneity: namely, that nonspontaneous changes or unnatural changes can be accomplished only by doing work on the system. Often there is no practical way to get work into the system and, therefore, many nonspontaneous changes will not occur at all.

As you recall from Chapter 3, the first law is commonly called the law of conservation of energy. It simply says that energy cannot be created or destroyed. Energy can manifest itself in several different forms, such as heat or work, and the first law permits calculations of the effects of energy as it is changed from one form to another. The amount of energy in any isolated system is constant or, in other words, energy is conserved in isolated systems. You will review how the concept of conservation of energy allows calculation of relationships between heat and work in many systems. One important example is the decrease in energy of a gas as it expands and does work against a constant resisting force such as the atmosphere. The concept of energy changes and accompanying pressure-volume changes is so basic to chemistry that a new variable, enthalpy (H), was defined to include both effects, $H = E + PV$. It is important to remember that $\Delta E = q_v$, the energy change is equal to the heat change for a constant-volume process, and also the parallel relationship, $\Delta H = q_p$, the change in enthalpy is equal to the heat change at constant pressure.

17-2 The second law

Understanding the second law of thermodynamics depends on understanding two variables connected with it: entropy and free energy. Your first introduction to thermodynamics may seem difficult because it deals with variables and concepts that are abstract. Even energy, a term we use almost daily, is difficult to comprehend in a thermodynamic sense. Terms like *enthalpy*, *entropy*, and *free energy* will seem challenging at first so you must allow time to read and study their definitions and uses several times if necessary. Strive to understand these terms and how they relate to each other. The second law introduces an additional abstract concept, entropy. Total entropy has the unique property of increasing in all spontaneous changes. You may be accustomed to dealing with physical variables that are conserved, such as energy, but probably not with a variable like entropy that tends to increase as a natural reaction takes place. Concentrating on relating entropy to probability and disorder will help you get by this hurdle.

17-3 Gibbs free energy and spontaneous change

The equation $\Delta G = \Delta H - T\Delta S$ relates the three most important variables in Chapter 17 and so is important to understand. The following definitions may help you understand the relationship among these variables.

ΔG	$=$	ΔH	$-$	$T\Delta S$
Energy available to do useful work		Total energy change		Energy not available to do work outside of the system

Reactions tending towards lowest energy and maximum increased entropy tend to be spontaneous. Both of these tendencies are combined in the concept of free energy in the equation above. Study the table in the text relating the signs of ΔG, ΔH, and ΔS to spontaneity of change to see the relationship between energy and randomness in determining whether or not a chemical change is thermodynamically allowed.

17-4 Changes in entropy and Gibbs free energy

Entropy changes for phase transitions are calculated with the equation

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{phase change}}}{T_{\text{phase change}}}$$

Changes in entropy for chemical reactions can be calculated using tabulated values of absolute entropies such as the values given in Table 17-1 in the text and the equation:

$$\Delta S^{\circ}_{\text{Rxn}} = \sum S^{\circ}_{\text{products}} = \sum S^{\circ}_{\text{reactants}}$$

Entropy is the only thermodynamic variable for which we can calculate an absolute value. The third law allows us to do this from absolute entropy values such as those in Table 17-1 in the text.

Changes in Gibbs free energy are calculated in a manner very similar to calculations of ΔH_{Rxn} introduced in Chapter 3. We can use the equation:

$$\Delta G^{\circ}_{\text{Rxn}} = \sum \Delta G^{\circ}_{f(\text{products})} - \sum \Delta G^{\circ}_{f(\text{reactants})}$$

Values of Gibbs free energy of formation, ΔG°_{f}, are obtained from Table 17-2 or Appendix G in the text.

17-5 Thermodynamics and equilibrium

Figure 17-7 in the text shows the relation between the minimum value of $\Delta G^{\circ}_{\mathrm{Rxn}}$ and equilibrium. This relation can be expressed algebraically as

$$\Delta G^{\circ} = -RT \ln K_p$$

This powerful relation between ΔG° and K_p unites Chapters 17 and 14 and allows us to convert thermodynamic data to equilibrium data and vice versa. You will work some problems showing how equilibrium constants can be calculated from tabulated thermodynamic values.

KEY EQUATIONS

17-1 The first law: a reconsideration

1. *The first law*

$$\Delta E = q + w$$

where ΔE = energy change of a system
q = heat gained by a system from its surroundings
w = work done by a system on its surroundings

2. *Work of expansion*

$$w = P_{\mathrm{ext}} \Delta V$$

where P_{ext} = external pressure acting on a system
ΔV = change in volume of the system (gas)

3. *Enthalpy definition*

$$H = E + PV$$

$$\Delta H = \Delta E + P\Delta V \text{ at constant pressure}$$

17-2 The second law

$\Delta S > 0$ for spontaneous change in an isolated system

where ΔS = entropy change of a system, J $\mathrm{mol^{-1}\ K^{-1}}$

17-3 Gibbs free energy and spontaneous change

$$\Delta G = \Delta H - T\Delta S$$

where ΔG = free energy change, or energy available to do work.

17-4 Changes in entropy and Gibbs free energy

1. *Entropy change for a phase change*

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m}$$

where ΔS_{fus} = entropy of fusion
ΔH_{fus} = enthalpy or heat of fusion
T_m = melting temperature, K

A similar equation applies to the entropy of vaporization.

2. *Calculation of absolute entropy of a reaction*

$$\Delta S^{\circ} = \Sigma\, S^{\circ}_{\text{products}} - \Sigma\, S^{\circ}_{\text{reactants}}$$

where S° = absolute entropy of a substance (see Text Table 17-1).

3. *Calculation of free-energy change of a reaction from tabulated values of free energy of formation.*

$$\Delta G^{\circ}_{\text{reaction}} = \Sigma(\Delta G^{\circ}_f)_{\text{products}} - \Sigma\,(\Delta G^{\circ}_f)_{\text{reactants}}$$

where ΔG°_f = standard free energy of formation (Text Table 17-2).

17-5 Thermodynamics and equilibrium

$$\Delta G^{\circ} = -RT \ln K_p$$

LEARNING OBJECTIVES

As a result of studying Chapter 17, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 300 of this *Study Guide*.

17-1 The first law: a reconsideration

1. Clearly distinguish between spontaneous and nonspontaneous changes in a thermodynamic sense. (Self Test 26)
2. Calculate the work done by a gas as it expands against a constant force. (Text Example 17-1; Text Probs. 17-2, 17-3, 17-7 to 17-9, 17-13, 17-14, 17-46) (New Skills Example 1; Self Test 17, 18)
3. Write a word statement and mathematical equation of the first law of thermodynamics. (Text Prob. 17-1) (Self Test 3, 4, 16)

4. Calculate heat, work, ΔE, and ΔH changes associated with the expansion of an ideal gas. (Text Example 17-2; Text Probs. 17-3, 17-10 to 17-14, 17-35, 17-46, 17-49) (New Skills Example 2; Self Test 1, 6, 7, 31, 32, 34)
5. Calculate ΔH for a system given ΔE, and vice versa. (Text Example 17-3; Text Probs. 17-13 to 17-15, 17-36, 17-37, 17-46) (Self Test 5)

17-2 The second law

1. Write a word statement and mathematical expression for the second law of thermodynamics. (Self Test 11, 24, 28, 42)
2. Predict the sign of entropy changes for physical and chemical processes. (Text Probs. 17-16, 17-21, 17-49) (New Skills Example 3; Self Test 7, 9, 22, 43, 45)
3. Relate entropy to disorder and probability. (Text Probs. 17-17, 17-38, 17-40) (Self Test 12, 14, 23, 25, 41)
4. Clearly distinguish between the entropy change of a system and the entropy change of the surroundings. (Text Prob. 17-41) (Self Test 33)

17-3 Gibbs free energy and spontaneous change

1. Explain why change in Gibbs free energy is a reliable criterion for predicting spontaneity of reactions based on its relationship to enthalpy and entropy. (Text Prob. 17-24)
2. Use the algebraic sign of ΔG to predict whether a reaction is spontaneous or nonspontaneous. (Text Prob. 17-43) (Self Test 5, 10, 15, 44)
3. Use the algebraic signs of ΔH and ΔS to predict the effects of temperature on the spontaneity of a reaction. (Text Probs. 17-25, 17-26, 17-30, 17-44) (New Skills Sec. 17-3; New Skills Example 7; Self Test 2, 13, 30, 40)

17-4 Changes in entropy and Gibbs free energy

1. Calculate entropy change of a phase transition. (Text Example 17-4; Text Probs. 17-18, 17-19, 17-39, 17-50) (New Skills Example 4; Self Test 9, 35)
2. Calculate entropy changes from tabulated third law entropy values or from tabulated values of enthalpy and free energy. (Text Example 17-5; Text Probs. 17-22, 17-23, 17-42) (Self Test 36)
3. Calculate free-energy changes from tabulated values of standard enthalpy of formation and absolute entropies. (Text Tables 3-2, 17-1; Text Example 17-6; Text Probs. 17-30, 17-44) (Self Test 21)
4. Calculate free-energy changes from tabulated values of free energy of formation. (Text Table 17-2; Text Example 17-7; Text Probs. 17-27 to 17-29) (New Skills Example 5; Self Test 8, 19, 37)

17-5 Thermodynamics and equilibrium

1. Explain the changes in free energy and entropy of a system as it approaches equilibrium. (Text Fig. 17-7) (Self Test 20)
2. Calculate equilibrium constants from tabulated thermodynamic data. (Text Example 17-8; Text Probs. 17-31 to 17-33) (New Skills Example 6; Self Test 39)
3. Calculate free-energy changes from equilibrium data. (Text Probs. 17-45, 17-47, 17-48)
4. Calculate the temperature at which a reaction is at equilibrium. (Text Prob. 17-44) (New Skills Example 7; Self Test 38)

NEW SKILLS

17-1 The first law: a reconsideration

1. Work of expansion

When a gas expands against a resisting force it does work. If the gas is the system, the work done by the system is a negative quantity. Example 17-1 in the text illustrates the calculation of this work. For a compression process V_{final} is less than V_{initial}, so ΔV is negative and w is positive. P_{ext} is the external pressure exerted to compress the gas.

• EXAMPLE 1

Problem: Calculate the work done to compress 1.0 mol of an ideal gas from 50 to 30 liters by a force exerting a pressure of 2.0 atm on the gas.

Solution:

$$w = -P_{\text{ext}}\Delta V$$

$$P_{\text{ext}} = 2.0\text{ atm}; \quad V_{\text{initial}} = 50\text{ L}; \quad V_{\text{final}} = 30\text{ L}$$

$$P_{\text{ext}}(V_{\text{final}} - V_{\text{initial}}) = 2.0\text{ atm }(30\text{ L} - 50\text{ L}) = 40\text{ L atm}$$

$$40\text{ L atm} \times 0.101\text{ kJ L}^{-1}\text{ atm}^{-1} = 4.0\text{ kJ} \quad \bullet$$

Parallel Problem: Calculate the change in volume of a gas when 10 kJ of work is done on the gas by a force exerting a pressure of 5.0 atm.
Ans: 20 L

2. Calculation of ΔE, q, or w using the first law

The first law can be used to calculate ΔE, q, or w if two of these quantities are known. Text Example 17-2 illustrates this calculation.

• EXAMPLE 2

Problem: If 2 mol of an ideal gas expand isothermally (at constant temperature) from 10.0 to 60.0 liters against a resisting pressure of 0.500 atm, calculate ΔE, q, and w for the expansion process.

Solution: The energy of an ideal gas is a function of its temperature only. If the temperature remains constant so does the energy. Therefore, for any constant-temperature expansion of an ideal gas.

$$\Delta E = 0$$

From the first law

$$\Delta E = 0 = q + w$$

$$q = -w$$

The heat added to an ideal gas during an isothermal expansion is equal to the work of expansion done by the gas.

$$w = -P_{ext}\Delta V = -0.500 \text{ atm}(60.0 \text{ L} - 10.0 \text{ L}) = -25.0 \text{ L atm}$$

$$-25.0 \text{ L atm} \times 0.101 \text{ kJ L}^{-1} \text{ atm}^{-1} = -2.53 \text{ kJ}$$

$$q = -w = 2.53 \text{ kJ} \bullet$$

Parallel Problem: If 5.0 mol of an ideal gas undergoes an isothermal compression from 20.0 to 10 liters by an external force exerting a pressure of 6.0 atm, what is ΔE, q, and w for the compression process?
Ans: $\Delta E = 0$, $q = -w = -6.1$ kJ

3. *Calculation of enthalpy changes*

The enthalpy change of a substance undergoing a physical change may be calculated by several different techniques. When the energy change is known, it is convenient to use the definition of enthalpy, $\Delta H = \Delta E + \Delta(PV)$. The $\Delta(PV)$ term is usually small unless a gas is involved, so ΔH and ΔE normally have very similar values in condensed systems. For processes taking place at constant pressure, the relationship $\Delta H = q_p = nC_p \Delta t$ can be used. Text Example 17-3 illustrates this calculation.

17-2 The second law

Entropy changes

As a system moves from an ordered state to a disordered state, the entropy increases. The entropy of a gas is higher than that of a liquid or solid. A solution has higher entropy than its unmixed components. Chemical or physical changes that cause disorder or mixing, generate gases, or substantially increase the number of moles will have a positive ΔS.

• EXAMPLE 3

Problem: Predict the sign of the entropy change for each of the following processes: (a) melting of ice (b) shuffling of a new deck of cards (c) conversion of amorphous sulfur to crystalline sulfur (d) burning of carbon monoxide to carbon dioxide (e) $2\ \text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$

Solution: (a) H_2O goes from an ordered solid state to a disordered liquid state. ΔS is positive.
(b) The cards go from an ordered state to a random distribution. ΔS is positive.
(c) The sulfur goes from a disordered amorphous state to an ordered crystalline state. ΔS is negative.
(d) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g)$ The number of moles of gas decreases from $1\frac{1}{2}$ to 1, so the system becomes more ordered. ΔS is negative. Note that Δn_{gas} equals the number of moles of gaseous products minus the number of moles of gaseous reactants so $\Delta n_{gas} = 1 - 1.5 = -0.5$. ΔS always has the same sign as Δn_{gas}.
(e) $\Delta n_{gas} = 0 - 1.5 = -1.5$ ΔS is negative. •

Parallel Problem: Predict the sign of the entropy change for each of the following processes: (a) condensing of steam (b) mixing red and green marbles (c) burning of wood (d) extraction of a metal from its ore (e) reaction between hydrochloric acid and calcium carbonate.
Ans: (a) negative (b) positive (c) positive (d) negative (e) positive

17-3 Gibbs free energy and spontaneous change

Free energy is a measure of the ability or capacity of a system to do work. The free energy of a system decreases during a spontaneous change so it loses its ability to do work. When all of the capacity to do work has been used, the system is at equilibrium and the free energy cannot decrease further. Another way of saying this is ΔG is negative for a spontaneous process and $\Delta G = 0$ at equilibrium. Since $\Delta G = \Delta H - T\Delta S$, either ΔH or ΔS can determine the sign of ΔG depending on the relative magnitude of ΔH and $T\Delta S$. Usually ΔH is larger than $T\Delta S$ so enthalpy (heat) considerations govern the sign of ΔG and determine whether or not a reaction or process is spontaneous. Occasionally ΔH is small and $T\Delta S$ may determine the sign of ΔG, so molecular ordering becomes the most important factor in deciding whether or not a reaction can proceed. If the temperature is high enough, the $T\Delta S$ term will become the deciding factor. When $\Delta H = T\Delta S$, the energy and molecular ordering exactly balance and $\Delta G = 0$. The system is at equilibrium.

17-4 Changes in entropy and Gibbs free energy

1. *Entropy change during phase transitions*

Entropy and enthalpy of phase changes are related by the expressions

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m} \quad \text{and} \quad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

• EXAMPLE 4

Problem: Calculate the entropy change for the condensation of 1 mol of water at 100°C. $\Delta H_{\text{vap}} = 40.7\ \text{kJ mol}^{-1}$.

Solution: The enthalpy of condensation is the negative of ΔH_{vap}.

$$\Delta S_{\text{cond}} = \frac{\Delta H_{\text{cond}}}{T_b} = \frac{-40.7\ \text{kJ mol}^{-1}}{373\ \text{K}} = -0.109\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$ •

Parallel Problem: Calculate the entropy change for the freezing of 2 mols of water.
Ans: $-22.0\ \text{J mol}^{-1}\ {}^{\circ}\text{C}^{-1}$

Example 17-4 in the text is a similar problem.

2. *Gibbs free-energy calculations*

Free-energy changes for a reaction can be calculated from tabulated free energies of formation using a manner similar to the way we calculated enthalpy changes in Chapter 3. This can be illustrated by the following example.

• EXAMPLE 5

Problem: Calculate the standard free energy for the conversion of graphite to diamond.

$$(\Delta G_f^{\circ})_{\text{graphite}} = 0$$

$$(\Delta G_f^\circ)_{\text{diamond}} = +2.91 \text{ kJ mol}^{-1}$$

Solution: The reaction for the process is

$$C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$$

The free-energy change for the reaction can be found from

$$\Delta G^\circ_{\text{reaction}} = \Sigma(\Delta G_f^\circ)_{\text{products}} - \Sigma(\Delta G_f^\circ)_{\text{reactants}}$$

$$= (\Delta G_f^\circ)_{\text{diamond}} - (\Delta G_f^\circ)_{\text{graphite}} = +2.91 \text{ kJ} - 0 = 2.91 \text{ kJ}$$

Since ΔG is positive the reaction is nonspontaneous. This is one explanation why many years and much effort were expended before a way to accomplish the conversion was found. Note that since the forward reaction is nonspontaneous, the reverse action (decomposition of diamond to graphite) is spontaneous! Do not worry about your diamond ring decomposing, though; thermodynamics only predicts the possibility of a reaction occurring. It says nothing about the rate of reaction. Decomposition of diamond to graphite *is* spontaneous, but the reaction is extremely slow. •

Parallel Problem: Calculate the standard free energy for the combustion of methane, $CH_4(g)$, to gaseous carbon dioxide and liquid water. See Text Table 17.2 for data.
Ans: –818 kJ mol^{-1}

Free energy of reaction can be calculated from tabulated values of free energy of formation. Example 17-7 in the text shows this calculation and Example 17-5 applies the technique used in Chapter 3 for calculation of $\Delta H^\circ_{\text{Rxn}}$ to calculation of absolute entropy.

17-5 Thermodynamics and equilibrium

1. Calculation of equilibrium constants from free-energy values

The concepts of equilibrium and thermodynamics are joined by the equation

$$\Delta G^\circ = -RT \ln K_p$$

You need to be able to calculate equilibrium constants from tabulated values of standard free energy of formation. This is illustrated by the following example.

• EXAMPLE 6

Problem: Calculate the equilibrium constant at 298 K for the reaction

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

given $(\Delta G_f^{\circ})_{CaCO_3(s)} = -1129 \text{ kJ mol}^{-1}$

$(\Delta G_f^{\circ})_{CaO(s)} = -604.2 \text{ kJ mol}^{-1}$

$(\Delta G_f^{\circ})_{CO_2(g)} = -394.4 \text{ kJ mol}^{-1}$

Solution: ΔG° for the reaction is found by

$$\Delta G^{\circ}_{\text{reaction}} = \Sigma(\Delta G_f^{\circ})_{\text{products}} - \Sigma(\Delta G_f^{\circ})_{\text{reactants}}$$

$$= (\Delta G_f^{\circ})_{CO_2} + (\Delta G_f^{\circ})_{CaO} - (\Delta G_f^{\circ})_{CaCO_3}$$

$$= -394.4 \text{ kJ} + (-604.2 \text{ kJ}) - (-1129 \text{ kJ}) = +130 \text{ kJ}$$

Note that since ΔG is positive the reaction is nonspontaneous. The equilibrium constant can be calculated from the relationship

$$\Delta G^{\circ} = -RT \ln K_p$$

First put this in the form

$$\ln K_p = \frac{-\Delta G^{\circ}}{RT} = \frac{-(+130{,}000 \text{ J mol}^{-1})}{(8.134 \text{ J mol}^{-1}\text{ K}^{-1})(298 \text{ K})} \doteq -52.5$$

$$K_p = e^{-52.5} = 1.6 \times 10^{-23}$$

The equilibrium expression for this reaction is $K_p = P_{CO_2}$. Therefore, the pressure of CO_2 in equilibrium with $CaCO_3$ (limestone) at standard conditions is 1.6×10^{-23} atm. •

Parallel Problem: Calculate the equilibrium constant at 25°C for the reaction:

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

Ans: $K_p = 2 \times 10^{-37}$

Thus we see that another interpretation of a nonspontaneous reaction is $K_p < 1.0$ so that the equilibrium concentrations strongly favor the reactants over the products.

2. *Free energy and the position of equilibrium*

What happens to the equilibrium constant in the foregoing example as the temperature increases? One would expect $CaCO_3$ to decompose if the temperature is high enough. In fact, this is the very process used to make lime (CaO) from limestone ($CaCO_3$) in a lime kiln.

• EXAMPLE 7

Problem: Calculate the temperature at which the decomposition of $CaCO_3$ becomes spontaneous at 1 atm pressure. $(\Delta H_f^{\circ})CaCO_3 = -1207 \text{ kJ mol}^{-1}$, $(\Delta H_f^{\circ})CaO = -635.5 \text{ kJ mol}^{-1}$, and $(\Delta H_f^{\circ})CO_2 = -393.5 \text{ kJ mol}^{-1}$.

Solution: To solve this problem we need to find how ΔG^o for the reaction varies with temperature. Using the relationship

$$\Delta G^o = \Delta H^o = T\Delta S^o$$

we can take advantage of the fact that ΔH^o and ΔS^o are essentially constant over a fairly wide temperature range. We can determine their values at 298 K from tabulated data and assume these values hold constant over the temperature range of interest.

First we find ΔH^o

$$\Delta H^o = \Sigma(\Delta H^o_f)_{\text{products}} - \Sigma(\Delta H^o_f)_{\text{reactants}}$$

$$= (\Delta H^o_f) + (\Delta H^o_f)_{CO_2} - (\Delta H^o_f)_{CaCO_3}$$

$$= (-393.5\text{ kJ}) + (-635.5\text{ kJ}) - (-1207\text{ kJ}) = +178\text{ kJ}$$

Now determine ΔS^o using the value of ΔG^o from Example 6.

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{178\text{ kJ} - 130\text{ kJ}}{298\text{ K}} = 0.161\text{ kJ K}^{-1}$$

We can substitute the values for ΔH^o and ΔS^o into the equation for ΔG^o to get an expression relating ΔG^o to temperature.

$$\Delta G^o = 178 - 0.161T$$

Since both ΔH^o and ΔS^o are positive, ΔG^o will become more negative as the temperature is increased. (See the table in Section 17-4 of the text.) If the temperature is high enough ΔG will become negative and the reaction will be spontaneous. At some temperature, ΔG^o will equal 0 and the reaction will be at equilibrium. In this case, you can see that equilibrium signifies $K_p = 1$, since when $\Delta G^o = 0 = -RT \ln K_p$, $\ln K_p = 0$ and $K_p = 1$. At any temperature above that which gives $\Delta G^o = 0$, the reaction will be spontaneous because ΔG^o will be negative.
If we set $\Delta G^o = 0$ in the expression relating ΔG^o to temperature, we find

$$\Delta G^o = 0 = 178 - 0.161\,T$$

$$T = \frac{178}{0.161} = 1100\text{ K} \quad \text{or} \quad \text{about } 830^\circ\text{C}$$

Therefore, at any temperature above 830°C, $CaCO_3$ will decompose to CaO and CO_2 with an equilibrium pressure of CO_2 greater than 1 atm. •

Parallel Problem: Calculate the temperature at which the reaction in the previous Parallel Problem becomes spontaneous.
Ans: 342°C

In general, we can say that the temperature at which a reaction is at equilibrium is given by:

$$\Delta G^o = 0 = \Delta H^o - T\Delta S^o$$

$$T_{\Delta G^o \to 0} = \frac{\Delta H^o}{\Delta S^o}$$

If ΔH^o and ΔS^o have the same algebraic sign, equilibrium will occur at some finite temperature.

KEY TERMS

17-1 The first law: a reconsideration

Enthalpy: A measure of the heat change of a process, defined as the sum of the energy and the pressure-volume product: $H = E + PV$.

First law of thermodynamics: The law of conservation of energy: $\Delta E = q + w$.

Laws of thermodynamics: Three laws which describe the energy changes of processes.

Thermodynamics: A study of the changes or transformations of energy which accompany physical and chemical changes of matter.

17-2 The second law

Boltzman constant: The ideal-gas constant expressed per molecule. $k = 1.38 \times 10^{-23}$ J K^{-1}

Disorder: A state of randomness or high probability often characterized by maximum freedom of molecules of a system.

Entropy: S. A thermodynamic quantity which measures the degree of disorder or randomness of a system.

Isolated system: A system which cannot exchange matter or energy with the surroundings.

Ordered state: A state of a system characterized by restricted arrangements and limited freedom of movement of molecules.

Second law of thermodynamics: There is a natural tendency for an isolated system to become more disordered and for its entropy to increase.

Spontaneous change: A process for which the change in Gibbs free energy is negative or the total entropy of system plus surroundings is positive.

Thermodynamic probability: The number of possible microstates for a system. It is proportional to the order or randomness of the system.

17-3 Gibbs free energy and spontaneous change

Free energy: G. A thermodynamic quantity which measures the energy of a system which is available for doing useful work, other than work of expansion. The free energy of a system is defined as the difference between the enthalpy and the temperature-entropy product. Same as Gibbs free energy.

Gibbs free energy: Same as free energy.

Nonspontaneous: A process for which the change in Gibbs free energy is positive or the total entropy of system plus surroundings is negative.

17-4 Changes in entropy and Gibbs free energy

Standard absolute entropy: Entropy calculated by the third law of thermodynamics for a substance in its standard state.

Standard free energy of formation: The change in free energy for the formation of one mole of a subsatnce from its elements in their standard state.

Third law of thermodynamics: The entropy of a perfect crystal at absolute zero is zero.

17-5 Thermodynamics and equilibrium

Entropy of mixing: The increase in entropy due to the disorder of a system caused by mixing pure components to form a solution.

Gibbs valley: The minimum point on a graph of free energy as a function of extent of reaction. The Gibbs valley corresponds to the point of equilibrium for the system.

Thermodynamic equilibrium constant: The true equilibrium constant expressed as a function of activities rather than concentrations or partial pressures.

SELF TEST

True or False

_____ 1. When a system does work its energy decreases.

_____ 2. Exothermic reactions are capable of doing work and therefore are spontaneous.

_____ 3. The total quantity of energy available in an isolated system is constant.

_____ 4. Every system in the universe tends toward a maximum in its potential energy.

_____ 5. For a system consisting entirely of condensed phases ΔH is approximately equal to ΔE.

_____ 6. The heat change of a system at constant pressure is equal to the enthalpy change of the system.

_____ 7. Entropy increases when a sugar cube dissolves in coffee.

_____ 8. The standard free energy of formation of an element is zero.

_____ 9. The entropy of one mole of gaseous water is less than the entropy of one mole of liquid water.

_____10. If the free energy change is less than zero, the change is spontaneous.

_____11. The energy of the universe is constant, but the entropy of the universe tends to increase.

_____12. As matter becomes more orderly or organized, entropy increases.

_____13. It is not possible for an endothermic reaction to proceed spontaneously if there is also a decrease in the entropy of the system.

_____14. The most probable state of an isolated system left to itself is the most disordered state.

_____15. A spontaneous change results in a decrease in free energy of the system.

Completion

16. A mathematical statement of the first law of thermodynamics is ________________.

17. The work done by a gas expanding into a vacuum is ________________.

18. When a gas expands against a constant pressure, P_{ext}, going from V_1 to V_2, the amount of work done is equal to ________________.

19. Write the chemical equation representing the formation of calcium carbonate from its elements: ________________.

20. For a system at equilibrium, the standard free energy is equal to ________________.

21. The equation that relates to ΔH, ΔS, and ΔG for a given system is ________________.

22. When air escapes from a pressurized cylinder, the entropy ________________ (increases/decreases).

23. The probability of a system being in a disordered state is ________________ (higher/lower) than the probability of its being in an ordered state.

24. There is a natural tendency for an isolated system to become more ________________ (ordered/disordered).

25. The most probable state of a system will have the ________________ (highest/lowest) entropy.

26. In order for a nonspontaneous change to occur, ________________ must be done on the system.

27. If a system absorbs heat from its surroundings and has work done on it by the surroundings, the sign of ΔE is ________________.

28. In an isolated system the sign of ΔS for a spontaneous change must be ________________.

29. A reaction for which both ΔH and ΔS are positive will be ________________ at high temperatures.

30. The energy of the universe is constant but the ________________ tends toward a maximum.

31. If a system absorbs heat from its surroundings and its energy remains constant, it must
    (a) do work on the surroundings
    (b) be compressed
    (c) expand into a vacuum
    (d) violate the first law of thermodynamics since energy cannot be conserved if heat is absorbed

32. One mole of ideal gas is allowed to expand into a vacuum. During the expansion, the temperature of the gas remains constant (an isothermal expansion). Which of the following statements is true?
    (a) $q = 0$; ΔE and w are positive numbers
    (b) $\Delta E = w = 0$; q is a positive number
    (c) $\Delta E = 0$; w and q are positive numbers
    (d) $\Delta E = w = q = 0$

33. In the process of photosynthesis, small molecules such as CO_2 and H_2O are combined to form large, ordered biological molecules in living plants. Which of the following statements is true?
    (a) This is an example of violation of the second law of thermodynamics since the entropy of the universe is decreasing as the plant grows.
    (b) The second law is not violated but thermodynamics does not apply in this case.
    (c) The second law is not violated because the entropy of the surroundings is increased.
    (d) The second law is not violated because the entropy of the universe remains constant.

34. What is ΔE for the evaporation of 1 mol of water at its normal boiling point? The molar heat of vaporization is 40.7 kJ mol^{-1}.
    (a) 40.7 kJ (b) −40.7 kJ (c) 37.6 kJ (d) 0

35. What is the entropy change when 2 mol of liquid water at 100°C are converted to vapor? The molar heat of vaporization is 40.7 kJ mol^{-1}.
    (a) 81.4 J K^{-1} (b) 218 J K^{-1} (c) −218 J K^{-1} (d) 814 J K^{-1}

36. What is the standard entropy change for formation of 1 mol of ammonia from its elements?

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$$

The third law entropies at 298 K are $S^{o}_{N_2(g)} = 191.5$ J mol^{-1} K^{-1}, $S^{o}_{H_2(g)} = 130.6$ J mol^{-1} K^{-1}, and $S^{o}_{NH_3(g)} = 192.3$ J mol^{-1} K^{-1}.
    (a) 0 (b) −129.8 J mol^{-1} K^{-1}
    (c) −198.7 J mol^{-1} K^{-1} (d) −99.4 J mol^{-1} K^{-1}

37. If the reaction

$$CO(g) + NO(g) \rightarrow CO_2(g) + \frac{1}{2}N_2(g)$$

were spontaneous, it might solve the problem of automobile exhaust emissions. It would remove two troublesome pollutants, CO and NO, by converting them to harmless $CO_2$and N_2. What is the value of ΔG for this reaction at standard conditions? $(\Delta G_f^{o})_{CO} = -137.2$ kJ mol^{-1}, $(\Delta G_f^{o})_{CO_2} = -394.4$ kJ mol^{-1}, and $(\Delta G_f^{o})_{NO} = +86.6$ kJ mol^{-1}.
    (a) +445 kJ (b) − 445 kJ (c) −343.8 kJ (d) +343.8 kJ

38. Above what temperature will Ag_2O decompose to silver and oxygen at 1 atm pressure? For Ag_2O, $\Delta H^\circ_f = -30.5$ kJ and $\Delta G^\circ_f = -10.9$ kJ.

(a) 463°C (b) 190°C (c) 165°C
(d) not enough data given for calculation

39. What is the equilibrium constant at 25°C for the decomposition reaction given in problem 38?
(a) −1.91 (b) 1.2×10^{-2} (c) 1.7×10^{-23} (d) 4.5×10^{-6}

40. Consider the following possible combinations of ΔH° and ΔS°. Which of these processes might be spontaneous at some temperature at 1 atm?

Process	ΔH°	ΔS°
1	−	+
2	+	−
3	−	−
4	+	+

(a) 1 and 2 are always spontaneous; 3 and 4 are uncertain.
(b) 3 and 4 are always spontaneous; 1 and 2 are uncertain.
(c) 1 is always spontaneous; 2 is always nonspontaneous; 3 and 4 are uncertain.
(d) 3 is always spontaneous; 4 is always nonspontaneous; 1 and 2 are uncertain.

41. Five molecules of a gas are placed in a container. What is the probability of finding all five molecules in the same half of the container?
(a) 1/5 (b) 1/2 (c) $(1/5)^2$ (d) $(1/2)^5$

42. Which one of the following is true for a spontaneous reaction?
(a) $\Delta S_{sys} = \Delta S_{surr}$ (b) $\Delta S_{univ} = 0$
(c) $\Delta S_{univ} > 0$ (d) $\Delta S_{univ} < 0$

43. For which one of the following processes is the change in entropy of the system not positive?
(a) gas → liquid (b) solid → liquid (c) solid → gas (d) liquid → gas

44. The reaction below has a ΔG° of −620 kJ. Which one of the following statements is not valid concerning this reaction?

$$X + Y \rightleftarrows A + B$$

(a) The reaction is thermodynamically favorable.
(b) The reaction is spontaneous as written.
(c) The reaction will proceed rapidly from left to right.
(d) The products are more stable than the reactants.

45. Which of the following processes are associated with an increase in entropy?
(1) condensing a vapor
(2) increasing temperature
(3) compressing a gas
(4) precipitation of a solid from aqueous solution
(a) 1 and 2 (b) 2 and 4 (c) 1 and 4 (d) 3 and 4

Chapter 18

ELECTROCHEMISTRY

CHAPTER OVERVIEW

This chapter discusses the relationship between chemical and electrical energies. We will learn the terms associated with electrodes and electrochemical cells and study their stoichiometry. The operation and applications of some practical cells are described.

18-1 Galvanic cells

Galvanic cells use a spontaneous chemical reaction to generate electricity. Theoretically, any spontaneous redox reaction could be used to generate electricity, but design problems have limited the number of practical galvanic cells to a few types. These are covered in Sec. 18-6. This section discusses the theory of their operation. To make a galvanic cell form any spontaneous redox reaction we simply physically separate the oxidation and reduction half-reactions into separate compartments and connect them electrically. This is shown for a zinc-copper cell in text Fig. 18-2. Study Fig. 18-2 to see how this electrical connection is made and how the electrons get from the oxidation half-cell to the reduction half-cell. Note how a salt bridge or porous plate is used to allow ions to migrate so electrical neutrality is preserved in the electrolyte solutions.

The voltage of most chemical cells is about 2 V or less. We will see how this voltage depends on the cell components and concentrations and can be calculated very accurately. Cell diagrams are shorthand notations showing how the cell is constructed. Practice writing cell reactions from cell diagrams, and vice versa. Electrodes are devices for providing electrical contact between the reacting ions in solution and the external circuit. Each cell has two electrodes and chemical reactions occur at the electrode surfaces. The type of electrode used depends on the state of the chemical species in the reaction, but they all serve the same purpose: to transfer electrons between the reacting chemical and the external circuit. Remember that oxidation always occurs at the anode and anions always flow toward the anode. A voltmeter in the external circuit measures the cell voltage. Galvanic cells always have a positive cell potential.

18-2 Electrolytic cells

An electrolytic cell uses electrical energy to force a nonspontaneous reaction to occur. Electrical energy (voltage) is used to overcome the positive ΔG for the reaction. Theoretically, any nonspontaneous redox reaction could be made to occur in an electrolytic cell, but there is not always a practical way to put electrical energy into the separate reduction and oxidation half-reactions. Many successful chemical reactions are carried out by electrolysis on a commercial basis, and the text discusses electrolysis of HCl and NaCl solutions and molten NaCl. Compare these systems so you can see how the products are formed and understand the electron-transfer processes. The cell potential of an electrolytic cell is always negative.

Faraday's laws are used to relate the amount of chemical reacting to the quantity of electricity (coulombs) flowing through the cell.

18-3 Standard electrode potentials

The sum of the half-cell potentials for the reduction and oxidation half-reactions gives the cell potential. Half-cell potentials for reduction half-reactions are given in Table 18-1 in the text. These values are relative to the standard hydrogen electrode. To determine the voltage of a cell, read the reduction half-cell potential directly from Table 18-1. Since oxidation half-cell reactions are found by reversing reduction half-cell reactions, the oxidation potential is the reduction potential times –1. Simply change the sign of the value given in Table 18-1 to get the oxidation half-cell potential. The cell potential or voltage is the sum of the oxidation and reduction half-cell potentials. Remember that cell voltages do not depend on amounts of material reacting, so Table 18-1 values are never multiplied or divided by stoichiometric coefficients.

Pay attention to the hints in the text on predicting spontaneity of reaction and strengths of oxidizing and reducing agents from the relative position of the reactants in Table 18-1. It may save you some time in working problems on exams. It is well worthwhile to become familiar with Table 18-1.

18-4 Free energy, cell voltage, and equilibrium

Thermodynamics and electrochemistry are related by

$$\Delta G = -nFE$$

The table in the text shows how the algebraic sign of E can predict spontaneity just as ΔG does. Note the opposite signs of the variables, however. The Nernst equation is used to calculate cell voltages for cells where concentrations are not 1 M. Temperature effects are also included in this equation. Since ΔG^o is related to both K and E^o, we have a powerful relationship between thermodynamics, equilibrium, and electrochemistry. You will be expected to work problems relating the basic constants of these three fields of study.

18-5 The electrochemical measurement of pH

The Nernst equation relates cell potential to the concentration of electrolyte. If the electrolyte is H^+, we can determine its concentration by measuring the cell potential with a voltmeter. Electrodes responding specifically to H^+ ions have been developed for use in pH meters. The same technique is employed using ion-specific electrodes for measuring the concentration of a wide variety of ionic species.

18-6 Commercial galvanic cells

The most important commercial galvanic cells (batteries) are the Leclanche dry cell, the mercury cell, the lead storage cell, and the NiCad (nickel-cadmium) cell. Study text Figs. 18-13 to 18-15 and the corresponding chemical reactions so you are familiar with their operation.

A fuel cell is simply a galvanic cell designed so the reactants can be supplied and the products removed to give continuous operation. The H_2—O_2 cell shown in Fig. 18-16 is typical of fuel cells. The use of fuel cells involves a dilemma: Those with high efficiencies require very expensive catalysts and fuel, while those operating on less expensive fuels or catalysts show poor operating characteristics. If design and development problems can be overcome, fuel cells offer great promise for power generation.

KEY EQUATIONS

18-2 Electrolytic cells

Faraday's laws:

$$1 \text{ faraday} = 9.65 \times 10^4 \text{ C}$$

$$\text{Coulombs} = \text{amperes} \times \text{seconds}$$

$$\text{No. of equivalents reacting} = \text{no. of faradays of electricity} = \frac{\text{amps} \times \text{seconds}}{9.65 \times 10^4 \; CF^{-1}}$$

18-3 Standard electrode potentials

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$$

18-4 Free energy, cell voltage, and equilibrium

$$\Delta G = -nFE$$

The Nernst equation (at 25°C): $E = E^{\circ} - \frac{0.0257}{n} \ln Q$

Equilibrium constant: $E^{\circ} = \frac{0.0257}{n} \ln K$

LEARNING OBJECTIVES

As a result of studying Chapter 18, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 315 of this *Study Guide*.

18-1 Galvanic cells

1. Tell how a galvanic cell differs from an electrolytic cell with respect to sign of ΔG of the cell reaction, sign of E°_{cell} and relationship between chemical and electrical energy. (Text Prob. 18-1) (Self Test 3, 6, 7)
2. Give an example showing how a redox reaction can be divided into two half-cell reactions.
3. Assign oxidation and reduction half-reactions to the correct electrode. (Text Probs. 18-2, 18-3) (Self Test 1)
4. List three functions of a salt bridge. (Text Probs. 18-8, 18-11) (Self Test 16, 33)
5. State two functions of electrodes. (Self Test 2, 23)
6. Give examples of a metal-metal ion electrode, a gas-ion electrode, and a metal-insoluble salt-anion electrode. (Self Test 5, 19)
7. Relate the voltage of a cell to the spontaneity of the cell reaction. (Text Example 18-7; Text Probs. 18-5, 18-42) (Self Test 21, 29)
8. Write cell diagrams given the cell reaction. (Text Probs. 18-5, 18-42) (New Skills Example 3; Self Test 4, 17, 32)

9. Write anode and cathode half-reactions given the overall reaction or the cell diagram. (Text Examples 3 to 7, 9, 10; Text Probs. 18-7, 18-14) (Self Test 20, 34)
10. Make a drawing of the cell compartments given the cell reaction. Show the anode, cathode, and direction of electron flow and give the half-cell reactions. (Text Probs. 18-3, 18-4, 18-6, 18-14, 18-43) (New Skills Example 4; Self Test 18, 31, 35)

18-2 Electrolytic cells

1. Show what must be done to convert a galvanic cell into an electrolytic cell and list the consequences of the change. (Text Prob. 18-1)
2. Explain the function of the electrolyte in an electrochemical cell. (Text Prob. 18-12) (Self Test 2)
3. Write the chemical reactions for the electrolysis of aqueous HCl, aqueous NaCl, and molten NaCl. (Text Probs. 18-13, 18-56) (Self Test 8, 24, 36)
4. Use Faraday's laws to calculate the amounts of chemicals reacting when a given quantity of electricity passes through a cell, and vice versa. (Text Examples 18-1, 18-2; Text Probs. 18-15 to 18-20, 18-39 to 18-41) (New Skills Example 1, 2; Self Test 9, 25 to 27, 37 to 39)

18-3 Standard electrode potentials

1. Use Table 18-1 in the text to find the standard electrode potentials of oxidation and reduction half-reactions. (Text Prob. 18-21) (New Skills Example 3; Self Test 11 to 13)
2. Calculate cell potentials given the cell reaction or cell diagram and Table 18-1 in the text. (Text Examples 18-5, 18-6; Text Probs. 18-22, 18-26, 18-53) (New Skills Example 4; Self Test 14, 22, 41)
3. Relate the strength of oxidizing and reducing agents to their position in Table 18-1 in the text. (Text Example 18-8; Text Probs. 18-24, 18-25) (Self Test 10, 28, 40)

18-4 Free energy, cell voltage, and equilibrium

1. Calculate ΔG from E and vice versa. (Text Example 18-9; Text Probs. 18-23, 18-32 to 18-36, 18-51, 18-52) (New Skills Example 5; Self Test 30)
2. Use the Nernst equation to calculate the cell potential of cells not at standard state. (Text Example 18-10; Text Probs. 18-27 to 18-31, 18-46 to 18-48, 18-52) (New Skills Example 6; Self Test 42, 43)
3. Calculate K from E^o, and vice versa. (Text Example 18-11; Text Probs. 18-37, 18-38, 18-54) (New Skills Example 7; Self Test 44)

18-5 The electrochemical measurement of pH

1. Explain how the Nernst equation is used to determine concentrations of ions from cell-potential measurements.
2. Describe how a hydrogen electrode or a glass electrode can be combined with a calomel reference electrode to form a cell used to measure pH.
3. Calculate the pH of a solution given the voltage measured by a glass electrode or a hydrogen electrode with a calomel reference electrode. (Text Example 18-12; Text Probs. 18-49, 18-50)

18-6 Commercial galvanic cells

1. Make sketches showing the operation and construction of the Leclanche cell, the mercury cell, the lead storage cell, the nickle-cadmium cell, and the H_2—O_2 fuel cell. Identify the anode and

cathode and show the direction of electron flow in each sketch. (Text Figs. 18-13 to 18-16; Text Prob. 18-44) (Self Test 15)

2. Write the half-cell and cell reactions for the cells in Learning Objectives 18-6:1. (Text Probs. 18-9, 18-45) (Self Test 45)

NEW SKILLS

This chapter presents the basic concepts involved in electrochemical cells. It is essential that you know the new terms used to describe the cells so you can concentrate on understanding how the cells work.

18-1 Galvanic cells

Cell diagrams

The structure and operation of electrochemical cells is conveniently represented in shorthand notation by a cell diagram. Cell diagrams are written so the anode reaction (oxidation) is on the left and the cathode reaction (reduction) is on the right. Boundaries between different phases are indicated by a single vertical line or slash and a salt bridge is represented by double vertical lines or slashes. Concentrations of reacting substances or pressures of gases are shown in parentheses after the chemical formulas. The electrodes are always written first for the anode and last for the cathode so they appear as the first and last items in the cell diagram.

For the Daniell cell operating at standard conditions where the concentrations of dissolved chemical species are 1.0 M, the anode reaction is $Zn \rightarrow Zn^{2+}$ (1 M) + 2 e^- and is represented in a cell diagram as Zn/Zn^{2+} (1 M) where the slash represents the base boundary between the solid Zn electrode and the Zn^{2+} electrolyte in solution. The cathode reaction is Cu^{2+} (1 M) + 2 $e^- \rightarrow Cu$ and is represented as Cu^{2+} (1M)/Cu. The cell diagram is written with the anode on the left and the cathode on the right separated by a salt bridge

$$Zn/Zn^{2+}(1\ M)//Cu^{2+}(1\ M)/Cu$$

• EXAMPLE 1

Problem: Write a cell diagram for an electrolytic cell in which an iron electrode is in contact with a 1.50 M solution of $FeCl_2$ in the anode compartment and 0.30 M HCl is reduced to H_2 at 2.0 atm at a platinum electrode in the cathode compartment. The anode and cathode compartments are connected through a salt bridge.

Solution: The anode reaction is represented on the left of the cell diagram with the electrode written first.

Anode: Fe/Fe^{2+} (1.50 M)

The cathode reaction is represented in the order: reactants, product, electrode as

Cathode: $H^+(0.30\ M)/H_2(2.0\ \text{atm})/Pt$

The two half cells are separated by a salt bridge, so the cell diagram is

$$Fe/Fe^{2+}(1.50\ M)//H^+(0.30\ M)/H_2(2.0\ \text{atm})/Pt \quad \bullet$$

Parallel Problem: Write a cell diagram for an electrolytic cell in which a cadmium electrode is in contact with a 0.500 M solution of $CdSO_4$ in the anode compartment and a copper electrode is

in contact with 0.750 *M* $CuSO_4$ solution in the cathode compartment. The compartments are connected by a salt bridge.
Ans: $Cd/Cd^{2+}(0.500\ M)//Cu^{2+}(0.050\ M)/Cu$

Study the cell diagram for the Daniell cell in conjunction with Fig. 18-2 in the text until you understand how the cell diagram conveys the same information about the cell as the figure. Become familiar with the order of terms in the cell diagram. You should be able to identify the anode, the anode reaction, where electrons leave the cell (anode), what kind of cell junction is used, what kind of electrodes are present, and the overall cell reaction by inspecting the cell diagram. Read the text discussion on cell diagrams until you see how they present all this information. Do not worry too much about the "sign" of the electrode. If you understand the operation of the cell you should be able to assign the "sign" according to the convention used by your instructor.

18-2 Electrolytic cells

The terms and symbols used in galvanic cells also apply to electrolytic cells. In electrolytic cells a voltage is applied which forces the electrons to flow in the reverse direction (compared to galvanic cells). As the text shows, this reverses the nature of the redox reactions and the electrodes.

Calculations involving Faraday's laws

Faraday's laws can be stated mathematically by the relationship

$$\text{Faradays} = \text{no. of equivalents of chemical reacting} = \frac{\text{Coulombs}}{9.65 \times 10^4\ \text{C}\ F^{-1}}$$

$$= \frac{\text{amps} \times \text{seconds}}{9.65 \times 10^4\ \text{C}\ F^{-1}}$$

• EXAMPLE 2

Problem: An electrical current of 10 amps passes through an electrochemical cell for 3 hours. How many moles of electrons pass through the cell?

Solution: One mole of electrons is a faraday. Faradays are related to coulombs by

$$\text{Faradays} = \frac{\text{C}}{9.65 \times 10^4\ \text{C}\ F^{-1}}$$

Since one coulomb is one ampere-second

$$\text{C} = \text{A} \times \text{s}$$

$$\text{Faradays} = \frac{\text{A} \times \text{s}}{9.65 \times 10^4\ \text{C}\ F^{-1}}$$

$$\text{Moles of electrons} = \text{faradays} = \frac{10.0\ \text{A}\ (3\ \text{H})\ (3600\ \text{sh}^{-1})}{9.65 \times 10^4\ \text{C}F^{-1}} = 1.12\ \text{mol}\ e^- \quad \bullet$$

Parallel Problem: Three faradays of electricity pass through an electrochemical cell in 10 hours. What is the amperage of the current?
Ans: 8.0 amps

• **EXAMPLE 3**

Problem: What length of time is required to deposit 0.100 g Cu from a $Cu(NO_3)_2$ solution using a current of 0.300 A?

Solution: The half-cell reaction for the reduction of Cu^{2+} at the cathode is

$$Cu^{2+} + 2\,e^- \rightarrow Cu$$

Thus the equivalent weight of Cu is

$$\text{Equiv wt} = \frac{\text{atomic wt}}{\text{No. of } e^- \text{ transferred}} = \frac{63.5}{2} = 31.8 \text{ g equiv}^{-1}$$

The number of equivalents of Cu is

$$\text{Equiv of Cu} = \frac{\text{g Cu}}{\text{equiv wt}} = \frac{0.100 \text{ g Cu}}{31.8 \text{ g Cu equiv}^{-1}} = 3.14 \times 10^{-3} \text{ equiv}$$

Now we use Faraday's laws to find the time required.

$$\text{Equiv} = \frac{\text{A} \times \text{s}}{9.65 \times 10^4 \text{ C } F^{-1}}$$

$$\text{s} = \frac{9.65 \times 10^4 \text{ C } F^{-1}}{\text{A}} = \frac{9.65 \times 10^4 \text{ C } F^{-1} (3.14 \times 10^{-3} \text{ equiv})}{0.300 \text{ A}}$$

$$= 1010 \text{ s} \quad \text{or} \quad 16.8 \text{ min} \quad \bullet$$

Parallel Problem: How many grams of Ni could be deposited from a $NiCl_2$ solution by 0.500 amps of current flowing for 2.00 hours?
Ans: 1.09 g

Examples 18-1 and 18-2 in the text give further illustrations of the use of Faraday's laws in calculations involving electrochemical cells.

18-3 Standard electrode potentials

Table 18-1 in the text can be used to find the standard cell potential of any cell composed of some combination of half-cell reactions included in the table.

• **EXAMPLE 4**

Problem: Write the anode and cathode half-reactions and the cell reaction, and use Table 18-1 to determine the standard cell potential for the electrolytic cell in Example 1.

Solution: Oxidation always occurs at the anode. In this case Fe is oxidized to Fe^{2+} so the anode half-reaction is

$$Fe \rightarrow Fe^{2+}\,(1.50\,M) + 2\,e^- \qquad E^{o}_{ox} = +0.44 \text{ V}$$

In Table 18-1 we find only cathode, or reduction, half-reactions. We must change the sign of the standard reduction potential found in the table to have it apply to an oxidation half-reaction. The numerical value is unchanged; only the sign is changed.
At the platinum cathode hydrogen ions are reduced to H_2, so the reaction is

$$2\,H^+\,(0.30\,M) + 2\,e^- \rightarrow H_2\,(2.0\text{ atm}) \qquad E^\circ_{red} = 0\text{ V}$$

The standard potential for a hydrogen half-cell is zero.
The cell reaction is found by adding the oxidation and reduction half-reactions, and the cell potential is found by adding the oxidation and reduction half-cell potentials.

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

Care must be taken to be sure the number of electrons lost in oxidation is equal to the number gained in reduction.

Anode (oxidation): $Fe \rightarrow Fe^{2+}\,(1.50\,M) + 2\,e^-$ $\qquad E^\circ_{ox} = +0.44\text{ V}$

Cathode (reduction): $2\,H^+\,(0.30\,M) + 2\,e^- \rightarrow H_2(2.0\text{ atm})$ $\qquad E^\circ_{red} = 0\text{ V}$

Cell reaction: $Fe + 2\,H^+\,(0.30\,M) \rightarrow Fe^{2+}\,(1.50\,M) + H_2\,(2.0\text{ atm})$ $\qquad E^\circ_{cell} = +0.44\text{ V}$ •

Parallel Problem: Write the anode and cathode half-reactions and the cell reaction, and use Table 18-1 or Appendix I to determine the standard cell potential for the electrolytic cell in the previous Parallel Problem.

Ans:
anode : $Cd \rightarrow Cd^{2+} + 2\,e^-$
cathode : $Cu^{2+} + 2\,e^- \rightarrow Cu$
cell : $Cd + Cu^{2+} \rightarrow Cd^{2+} + Cu$
E°_{cell} = 0.740 volts

Examples 18-5 and 18-6 in the text give additional illustrations of the use of Table 18-1 to find cell potentials.

18-4 Free energy, cell voltage, and equilibrium

This section presents some simple equations that relate thermodynamics, electrochemistry, and equilibrium. We will learn how the basic constants of these fields are closely related, and we will use the Nernst equation to calculate cell potentials of cells not at standard state.

1. Relationship between free energy and cell potential

The relationship between thermodynamics and electrochemistry is given by the simple equation

$$\Delta G^\circ = nFE^\circ$$

where ΔG° = standard Gibbs free energy
n = moles of electrons transferred
F = Faraday's constant = $9.65 \times 10^4\ C\,F^{-1}$
E° = standard cell potential

The relationship also applies when the system is not at standard state.

• EXAMPLE 5

Problem: For the reaction

$$2\ \mathrm{Fe}(s) + 3\ \mathrm{Cu}^{2+}(aq) \rightleftarrows 2\ \mathrm{Fe}^{3+}(aq) + 3\ \mathrm{Cu}(s)$$

the standard free energy is –218 kJ. What is the standard cell potential for this reaction?

Solution: We need to determine the value of n for the reaction. First separate the reaction into half-cell reactions. These are

Oxidation: $2\ \mathrm{Fe}(s) \rightarrow 2\ \mathrm{Fe}^{3+}(aq) + 6\ e^-$

Reduction: $3\ \mathrm{Cu}^{2+}(aq) + 6\ e^- \rightarrow 3\ \mathrm{Cu}(s)$

There are six electrons transferred in the reaction so $n = 6\ F$ or 6 mol of electrons.

$$E^o = \frac{-\Delta G^o}{nF} = \frac{-(-218{,}000\ \mathrm{J})}{(6F)(9.65 \times 10^4\ \mathrm{C}\ F^{-1})} = 0.377\ \mathrm{J\ C^{-1}} \quad \text{or} \quad 0.377\ \mathrm{V}$$ •

Parallel Problem: What is the standard free energy of reaction for the cell in the previous Parallel Problem?
Ans: –143 kJ $\mathrm{mol^{-1}}$

Text Example 18-9 shows the calculation of ΔG^o from tabulated standard reduction potentials.

2. *The Nernst equation: calculating the effect of concentration on cell voltage*

The voltage of a cell is a function of the logarithm of the concentrations of reactants and products. This dependence is given quantitatively by the Nernst equation.

$$E = E^o - \frac{0.0257}{n} \ln Q \quad \text{at } 25^\circ\mathrm{C}$$

where E = cell voltage at conditions given
E^o = cell voltage at standard conditions
n = moles of electrons transferred
Q = mass-action expression

Review Sec. 14-2 if you do not remember the meaning of the mass-action expression.

Table 18-1 in the text can be used to determine E^o, the cell potential at standard conditions where all concentrations are 1 M and all gases are present at 1 atm partial pressure. At other concentrations the Nernst equation is used to determine E, the cell potential when the system is not at standard conditions.

• EXAMPLE 6

Problem: Calculate the voltage at 25°C for the reaction

$$2\ \mathrm{H}^+(aq) + \mathrm{Zn}(s) \rightarrow \mathrm{H_2}(g) + \mathrm{Zn}^{2+}(aq)$$

when $[\mathrm{H^+}] = 3.0 \times 10^{-3}\ M$, $[\mathrm{Zn^{2+}}] = 0.50\ M$, and the $\mathrm{H_2}$ partial pressure is 0.75 atm.

Solution: First use the half-cell potentials in Text Table 18-1 to determine the standard cell potential. The half-cell reactions are

Oxidation:	$Zn(s)$	$\rightarrow$	$Zn^{2+}(aq) + 2\,e^-$	$E^o_{ox} = +0.76$ V
Reduction:	$2\,H^+(aq) + 2\,e^-$	$\rightarrow$	$H_2(g)$	$E^o_{red} = 0$
Cell:	$2\,H^+(aq) + Zn(s)$	$\rightarrow$	$H_2(g) + Zn^{2+}(aq)$	$E^o_{cell} = +0.76$ V

We see that $n = 2$ for the reaction, so the Nernst equation becomes

$$E = E^o - \frac{0.0257}{n} \ln \frac{P_{H_2}[Zn^{2+}]}{[H^+]^2}$$

$$= 0.76 - \frac{0.0257}{2} \ln \frac{0.75\,(0.50)}{(3.0 \times 10^{-3})^2} = 0.76 - \frac{0.0257}{2} \ln (4.2 \times 10^4)$$

$$= 0.76 - \frac{0.0257}{2} (10.64) = 0.76 - 0.14 = 0.62 \text{ V}$$

The cell potential is reduced 0.14 V compared to the standard state potential. •

Parallel Problem: Calculate the actual cell potential for the cell in the Parallel Problem after Exercise 1.
Ans: 0.71 volts

Example 18-10 in the text is a similar problem.

3. *Determination of equilibrium constants from standard cell potentials*

The relationship between the equilibrium constant of a reaction and its standard cell potential is given by the expression

$$E^o = \frac{0.0257}{n} \ln K$$

where K is the type of equilibrium constant appropriate to the chemical reaction considered.

• EXAMPLE 7

Problem: Calculate the solubility product constant for AgCl at 25°C.

Solution: The K_{sp} of AgCl is the equilibrium constant for the reaction

$$AgCl(s) \rightleftarrows Ag^+ + Cl^-$$

The cell potential for this reaction is related to K_{sp} by the equation

$$E^o_{cell} = \frac{0.0257}{n} \ln K_{sp}$$

The cell diagram for the solubility equilibrium would be

$$Ag(s)/Ag^+(aq)//Cl^-/AgCl(s)/Ag(s)$$

which is a silver-silver ion electrode in the anode compartment connected to a silver-silver chloride electrode in the cathode compartment. The half-cell reactions and potentials are

Oxidation:	$Ag(s)$	$\rightarrow Ag^+(aq) + e^-$	$E^o_{ox} = -0.80$ V
Reduction:	$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-(aq)$	$E^o_{red} = +0.22$ V
Cell:	$AgCl(s)$	$\rightarrow Ag^+(aq) + Cl^-(aq)$	$E^o_{cell} = -0.58$ V

The standard potential for the silver-silver ion electrode is given in text Table 18-1. The potential for the silver-silver chloride electrode is in Text Appendix 1. The equation for K_{sp} becomes

$$-0.58 = \frac{0.0257}{1} \ln K_{sp}$$

$$\ln K_{sp} = \frac{-0.58}{0.0257} = -22.57$$

$$K_{sp} = 1.6 \times 10^{-10}$$

This compares favorably with the value of 1.7×10^{-10} given in Table 16-1. •

Parallel Problem: Calculate the solubility product constant for AgBr.
Ans: 4.7×10^{-13}

Example 18-11 in the text is an additional example of using electrochemical data to calculate equilibrium constant values.

KEY TERMS

18-1 Galvanic cells

Anode: The electrode at which oxidation occurs.

Cathode: The electrode at which reduction occurs.

Cell diagram: A shorthand notation for representing electrochemical cells.

Compartment: One-half of a galvanic cell in which either oxidation or reduction takes place.

Danielle cell: Any voltaic cell involving the oxidation of zinc and the reduction of copper(11) ions.

Electrical potential: The voltage between the electrodes of an electrochemical cell.

Electrochemical cell: A device which converts chemical energy into electrical energy or vice versa.

Electrode: The surface at which oxidation or reduction takes place in an electrochemical cell.

Electrolytic cell: An electrochemical cell in which electrical energy produces a chemical change. A cell in which electrolysis takes place.

Galvanic cell: An electrochemical cell in which a spontaneous chemical reaction is used to produce electrical energy. Same as voltaic cell.

Half-cell: The half of an electrochemical cell in which either oxidation or reduction takes place. The anode or cathode compartment.

Liquid-junction potential: The voltage produced across the interface between two different liquids.

Plating out: The reduction of a metal at the surface of a cathode.

Salt bridge: A U-shaped tube filled with a conducting solution which connects the anode and cathode compartments of an electrochemical cell and allows migration of ions between the compartments.

Voltaic cell: Same as galvanic cell.

18-2 Electrolytic cells

Coulomb: C. An SI derived unit of electrical charge. The quantity of charge equal to a current of one ampere flowing for one second.

Decomposition potential: The minimum voltage which must be applied across a pair of immersed electrodes in order to cause electrolysis.

Electrolysis: The use of electrical energy to cause a chemical change.

Faraday: One mole of electrons. One faraday equals 9.65×10^4 coulombs.

Faraday's laws of electrolysis: Quantitative relations involving changes in electrochemical processes. (1) The quantity of a substance produced by electrolysis is proportional to the quantity of electricity consumed. (2) The amount of substance produced by a given quantity of electricity is proportional to the equivalent mass of the substance.

Ion current: The migration of ions between the electrode compartments of an electrochemical cell.

Overvoltage: The voltage greater than the theoretical cell potential which must be applied to initiate electrolysis.

18-3 Standard electrode potentials

Electrode potential: The voltage assigned to a half-cell for a reduction process.

Standard electrode potential: The voltage assigned to a reduction half-reaction with all chemical species in the standard state. Same as standard reduction potential.

Standard hydrogen electrode: A half-cell consisting of a platinum-black coated platinum electrode in contact with hydrogen gas at one atmosphere pressure and hydrogen ions in a one-molar aqueous solution. The voltage of the standard hydrogen electrode is arbitrarily defined to be zero.

Standard reduction potential: Same as standard electrode potential.

18-4 Free energy, cell voltage, and equilibrium

Nernst equation: An equation giving the dependence of cell voltage on the concentrations of substances involved in the cell reactions.

18-5 The electrochemical measurement of pH

Glass electrode: An electrode incorporating a glass membrane which developes a voltage in response to difference in pH of solutions on either side of the membrane.

pH meter: A voltmeter calibrated to read in pH. It generally uses a glass electrode and a reference electrode which may be combined into a single unit.

Saturated calomel electrode: A very stable and commonly used reference electrode which uses a mercury(I) chloride/mercury electrode.

18-6 Commercial galvanic cells

Amalgam: An alloy containing mercury.

Battery: (1) Galvanic cells connected in series. (2) A single commercial galvanic cell.

Dry cell: A common flashlight battery using a Zn/MnO_2 cell reaction also known as a Leclanche cell.

Lead storage cell: A cell of the common automobile battery. It uses a lead/lead sulfate/sulfuric acid cell.

Leclanche cell: The common flashlight battery or dry cell.

Mercury cell: The common watch or hearing aid battery. It uses a zinc amalgam/mercury(II) oxide cell.

Primary cell: A nonrechargeable cell.

Secondary cell: A rechargeable cell.

SELF TEST

True or False

_____ 1. Oxidation takes place at the anode in any kind of electrochemical cell.

_____ 2. Positive ions are called cations because they migrate toward the cathode.

_____ 3. A galvanic cell converts chemical energy to electrical energy.

_____ 4. Cell diagrams generally give the cathode first.

_____ 5. Since gases are nonconductors they cannot be used as electrodes.

_____ 6. The overall reaction in a galvanic cell is always spontaneous.

_____ 7. The standard cell potential for an electrolytic cell is always positive.

_____ 8. Electrolysis of NaCl always yields sodium and chlorine.

_____ 9. In the electrolysis of $CuSO_4$, one faraday of electricity is required to produce one mole of copper.

_____10. The standard hydrogen electrode potential is 0.00 volts because it has no potential.

_____11. Standard reduction potentials are always positive.

_____12. For any half-reaction the oxidation potential is the negative of the reduction potential.

_____13. Na^+ lies below Mg^{2+} in the table of standard reduction potentials. This means that Na^+ will reduce Mg^{2+} to Mg.

_____14. Voltages produced by cells do not depend on quantities of reactants or products.

_____15. Galvanic cells can be used in rechargeable batteries only when the overall cell reaction is reversible.

Completion

16. Three functions of a salt bridge are ____, ______________________________________, and _________________________________.

17. The cell diagram for the Daniell cell is ____.

18. In the Daniell cell, _______________ is the anode, _______________ is the cathode, and electrons leave the cell at the __________________ electrode.

19. The electrodes in the Daniell cell are ___________________ type electrodes.

20. The half reaction which takes place at the anode during the electrolysis of water is ______________________.

21. If the overall chemical reaction is spontaneous, the cell potential will be ________________________.

22. The cell potential is the sum of the __________________ and __________________ half-cell potentials.

23. _____________________________ charged ions are attracted to the anode where they are _____________________________ in an electrolytic cell.

24. The electrolysis of molten NaCl yields ____________________ at the cathode.

25. The quantity of substance produced by electrolysis is proportional to ________________.

26. A mole of electrons is called a ______________________.

27. A coulomb is one _________________ per __________________.

28. The strongest reducing agents are at the ____________ (left, right)) of the half-cell reactions at the ______________ (top, bottom) of a table of standard reduction potentials.

29. If the cell potential is negative, the cell reaction must be ______________________.

30. The equation relating free energy and cell potential is ____________________.

Multiple Choice

31. In a galvanic cell, the electrons flow
(a) from anode to cathode (b) through the salt bridge
(c) from cathode to anode (d) from the battery to the cathode

32. The cell diagram for the reaction $Ag^+(aq) + H_2(g) \rightarrow Ag(s) + 2\,H^+(aq)$ is
(a) $H_2/Ag^+//Ag/H^+$ (b) $Pt/H_2/H^+//Ag^+/Ag$
(c) $H_2/H^+//Ag^+/Ag$ (d) $Ag/H_2//Ag^+/H^+$

33. The salt bridge in the cell in problem 32 preserves electrical neutrality in the cell by permitting
(a) electrons to flow from the anode to the cathode
(b) cations to migrate from the cathode to the anode compartment
(c) anions to migrate from the anode to the cathode compartment
(d) cations to migrate from the anode to the cathode compartment

34. For the cell $Al(s)/AlCl_3(aq)/Cl_2(g)/Pt$ the cell reaction is
(a) $Pt + 2\,AlCl_3 \rightarrow 3\,PtCl_2 + 2\,Al$
(b) $2\,AlCl_3 + PtCl_2 \rightarrow 2\,Al + Pt + 4\,Cl_2$
(c) $2\,Al + 3\,Cl_2 \rightarrow 2\,AlCl_3$
(d) No reaction is possible because there is no salt bridge.

35. In the Daniell cell, cations
(a) move toward the Zn electrode
(b) move toward the Cu electrode
(c) are formed in the $ZnSO_4$ solution
(d) are removed from the $CuSO_4$ solution

36. When aqueous NaCl is electrolyzed
(a) Na is produced at the anode
(b) Na is produced at the cathode
(c) O_2 is produced at the cathode
(d) H_2 is produced at the cathode

37. 9.65×10^4 coulombs
(a) will oxidize 1 mol of Na^+ to Na
(b) will reduce 1 mol of Cl_2 to Cl^-
(c) will reduce 1 equivalent of CO_2 to C
(d) is 1 amp flowing for 1 hour

38. One faraday will reduce how many grams of Fe^{3+} to Fe?
(a) 19 (b) 28 (c) 56 (d) 168

39. How many amperes would be needed to reduce 0.10 g of Ni^{2+} to Ni in 10 minutes?
(a) 1.85 (b) 1.08 (c) 0.54 (d) 0.27

40. Na^+ is below Zn^{2+} in the table of standard reduction potentials. This means that
(a) Na^+ is a better reducing agent than Zn^{2+}
(b) Na will reduce Zn
(c) Na is a better reducing agent than Zn
(d) Na^+ will reduce Zn^{2+}

41. The standard reduction potentials of Sn^{2+} and Cu^{2+} are –0.14 and +0.34 volts respectively. The cell potential for a galvanic cell containing these two ions would be
(a) 0.48 V (b) –0.48 V (c) 0.20 V (d) –0.20 V

42. For the reaction $8\ H^+ + 2\ NO_3^- + 3\ Cu \rightarrow 2\ NO + 3\ Cu^{2+} + 4\ H_2O$ the value of *n* in the equation $\Delta G = -nFE$ is
(a) 1 (b) 2 (c) 6 (d) 8

43. What is the potential at 25°C for the cell $Zn/Zn^{2+}(0.50\ M)//H^+(0.020\ M)/H_2(0.30$ atm)/Pt? The standard reduction potential of Zn is –0.76 volts.
(a) 0.68 V (b) 0.73 V (c) 0.76 V (d) –0.84 V

44. The equilibrium constant for the cell reaction in Problem 43 is
(a) 3.1×10^{11} (b) 6.9×10^{12} (c) 9.4×10^{22} (d) 4.7×10^{25}

45. When a lead storage cell is discharged, $PbSO_4$ is
(a) produced at the anode (b) produced at the cathode
(c) produced at both electrodes (d) removed from both electrodes

Chapter 19

COVALENT BONDING

19-1 Valence-bond theory and orbital overlap

The valence-bond theory was developed to help explain and understand covalent bonding. The theory considers bonding pairs of electrons to occupy atomic orbitals on the bonded atoms. Bonding is the result of overlap of these atomic orbitals. Valence-bond theory helps explain overall molecular geometry.

The concepts of σ (sigma) and π (pi) bonds are very important. Make sure you understand how each arises from atomic orbitals, which orbitals give σ and which give π bonds, and how the atomic orbitals overlap to make σ and π molecular orbitals. Remember that one bond of a double or triple bond is always a σ bond; additional bonds are π bond(s).

19-2 Hybrid orbitals

The geometry and bonding of many molecules cannot be explained from simple atomic orbitals. According to the valence-bond theory, atomic orbitals merge (hybridize) to form new orbitals as molecular bonding takes place. Several types of possible hybrid orbitals are summarized in Table 19-1 of the text. The type of hybridization is determined by the geometry of the molecule, so try to relate these two concepts as you study. Remember: The number of hybrid orbitals obtained during hybridization must equal the number of atomic orbitals used. Hybrid orbitals are a powerful aid in explaining the geometry and bonding in molecules.

19-3 The molecular-orbital model

Two separate and distinct theories describe covalent bonds and electronic structure of molecules. Each theory has its own advantages and limitations and each explains certain observations well.

1 Valence-bond (VB) theory considers a bonding pair to occupy atomic orbitals on the bonded atoms. Bonding is the result of overlap of the atomic orbitals.
2 Molecular-orbital (MO) theory considers the atomic orbitals to be replaced by new molecular orbitals. Bonding is determined by the number of electrons in certain molecular orbitals.

The VB theory explains molecular geometry best while MO theory explains molecular spectra, bond strength, and magnetic properties best.

A molecular orbital (MO) is formed by mixing atomic orbitals of two bonding atoms. The resulting MO can either increase or decrease the density of electrons between the bonding nuclei. If the electron density is increased, the MO is bonding and the nuclei are drawn closer together. If it is decreased, the MO is antibonding and the nuclei repel each other. An asterisk (*) is used to designate antibonding orbitals and is read as "star", so π^* is read "pi star."

The relationship between energies of the molecular orbitals and the atomic orbitals from which they were derived is shown in Figs. 19-19 to 19-21 in the text. Note that the bonding MO is always lower in energy (more stable) than the atomic orbitals that generated it, while the antibonding MO is always higher in energy than the atomic orbitals. Molecular orbitals are filled with electrons by an Aufbau-type procedure to give molecular electronic configurations for homonuclear molecules of second-period elements. Figures 19-22 to 19-27 and Table 19-2 in the text show the filling order.

If the bond order is greater than 0, the molecule should exist; otherwise it will not. The strength and utility of the MO theory is best seen in the successful predictions of stable molecules, bond energies, and magnetic properties which correlate well with experimental observations.

LEARNING OBJECTIVES

As a result of studying Chapter 19, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 328 of this *Study Guide*.

19-1 Valence-bond theory and orbital overlap

1. Use the VB theory to explain how molecular bonds result from overlap of atomic orbitals on adjacent atoms. (Text Probs. 19-4, 19-19) (Self Test 1, 33)
2. Show what type of overlap of atomic orbitals results in σ bonds and what type results in π bonds. (Text Probs. 19-2 to 19-4, 19-17, 19-18) (Self Test 5, 17, 18, 26)
3. Sketch the arrangement of σ and π bonds in single, double, and triple bonds. (Text Prob. 19-4) (Self Test 6, 19, 36, 38)

19-2 Hybrid orbitals

1. Understand that hybrid orbitals are generated from atomic orbitals to describe covalent bonding in molecules. Other methods are used to predict geometry for the entire molecule. (Text Probs. 19-7, 19-8) (Self Test 4, 20)
2. Know the types of hybrid orbitals listed in Table 19-1, and how they arise from atomic orbitals. (Text Probs. 19-5, 19-6) (Self Test 3, 20, 21)
3. Predict which hybrid orbitals will be used in bonding by elements in period 2 of the periodic table. (Text Probs. 19-8, 19-21, 19-30 to 19-33) (New Skills Example 1; Self Test 31, 32, 34, 42 to 44)
4. Understand the geometric terms in text Table 19-1 and sketch the arrangement of atoms for each of these geometries. (Text Prob. 19-5)
5. Match types of hybrid orbitals with a given type of geometry. (Text Table 19-1; Text Probs. 19-5, 19-22, 19-30 to 19-33) (Self Test 22)

19-3 Molecular-orbital theory

1. Explain the basic difference in VB and MO theories with respect to atomic orbital overlap and formation of molecular orbitals. (Self Test 2, 16, 33)
2. Illustrate how molecular orbitals (MOs) in molecules are analogous to atomic orbitals (AOs) in atoms and how they are different. (Self Test 2, 7)
3. Know which MOs are generated from mixing given *s* and *p* atomic orbitals. (Text Probs. 19-14, 19-28) (Self Test 7, 24, 45)
4. Know the filling order of MOs for period-2 elements. (Text Figs 19-19 to 19-21; Text Prob 19-33) (Self Test 9)
5. Understand the difference between bonding and antibonding MOs. (Text Prob. 19-9) (Self Test 8, 23, 24, 35, 41)
6. Use the Aufbau type procedure to write the configuration of valence electrons in MOs for homonuclear molecules of period 2. (Text Figs 19-23 to 19-27; Text Probs. 19-10, 19-11, 19-27) (New Skills Example 2; Self Test 15, 27)
7. Explain why the sequence of filling MOs changes between N_2 and O_2 as you proceed across period 2. (Self Test 9, 30)
8. Extend the filling sequence of MOs to heteronuclear molecules or diatomic ions of period-2 elements. (Text Probs. 19-12, 19-23) (New Skills Example 2; Self Test 28, 37, 39, 40)
9. Determine bond order and relate it to the stability of a molecule. (Text Table 19-2; Text Example 19-1; Text Probs. 19-11, 19-13, 19-20, 19-24 to 19-26) (New Skills Examples 3, 4; Self Test 10 to 14, 28, 29, 39, 40)

NEW SKILLS

19-2 Hybrid orbitals

Hybrid orbitals for second-period elements

In Sec. 8-6 we learned how to use Lewis structures and the VSEPR method to determine the geometry of molecules. The atomic orbital overlap described in Sec. 19-1 successfully describes the bonding in diatomic molecules but is inadequate for polyatomic molecules. The text describes why tetrahedral geometry of CH_4 with four equivalent C—H bonds cannot be explained with simple atomic orbitals.

According to Table 19-1 in the text, BF_3 is a trigonal planar molecule. There are three B—F bonds, all in the same plane, and 120° apart. However, the boron atomic orbitals are not in the same plane and not 120° apart. For instance, the three $2p$ orbitals are 90° apart. The trigonal planar geometry is quite different from the simple atomic orbital geometry. The correct geometry for BF_3 is described by mixing atomic orbitals to form new orbitals oriented toward the bonded atoms. The new orbitals are called hybrid orbitals, and the process of mixing is called hybridization. The text illustrates the hybridization process for several second-period elements. The number of hybrid orbitals generated is always equal to the number of atomic orbitals used, and all hybrid orbitals on an atom are equivalent. Second-period elements do not have d-orbital electrons, so they only form hybrid orbitals from s and p atomic orbitals. The type of hybridization is determined by the steric number (number of bonded atoms plus number of lone pairs on the central atom). The geometry of some common hybrid orbitals is shown in Table 19-1 in the text.

• EXAMPLE 1

Problem: Determine the hybridization on the central atom of each molecule in Examples 7 and 8 from the New Skills section of Chapter 8 in this *Study Guide.*

Solution: The steric number determined by the VSEPR method from Chapter 8 gives the number of atomic orbitals that must be combined to form hybrid orbitals. The number of hybrid orbitals is the number of lobes on the hybrid orbital geometry illustrated in Table 19-1 in the text. Once the hybrid orbital geometry is identified, the type of hybridization on the central atom can be determined from Text Table 19-1.

Compound	Steric number	Molecular geometry	Hybrid orbital geometry	Hybridization
XeF_4	6	Square planar	Octahedral	d^2sp^3
CO_2	2	Linear	Linear	sp
SO_2	3	Angular	Trigonal planar	sp^2
NF_3	4	Trigonal pyramidal	Tetrahedral	sp^3
ClF_3	5	T-shaped	Trigonal bipyramidal	dsp^3

Hybrid orbital geometry is different from molecular geometry when lone pairs of electrons are present on the central atom. Hybrid orbital geometry includes the lone pairs but molecular geometry ignores them. Be sure to include lone pairs when you determine the hybrid orbital geometry. •

Parallel Problem: Determine the hybridization on the central atom of each of the following molecules. Refer to the Parallel Problems following Examples 7 and 8 in Chapter 8 of this *Study Guide* for steric numbers and molecular geometries.

(a) AsF_5 (b) SnF_4 (c) IF_2^+ (d) I_3^- (e) PH_3

Ans:		
	(a) AsF_5	*dsp*^{3}
	(b) SnF_4	*sp*^{3}
	(c) IF_2^+	*sp*^{3}
	(d) I_3^-	*dsp*^{3}
	(e) PH_3	*sp*^{3}

19-3 Molecular-orbital theory

Writing molecular orbital configurations for diatomic molecules and ions

The filling order of MOs for homonuclear molecules H_2 through N_2 is

$$\sigma_{1s},\ \overset{*}{\sigma}_{1s},\ \sigma_{2s},\ \overset{*}{\sigma}_{2s},\ \pi_{2py},\ \pi_{2pz},\ \sigma_{2px},\ \overset{*}{\pi}_{2py}$$

From O_2 to Ne_2 the σ_{2px} MO has lower energy than the π_{2py} and π_{2pz} MOs so the filling order becomes

$$\sigma_{1s},\ \overset{*}{\sigma}_{1s},\ \sigma_{2s},\ \overset{*}{\sigma}_{2s},\ \sigma_{2px},\ \pi_{2py},\ \pi_{2pz},\ \overset{*}{\pi}_{2py},\ \overset{*}{\pi}_{2pz},\ \overset{*}{\sigma}_{2px}$$

The molecular electronic configurations for these homonuclear diatomic atoms are given in Table 19-2 of the text.

The same general rules apply for filling molecular orbitals as for the Aufbau procedure with atomic orbitals. Each of the orbitals holds two electrons and electrons enter the available orbital with lowest energy first. The π_{2py} and π_{2pz} orbitals have equal energy so they are each occupied by single electrons before electron pairing takes place. The same is true for $\overset{*}{\pi}_{2py}$ and $\overset{*}{\pi}_{2pz}$.

The filling order for homonuclear molecules can be used for heteronuclear molecules or ions as long as the atoms are close together in the periodic table and the total number of valence electrons is consistent with the filling order for homonuclear molecules.

• EXAMPLE 2

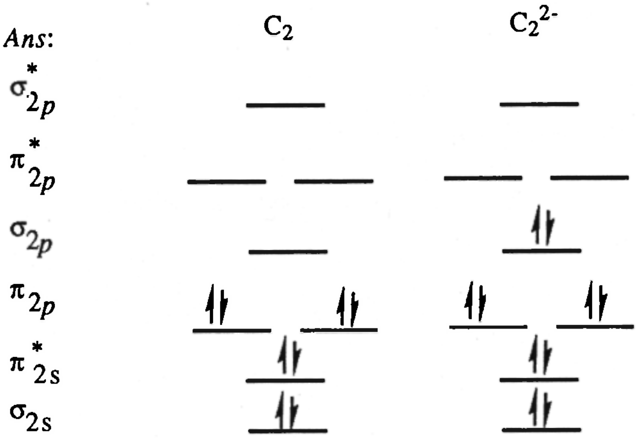
Problem: Write the molecular electronic configuration for N_2, N_2^-, and N_2^+.

Solution: The valence-shell MO population diagram for N_2 shown in Fig. 19-26 in the text can be used for each of these. KK designates the inner core 1*s* electrons.

N_2^+	9 valence electrons	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\pi_{2py})^2(\pi_{2pz})^2(\sigma_{2px})^1$
N_2	10 valence electrons	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\pi_{2py})^2(\pi_{2pz})^2(\sigma_{2px})^2$
N^-	11 valence electrons	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\pi_{2py})^2(\pi_{2pz})^2(\sigma_{2px})^2(\overset{*}{\pi}_{2py})^1$ •

Parallel Problem: Molecules of calcium carbide, CaC_2, contain the acetylide ion C_2^{2-}. Write MO population diagrams for C_2 and C_2^{2-}.

Ans:



• EXAMPLE 3

Problem: Find the bond order for each of the particles in the previous example.

Solution: Antibonding electrons are those in the "star" orbitals.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2}$$

Particle	Bonding electrons	Antibonding electrons	Bond order
N_2^+	7	2	$\frac{5}{2}$
N_2	8	2	3
N_2^-	8	3	$\frac{5}{2}$

•

Parallel Problem: Find the bond order for each of the particles in the previous parallel problem.
Ans: C_2 bond order is 2, C_2^{2-} bond order is 3

• EXAMPLE 4

Problem: Compare the bond energies and bond lengths of the particles in the previous example.

Solution: Bond order is a measure of the strength of the bond. For bonding atoms of similar atomic number, the bond length is inversely proportional to bond order. A strong bond pulls the nuclei closer together and gives a shorter bond. In the above example, N_2 has the strongest bond. Its bond energy will be highest and its bond length shortest. N_2^+ and N_2^- should have similar bond energies and bond lengths. •

Parallel Problem: Compare bond energies and bond lengths of the particles in the previous parallel problem.
Ans: The bond in C_2^{2-} is shorter and stronger than the bond in C_2.

KEY TERMS

19-1 Valence-bond theory and orbital overlap

Axial symmetry: A symmetrical orientation of the charge cloud of a shared electron pair around the bond axis, characteristic of sigma bonds.

Double bond: Sharing of two electron pairs by the same two atoms. A double bond consists of one sigma bond plus one pi bond.

Molecular orbital: MO. An electronic energy level in a molecule and the corresponding charge-cloud distribution in space.

Molecular orbital theory: A model of covalent bonding in molecules based on the replacement of atomic orbitals on bonded atoms with molecular orbitals. A shared pair of electrons occupies the new molecular orbitals.

Overlap: The volume of space simultaneously occupied by atomic orbitals of two bonded atoms. The increased electronic density in the overlap results in a sigma or a pi bond.

Pi bond: A covalent bond in which the charge cloud of the shared electron pair is located in two regions on opposite sides of the bond axis.

Shared electron pair: A pair of electrons which simultaneously occupies an orbital of each of two bonded atoms as a result of orbital overlap.

Sigma bond: A covalent bond in which the charge cloud of the shared electron pair is centered on the bond axis and has axial symmetry around it.

Single bond: Sharing of an electron pair between two atoms. A sigma bond.

Triple bond: Sharing of three electron pairs by the same two atoms. A triple bond consists of one sigma bond plus two pi bonds located at 90 degrees to each other.

Valence-bond theory: A model of covalent bonding in molecules based on the assumption that a shared pair of electrons occupies overlapping atomic orbitals on two bonded atoms.

19-2 Hybrid orbitals

Hybrid orbital: An orbital formed by combining or mixing two or more atomic orbitals.

Hybridization: Mixing of atomic orbitals on an atom to form new hybrid orbitals oriented in different directions from the original atomic orbitals.

19-3 Molecular-orbital theory

Antibonding orbital: A molecular orbital of higher energy than the corresponding atomic orbitals. Antibonding orbitals are characterized by a low electron probability density between the bonded atoms, producing a destabilizing effect on the molecule.

Bond order: The relative number of bonding and antibonding electrons in a molecule.

Bonding orbital: A molecular orbital in which electrons have lower energy than in the corresponding atomic orbitals. Bonding orbitals are characterized by a region of high electron probability density between the bonded atoms, leading to a stabilizing effect on the molecule.

Heteronuclear: Molecules containing two or more different elements.

Homonuclear: Molecules containing only one element.

Isoelectronic: Molecules which have the same number of electrons.

LCAO: Linear combination of atomic orbitals.

SELF TEST

True or False

_____ 1. VB theory considers bonding to be the overlap of existing atomic orbitals.

_____ 2. MO theory considers molecular orbitals to result from the overlap of atomic orbitals.

_____ 3. Mixing *s* and *p* atomic orbitals always results in *sp* hybrid orbitals.

_____ 4. The nitrogen atom in ammonia has four pairs of valence-shell electrons oriented toward the corners of the tetrahedron but the molecular geometry of ammonia is pyramidal.

_____ 5. According to valence-bond theory the sigma bond in N_2 results from the overlap of the 2_{px} atomic orbital of one N atom with the 2_{px} atomic orbital of the other N atom.

_____ 6. The triple bond in N_2 results from one N—N sigma bond and one N—N pi bond.

_____ 7. Molecular orbitals are obtained by mixing atomic orbitals of bonded atoms.

_____ 8. For each bonding molecular orbital there is a corresponding antibonding MO.

_____ 9. σ_{2p} MOs are always lower energy than π_{2p} MOs.

_____10. The C_2 molecule is more stable than the B_2 molecule.

_____11. MO theory predicts Be_2 does not exist.

_____12. Bond length is directly proportional to bond order.

_____13. Bond strength is directly proportional to amount of atomic orbital overlap.

_____14. The Li_2^+ ion has bond order of 1/2.

_____15. The electron configuration of He_2^+ is $(\sigma_{1s})^2(\sigma^*_{1s})^1$

Completion

16. ________________ theory explains molecular geometry best, while ____________ theory explains bond strength best.

17. The overlap of two atomic *s*-orbitals gives a ________________ bond.

18. Sideways overlap of two atomic *p*-orbitals gives a ________________ bond.

19. A double bond always contains one ______________ bond and one ______________ bond.

20. Mixing three atomic orbitals always produces ___________ (number of) hybrid orbitals.

21. Combination of an *s* atomic orbital with two *p* orbitals gives ___________________ hybridization.

22. sp^3 hybrid orbitals point toward the corners of a ____________________.

23. Molecular orbitals that increase the density of electrons between bonding atoms are called _______________ orbitals.

24. A π^*_{2p} MO is a (an)_________________ orbital resulting from the combination of two _______________ type atomic orbitals.

25. The symbol σ^*_{2s} is read ____________________________.

26. End-to-end overlap of two *p* orbitals leads to a ____________________ bond.

27. The last valence electron in F_2 enters a ___________________ MO.

28. The bond order of CO is _________________________.

29. MO theory predicts the molecule Be_2 is ____________________(stable, unstable).

30. MO theory predicts O_2 has two unpaired electrons in ________________ (bonding, antibonding) MOs.

Multiple Choice

31. *sp*^{3} hybridization is present in
(a) H_2O (b) BeF_2 (c) BH_3 (d) SF_6

32. The hybridization on PCl_3 is
(a) *sp* (b) *sp*^{2} (c) *sp*^{3} (d) *dsp*

33. Which of the following is incorrect about valence-bond theory?
(a) Bonding electrons occupy atomic orbitals on two different atoms at the same time.
(b) It successfully explains the geometry of molecules.
(c) Mixing of atomic orbitals results in bonding and antibonding molecular orbitals.
(d) Bonding results when two atomic orbitals of similar energy overlap.

34. Since we know the $BeCl_2$ molecule is linear, the hybridization on Be must be
(a) *sp* (b) *sp*^{2} (c) *sp*^{3} (d) *sp*^{3}*d*^{2}

35. Which of the following designates an antibonding orbital?
(a) σ (b) σ_{px} (c) σ^* (d) σ_{py}

36. Which molecule has no π bonds?
(a) SO_2 (b) NH_4Br (c) CO_2 (d) N_2

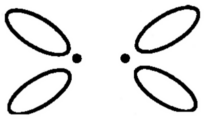
37. How many antibonding electrons are in NO^+?
(a) 1 (b) 2 (c) 4 (d) 8

38. How many sigma bonds are in the molecule $H—C\equiv C—H$?
(a) 2 (b) 3 (c) 4 (d) 5

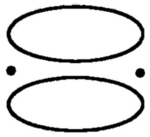
39. Which of the following has the lowest bond order?
(a) NF (b) BN (c) BeC (d) He_2^+

40. Which of the following has the shortest bond length?
(a) O_2 (b) O_2^+ (c) O_2^- (d) O_2^{2-}

41. Which picture best represents a π_{2p} bonding molecular orbital?

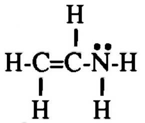
(a)


(b)


(c)


(d)


(e)


42. In the compound  $H-\underset{H}{\overset{}{C}}=\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\bullet\bullet}{N}}-H$ the carbon to nitrogen bond results from the overlap of
(a) a carbon *sp*^{3} with a nitrogen *sp*^{2}
(b) a carbon *sp*^{2} with a nitrogen *sp*^{3}
(c) a carbon *sp*^{3} with a nitrogen *sp*^{3}
(d) a carbon *sp*^{2} with a nitrogen *sp*^{2}
(e) a carbon *sp* with a nitrogen *sp*^{2}

43. What hybrid orbitals would be used by the xenon atom in the square planar complex, XeF_4?
(a) *sp*^{3} (b) *dsp*^{2} (c) *sp*^{2} (d) *d*^{2}*sp*^{3}

44. The hybridization of nitrogen in $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\text{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\text{-}\overset{\cdot\cdot}{N}{=}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$ is
(a) sp^2d (b) sp (c) sp^3 (d) sp^3d
(e) sp^2

45. Which one of the following is not true concerning molecular orbitals?
(a) Combination of two atomic orbitals results in the formation of two molecular orbitals.
(b) Bonding molecular orbitals have high electron density between the two nuclei of the bonded atoms.
(c) Antibonding molecular orbitals are less stable than bonding molecular orbitals.
(d) Combination of two $1s$ atomic orbitals results in the formation of σ and σ^* MOs.
(e) The molecular orbitals will be identical in energy to the atomic orbitals from which they are formed.

Chapter 20

THE NONMETALS

CHAPTER OVERVIEW

If you have been progressing through the text chapter by chapter, you will note a dramatic change in the nature and presentation of material beginning with this chapter. We leave the area where basic principles are emphasized and enter a study (known as descriptive chemistry) of the properties and reactions of substances. The approach will be less mathematical, but still requires an intensive effort to master the large amount of material presented. Your instructor should guide you about the extent of memorization work expected. The *Study Guide* is designed to help you organize the material and recognize the important correlations and trends. This chapter is mainly concerned with the properties and chemistry of ten nonmetallic elements. First we proceed to a systematic study of nomenclature in inorganic compounds.

20-1 Inorganic nomenclature

Naming inorganic compounds is largely a matter of attaching the correct prefix and suffix to the root name. The prefix tells the number of atoms per molecule and the suffix indicates the oxidation state. It is obvious that you must learn the meaning of the prefixes and suffixes before you can use them fluently. The prefixes are very straightforward and are given in Chapter 2, Section 10 and also in Appendix C in the text, so you should have no problem learning them. There are two different systems of suffixes for cations: the *ous-ic* system and the Stock or roman numeral system. Since both are widely used you need to learn both systems. Oxidation states of anions are indicated by the *-ide*, *-ite*, and *-ate* suffixes. The text examples for the oxoanions of chlorine illustrate the use of these suffixes. Oxoanions of bromine and iodine are named in the same way. It will be well worthwhile to memorize the names and formulas of the polyatomic ions in Table 20-1 in the text. Learning inorganic nomenclature is essential so the names do not become a stumbling block as you study the chemistry of these compounds in the remaining chapters. Be sure to refer to Section 2-10 and Appendix C in the text for helpful hints and examples of inorganic nomenclature.

20-2 Hydrogen

Hydrogen is present in more compounds than any other element, but most of it is simply combined with oxygen in water. Hydrogen gas is prepared by the electrolytic or chemical reduction of hydrogen in water. It is usually found in the +1 oxidation state. The hydride ion, H^-, exists only in compounds with reactive metals.

20-3 Oxygen

Oxygen is the most abundant element on earth. It occurs combined with metals and nonmetals or uncombined as O_2 or O_3. O_2 is prepared by the distillation of air or electrolytic or chemical oxidation of oxygen in oxygen-containing compounds. Important compounds of oxygen in the –2 oxidation state include metal and nonmetal oxides, hydroxides, oxoacids, and oxosalts. Peroxides contain oxygen in the –1 oxidation state, while superoxides contain the superoxide ion, O_2^-, where the oxidation state is –1/2. Positive oxidation states are found only in compounds containing fluorine.

20-4 Water

Properties of water were discussed in Section 11-4 of the text. This section should be studied in conjunction with Section 11-4. Water molecules combine with many salts to form hydrates.

20-5 The halogens

In this section you will study the group VIIA elements, or halogens. Their chemistry is very similar and follows the periodic behavior and trends discussed in Chapter 7. As you proceed down the group from fluorine to iodine the atomic radius increases so the ionization potential decreases and the elements become progressively more metallic. Fluorine differs from the other halogens in several ways because of its small size and high electronegativity. The text discusses the preparation, chemical properties, and compounds of each oxidation state for F, Cl, Br, and I. Interhalogen compounds are also possible. Since the halogens show a strong tendency to follow predicted periodic behavior, we can expect their compounds to follow the same trends. As you study the compounds, notice how the expected periodic trends gradually change the properties and reactions as you proceed through the halogens.

20-6 The chalcogens, especially sulfur

The group VIA elements show a strong periodic trend from nonmetallic to metallic, as one proceeds from top to bottom in the group. Changes due to this trend are more pronounced than in the halogens so chemical properties are not as similar among the chalcogens as they are among the halogens. Oxygen is quite different from the other elements in group VIA in physical and chemical properties. It is the only element of the group which is a gas under normal conditions. It is found mostly in the –2 oxidation state as the oxide of many elements in nature. Selenium and tellurium show considerable metallic behavior and are usually classed as metalloids. Sulfur shows several stable oxidation states from –2 to +6, and much of sulfur chemistry is not shared by other members of the group. For these reasons it is not as convenient to study the chalcogens as a group as it was for the halogens. This section focuses mainly on sulfur. The text discusses the Frasch method for mining sulfur, its several allotropic forms, and the chemistry of its different oxidation states. Like the halogens, sulfur can form numerous oxoacids and oxosalts.

20-7 The group VA nonmetals: nitrogen and phosphorus

The trend from nonmetallic to metallic behavior as one proceeds from top to bottom of group VA is very pronounced. The elements As, Sb, and Bi show metallic behavior not observed for N and P. Nitrogen is the smallest element in the group and (like fluorine and oxygen) has physical and chemical properties unique among its group.

Nitrogen is the only gaseous element in group VA. In spite of its high electronegativity, it is relatively inert, but shows a wide variety of oxidation states when combined. The text discusses the reactions and properties of nitrogen in several oxidation states. The most important compounds of nitrogen are ammonia and nitric acid. Pay close attention to the chemistry and properties of these two compounds. Concentrated nitric acid acts as an oxidizing agent in reactions in addition to showing usual acid behavior. The typical reactions with Cu and Zn given in the text show how different products can be formed when nitric acid is reduced, depending on the reaction conditions.

Phosphorus does not show the metallic behavior of As, Sb, and Bi, and is much more chemically active than nitrogen. The main reactions discussed include preparation of elemental phosphorus, reaction with oxygen to produce phosphorous oxides, and further reaction with water to produce a family of oxoacids.

20-8 Carbon

Carbon is the smallest member of group IVA and shows properties different from the other members of the group because of this size difference. It is the only nonmetallic member of the group. It has the unique capability of bonding with itself to form long chains; this property gives rise to the field of organic chemistry to be discussed in Chapter 23. This section is concerned with the element and its inorganic compounds.

20-9 The noble gases

Before 1962, it was generally believed that the noble gases were chemically inert. The chemistry presented in this section was not known until the generalities associated with group behavior of the noble-gas elements were disregarded by those doing basic research. Classifying chemicals according to group behavior is an aid to understanding present knowledge, but can be a barrier to developing new ideas.

LEARNING OBJECTIVES

As a result of studying Chapter 20, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 337 of this *Study Guide*.

20-1 Inorganic nomenclature

1. Use suffixes and prefixes correctly in names of compounds and ions. (Text Section 2-10, App. C; Text Probs. 20-1 to 20-4, 20-11) (Self Test 1 to 3, 17)
2. Write the names of binary salts and acids. (Text Section 2-10, App. C; Text Probs. 20-5, 20-6, 20-10) (Self Test 16, 18)
3. Write the names and formulas of common polyatomic ions. (Text Table 20-1, App. C; Text Probs. 20-8, 20-9) (Self Test 2, 16, 32)
4. Write the names and chemical formula of oxosalts and oxoacids. (Text Section 2-10, Table 20-1, App. C; Text Probs. 20-7, 20-10, 20-11) (Self Test 4, 16, 17, 33, 34)

20-2 Hydrogen

1. Name and give properties for the isotopes of hydrogen. (Text Table 20-2; Text Probs. 20-12, 20-13, 20-15, 20-61) (Self Test 6)
2. Write chemical equations for the preparation of H_2. (Text Probs. 20-14, 20-16, 20-17) (Self Test 5, 35)

20-3 Oxygen

1. Compare the VB and MO explanations of bonding in O_2 and related compounds. (Text Table 20-4; Text Fig. 19-27; Text Probs. 20-18, 20-73, 20-77) (Self Test 36)
2. Explain the differences between ionic oxides and molecular oxides. (Text Prob. 20-20)
3. Write the chemical equations for the preparation of O_2 and its reactions to form oxides. (Text Probs. 20-22, 20-25)

20-4 Water

1. Explain the differences and similarities between the structures of liquid and solid water. (Text Fig. 20-2; Text Prob. 20-23) (Self Test 9)
2. Explain how clathrates are formed. (Text Prob 20-24)

20-5 The halogens

1. Apply the periodic law to explain trends in physical and chemical properties of the halogen compounds. (Text Probs. 20-27, 20-62, 20-68) (Self Test 10, 21, 37)
2. Use the VSEPR theory to predict the shape of oxohalogen and interhalogen compounds. (Text Probs. 20-29, 20-78)
3. Write chemical equations for reactions of halogens and halogen compounds. (Text Probs. 20-28, 20-31 to 20-33, 20-63, 20-64, 20-72, 20-81) (Self Test 11, 23, 38)

20-6 The chalcogens, especially sulfur

1. Describe the changes in physical properties and chemical structure that take place as sulfur is heated. (Text Prob. 20-34)
2. Write Lewis structures for various oxosulfur compounds and ions. (Text Prob. 20-37)
3. Write chemical equations for the production of H_2SO_4. (Text Prob. 20-38) (Self Test 24)
4. Use the VSEPR theory to predict bonding and geometry in covalent sulfur compounds. (Text Probs. 20-35, 20-83)
5. Write chemical equations for reactions of compounds containing sulfur. (Text Probs. 20-36, 20-39, 20-75) (Self Test 39)

20-7 The group VA nonmentals: nitrogen and phosphorus

1. Use the principles of chemical equilibrium of Chapter 14 to predict optimum conditions of temperature and pressure for the Haber and Ostwald processes. (Text Prob. 20-40) (Self Test 26)
2. Draw Lewis structures for the nitrogen oxides. (Text Prob. 20-43)
3. Explain how the formation of N_2O_4 affects properties of NO_2 at low temperatures. (Text Prob. 20-44)
4. Explain why reduction of nitric acid gives nitrogen products of lower oxidation state when dilute acid is used. (Text Prob. 20-45) (Self Test 5, 14, 42)
5. Account for the presence of a strong triple bond in N_2 but not in phosphorus on the basis of orbital overlap in second-period but not in third-period elements. (Text Prob. 20-82)
6. List the properties of the allotropes of phosphorus. (Text Probs. 20-46, 20-47)
7. Write chemical equations for the formation and hydrolysis of phosphorus oxides. (Text Probs. 20-48, 20-51) (Self Test 15, 27, 43)
8. Write chemical equations showing reactions of nitrogen compounds. (Text Probs. 20-42, 20-50) (Self Test 13, 25, 26)
9. Write chemical equations showing reactions of salts containing phosphorus. (Text Probs. 20-49, 20-51) (Self Test 27)

20-8 Carbon

1. Compare the properties and structures of allotropes of carbon. (Text Probs. 20-52, 20-54) (Self Test 28, 44)
2. Write equations showing equilibria in the CO_2-HCO_3 -CO_3^{2-} system. (Text Probs. 20-56, 20-60) (Self Test 29)
3. Draw Lewis structures for inorganic carbon compounds. (Text Prob. 20-55)

4. Explain the effect of hydrogen bonding in HCN. (Text Prob. 20-67)
5. Write chemical equations for reactions of inorganic carbon compounds. (Text Probs. 20-53, 20-57)

20-9 The noble gases

1. Predict the structure of xenon compounds using the VSEPR theory. (Text Prob. 20-59) (Self Test 45)

KEY TERMS

20-2 Hydrogen

Deuterium: The isotope of hydrogen having one neutron in the nucleus.

Hydride: A compound containing hydrogen in the –1 oxidation state.

Hydrogen embrittlement: The brittle nature of metals caused by lattice distortion from dissolved hydrogen in the lattice interstices.

Isotope effect: Differences in chemical and physical properties of isotopes of an element due to difference in masses of the isotopes.

Protium: The most abundant isotope of hydrogen, $^{1}_{1}H$.

Tritium: The isotope of hydrogen having two neutrons in the nucleus.

20-3 Oxygen

Anhydride: A compound from which the elements of water have been removed.

Disproportionation: The self-oxidation and -reduction of a compound.

Ozone shield: The ozone layer in the stratosphere which abosrbs UV-B radiation.

Refractory: A compound with a very high melting or decomposition temperature.

20-4 Water

Clathrate: A "cage compound" in which particles are trapped in a cage of solvent molecules.

Flickering cluster: Briefly existing regions of tiny solid crystals existing at low temperature in a liquid.

Hydrate: A solid compound which incorporates water in its crystal structure.

20-5 The halogens

Charge-transfer complex: A complex which has received an electronic charge from solvent molecules.

Free radical: A molecule with an unpaired electron. A highly reactive species.

Halogen: A member of group VIIA.

20-6 The chalogens, especially sulfur

Chalcogen: A member of group VIA.

Contact process: The catalytic process for preparation of sulfuric acid from sulfur.

20-7 The group VA nonmetals: nitrogen and phosphorus

Pnicogen: A member of group VA.

20-8 Carbon

Dispersion: The separation of wavelengths of light when the angle of refraction from a surface varies with wavelength.

Refractive index: A measure of the bending of the path of light as it passes through a transparent substance.

SELF TEST

True or False

_____ 1. Another name for the Sn(II) ion is stannic.

_____ 2. The perchlorate ion contains chlorine in its highest oxidation state.

_____ 3. The suffix *-ate* refers to the higher oxidation state of a cation.

_____ 4. BiOCl is bismuth hypochlorite.

_____ 5. A metal plus an acid always gives hydrogen as a product.

_____ 6. H_2O dissociates to a greater extent than D_2O.

_____ 7. Compounds with oxygen in a positive oxidation state always have fluorine present.

_____ 8. Solutions of nitric acid in water slowly turn brown because of decomposition of the HNO_3.

_____ 9. The maximum density of water is at its freezing point.

_____10. HF, HCl, and HBr are all strong acids.

_____11. Chlorine water contains the OCl^- ion.

_____12. Hydrogen bonding in H_2O and H_2S are responsible for their relatively high boiling points.

_____13. NH_4NO_2 can be heated carefully to produce NO_2.

_____14. Concentrated nitric acid is a powerful oxidizing agent.

_____15. H_3PO_3 is a diprotic acid.

Completion

16. The formula is

______________________________ for copper(II) sulfate

______________________________ for nitrous acid

______________________________ for sodium bromate

______________________________ for calcium carbide

______________________________ for bromous acid

______________________________ for the permanganate ion

______________________________ for aluminum bisulfate

______________________________ for silver carbonate

17. The stock name is

____________________________________ for CuI

____________________________________ for $Pb(OCl)_2$

____________________________________ for $CoPO_4$

____________________________________ for $Sn(NO_2)_4$

18. Ionic compounds between metals and hydrogen in the –1 oxidation state are known as ____________________________________.

19. The two most common allotropes of oxygen are __________________________ and __________________________.

20. The net reaction for the disproportionation of H_2O_2 is __________________________.

21. The halide ion easiest to oxidize is ________________________.

22. The strongest of all acids is ________________________.

23. ________________________ is the only halogen that can not be prepared by chemical oxidation of the halide.

24. The chemical reactions in the contact process are ______________________________.

25. NH_4NO_3 can be heated carefully to produce ______________________________.

26. The first step in the Ostwald process is the oxidation of __________________________.

27. Elemental phosphorus is obtained by heating ________________ with ____________ and __________________ in an electric furnace.

28. Two allotropic forms of carbon are __________________ and __________________.

29. Carbonic acid forms two series of salts: the _______________ and the ____________.

30. Most of the known compounds of noble gases contain ___________________ plus __________________ or ___________________.

Multiple Choice

31. Which of the following is a correct name for a solution of NH_3 in water?
(a) ammonium water (b) ammonia hydroxide
(c) aqueous ammonia (d) liquid ammonia

32. Which of the following is the correct name for HPO_3^{2-}?
(a) phosphite ion (b) hydrogen phosphite ion
(c) hydrogen phosphorus trioxide ion (d) hydrogen phosphate ion

33. What is an acceptable alternate name for iron(II) hypochlorite?
(a) iron(II) oxide chloride (b) ferrous oxide chloride
(c) ferrous dihypochlorite (d) ferrous hypochlorite

34. Which of the following is the correct formula for calcium hydrogen sulfite?
(a) $CaHSO_2$ (b) $CaHSO_3$ (c) $Ca(HSO_3)_2$ (d) $Ca(HSO_2)_3$

35. Which of the following metals is least effective in reducing water?
(a) Zn (b) Ca (c) K (d) Rb

36. Which of the following gives the best interpretation of the structure and properties of O_2?
(a) valence-bond theory (b) Lewis structure
(c) atomic-orbital theory (d) molecular orbital theory

37. Which of the following compounds has not been observed?
(a) HOF (b) $HOCl_3$ (c) $HOBr_2$ (d) HOI

38. An aqueous solution of chlorine contains each of the following except
(a) Cl^- (b) ClO_2^- (c) ClO^- (d) Cl_2

39. Which of the following does not apply to sulfuric acid?
(a) strong acid (b) dehydrating agent
(c) reducing agent (d) anhydride of sulfur trioxide

40. Which of the following is not a common oxidation state of sulfur in its compounds?
(a) −2 (b) +2 (c) +4 (d) +6

41. Which of the following is a property of nitrous acid?
(a) weak acid (b) stable compound
(c) good solvent for metals (d) nontoxic

42. When zinc reacts with dilute nitric acid, which of the following is likely to be a product?
(a) H_2 (b) N_2O (c) NO (d) NO_2

43. When water is added to phosphorus pentoxide which of the following is likely to be a product?
(a) HPO_3 (b) $H_4P_2O_7$ (c) H_3PO_4 (d) all of these

44. Which of the following is a property of graphite?
(a) contains carbon with sp^3 hybridization
(b) has a semimetallic luster
(c) has equal carbon-carbon bonds
(d) good lubricant in vacuum systems

45. The highest oxidation state of xenon in its compounds is
(a) +2 (b) +4 (c) +6 (d) +8

Chapter 21

THE REPRESENTATIVE METALS AND METALLOIDS

CHAPTER OVERVIEW

There are less than 20 nonmetal elements and over 80 metals and semimetals. This chapter presents the representative metals (A-group metals). Review the properties of metals in Sec. 9-5 and note how elements that show strong metallic behavior in a chemical sense are not necessarily the common and familiar metals. From a chemical standpoint, metals are elements that lose electrons to become positive ions. The group IA elements (alkali metals) have the lowest first-ionization energies and therefore show strong metallic behavior. In general, metallic behavior decreases from left to right across the periodic table and the metalloids represent the transition from metallic to nonmetallic behavior.

21-1 The alkali metals

The group IA, or alkali, metals all show strong metallic behavior. They have high electrical conductivity and crystallize in body-centered-cubic structures. They are strong reducing agents and so are readily oxidized to the +1 state. Periodic trends are very pronounced in the alkali metals, so you can observe a gradual increase in metallic behavior from top to bottom in the group. Lithium is the smallest alkali metal and shows the deviation from group behavior expected for second-period elements. The text discusses historical aspects of the metals; methods of preparation; their reactions with H_2O, O_2, and N_2; and properties and uses of their compounds.

21-2 The alkaline-earth metals

The Group IIA, or alkaline-earth, metals show only the +2 oxidation state in compounds. They are less reactive than the alkali metals but are still strong reducing agents. Periodic trends are very pronounced in the group and metallic behavior decreases from bottom to top in the group to the extent that beryllium forms mostly covalent bonds and shows less reactivity than other members of the group. The text explains why only the +2 oxidation state is observed and discusses the preparation, reactions, and properties of some compounds.

The Ca^{2+}, Mg^{2+}, and Fe^{3+} ions are responsible for hardness in water. They form deposits in water lines, appliances, heat exchangers, and boilers. Temporary hardness results when HCO_3^- ions are present. This is a troublesome problem in industrial and home water heaters because heating results in precipitation of $CaCO_3$ or $MgCO_3$. Permanent water hardness is generally removed by the lime-soda method in industrial applications or by ion-exchange water softeners for domestic uses.

21-3 The group IIIA metals

In group IIIA we have moved far enough across the periodic table so that metallic behavior is much less pronounced than in groups IA and IIA. The smallest member of the group shows considerable nonmetallic behavior and forms only covalent bonds. It is classed as a metalloid. Thallium has a stable +1 oxidation state in addition to the +3 oxidation state common for the group. Aluminum is by far the most important metal in group IIIA. It is the most abundant metal in the earth's crust and is extracted from the mineral bauxite by the Bayer process and reduced to the metal electrolytically by the Hall process. Aluminum is a highly reactive element and finds widespread use as a metal only because it forms a dense protective layer of Al_2O_3 on its surface, which prevents further oxidation. Reactions and uses of aluminum are discussed in the text.

21-4 Other representative metals

The representative metals in groups IVA and VA are tin, lead, and bismuth. These metals are far to the right in the periodic table and have high electronegativities for metals. They form either ionic or covalent bonds. Tin has three stable allotropes, only one of which has the metallic properties commonly associated with tin. Tin exists in the +2 and +4 states in compounds and its reactions are discussed in the text.

Lead occurs in most common compounds in the +2 state. PbO_2, in which lead has a +4 oxidation state, is important for its use in lead storage cells. Reactions and uses of lead and its compounds are discussed in the text.

Bismuth is a hard, brittle metal whose main use is in low-melting alloys. It exists in the +3 or +5 oxidation states in compounds, with the +3 state being common.

21-5 The metalloids

Metalloids show either metallic or nonmetallic behavior depending on their chemical environment. They are located on a diagonal to the right of the center of the periodic table as show in text Figure 21-4. The most important metalloids from a chemical standpoint are boron and silicon. The chemistry of boron halides, borates, and boranes is discussed in the text. The chemistry of silicon is quite complex, but you should note that many common minerals are silicates. Arsenic and antimony resemble phosphorus and bismuth in chemical behavior. They each form a series of oxides and oxoanions. Selenium and tellurium resemble sulfur in chemical reactions and form similar compounds.

LEARNING OBJECTIVES

As a result of studying Chapter 21, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 345 of this *Study Guide*.

21-1 The alkali metals

1. Write equations showing the preparation of the alkali-metal elements. (Text Prob. 21-3)
2. Write equations showing the different reactions of the alkali metals with O_2. (Text Prob. 21-35) (Self Test 4, 33)
3. Recognize the similarities and differences in properties and reactions within the group. (Text Probs. 21-2, 21-4, 21-37) (Self Test 2, 3, 5, 32)
4. Write equations for reactions of the alkali metals and their compounds. (Text Probs. 21-5, 21-6, 21-34, 21-36) (Self Test 9, 17)

21-2 The alkaline-earth metals

1. Compare the chemical properties and reactions of alkaline-earth and alkali metals. (Text Probs. 21-7, 21-40) (Self Test 8, 34, 35)
2. Explain the similarities and differences in chemical properties and reactions among members of the group. (Text Probs. 21-41 to 21-43) (Self Test 6, 19)
3. Write equations for reactions of the alkaline-earth metals and their compounds. (Text Probs. 21-8, 21-10, 21-11, 21-44) (Self Test 7, 9, 20)
4. Explain what causes hard water and some of its effects. Describe the different types of hard water and how each type of hardness can be removed. (Text Probs. 21-12 to 21-14) (Self Test 10, 21, 22, 23, 36, 37)

21-3 The group IIIA metals

1. Write reactions for the Bayer and Hall processes for production of aluminum. (Text Probs. 21-16, 21-18, 21-48) (Self Test 25, 26, 38)
2. Explain the trends in chemical properties and reactions among members of the group. (Text Prob. 21-15)
3. Describe the properties and characteristics of aluminum and its compounds. (Text Probs. 21-17, 21-46) (Self Test 11, 12, 27, 39)
4. Explain the covalent nature of many aluminum compounds. (Text Probs. 21-19, 21-47)
5. Write equations for the reactions of group IIIA metals and their compounds. (Text Prob. 21-20)

21-4 Other representative metals

1. Relate the allotropic forms of tin to tin disease. (Text Prob. 21-22) (Self Test 28, 40)
2. Explain the amphoteric behavior of group IVA and VA metal hydroxides. (Text Probs. 21-23, 21-24)
3. Show the effect of complex ions containing lead on the chemistry of lead compounds. (Text Probs. 21-49, 21-50)
4. Write equations showing reactions for Sn, Pb, and Bi and their compounds. (Text Probs. 21-21, 21-25, 21-45) (Self Test 14, 29, 43)

21-5 The metalloids

1. Draw Lewis structures for boranes and BF_3 and interpret the results in terms of electronic bonding in these compounds. (Text Probs. 21-26, 21-27, 21-52, 21-53) (Self Test 30)
2. Compare the allotropes of boron nitride to the allotropes of carbon. (Text Prob. 21-54)
3. Draw structures showing discrete and extended silicate ions. (Text Probs. 21-28 to 21-31, 21-55) (Self Test 45)
4. Use the VSEPR theory to predict the structure of covalent silicon compounds. (Text Prob. 21-56)
5. Explain the differences and similarities in chemical properties and reactions among group IVA, VA and VIA metalloids on the basis of periodic trends. (Text Probs. 21-57 to 21-59)
6. Write equations for reactions of compounds of the metalloids. (Text Prob. 21-33)

KEY TERMS

21-1 The alkali metals

Alkali metal: A member of group IA in the periodic table.

Hydration energy: The energy released when a gaseous ion becomes hydrated in an aqueous solution.

Ionization energy: The energy required to remove an electron from an isolated, gaseous atom.

Oxidation potential: The voltage generated by an oxidation half-cell coupled to a standard hydrogen electrode.

21-2 The alkaline-earth metals

Alkaline earth metal: A member of group IIA in the periodic table.

Gypsum: Calcium sulfate dihydrate.

Ion exchange: The replacement of one ion in solution by a different ion, ordinarily accomplished by an exchange site called an ion-exchange resin.

Lime: Calcium oxide

Lime-soda method: Use of slaked lime to remove temporary water hardness, then adding washing soda to remove permanent hardness.

Permanent water hardness: Water hardness accompanied by an anion other than HCO_3^-.

Slaked lime: Calcium hydroxide

Temporary water hardness: Water hardness accompanied by the HCO_3^- anion.

21-3 The group IIIA metals

Alum: Hydrated potassium aluminum sulfate.

Alumina: Aluminum oxide

Aluminate ion: The hydrated AlO_2^- ion.

Bayer process: A method for converting impure bauxite into pure alumina.

Carborundum: A naturally occurring alumina.

Hall process: The electrolytic process for converting alumina from the Bayer process to metallic aluminum.

Thermite reaction: A highly exothermic reaction in whch aluminum is oxidized to alumina by iron(III) oxide.

21-4 Other representative metals

Bronze: An alloy of tin and copper.

Galena: A natural mineral of PbS.

Pewter: A low melting alloy of tin and lead.

Roasting: Heating a metal ore in air to produce the metal.

Solder: An alloy of tin and lead.

21-5 The metalloids

Addition compound: A compound formed when one molecule adds to another with no loss of atoms from either. Same as adduct.

Adduct: Same as addition compound.

Amphibole: An anion consisting of cross-linked silicate chains with half the silicon atoms with three bridging oxygens and half with two bridging oxygens.

Borazon: Boron nitride in the diamond cubic crystal structure.

Electron-deficient compound: Compounds such as diborane which have fewer valence electrons than is necessary to provide a pair of electrons for each bond.

Infinite band: The cross-linked silicate chains found in amphiboles.

Infinite chain: Extended chains of SiO_3^{2-} found in pyroxene minerals.

Infinite sheet: A two-dimensional anion with formula $Si_2O_5^{2-}$ formed when three of the four oxygen atoms surrounding each silicon atom are bridging oxygens. These anions are found in talcs, clays, and micas.

Metalloid: An element which has properties intermediate between metals and nonmetals. Same as semimetal.

Metasilicate: Anion consisting of one or more SiO_3^{2-} units.

Orthosilicate: Anion consisting of one or more SiO_4^{4-} units.

Semimetal: Same as metalloid.

Silica: Silicon dioxide

Silicone: A chain of alternating silicon and oxygen atoms with CH_3^- groups attached to the chain.

SELF TEST

True or False

_____ 1. There are about four times as many metallic elements as nonmetallic.

_____ 2. Lithium ions have a stronger tendency to undergo hydrolysis than potassium ions.

_____ 3. Lithium has the highest ionization energy and yet is the easiest to oxidize of the alkali metals.

_____ 4. Alkali metals react with oxygen to form oxides.

_____ 5. Lithium compounds are generally less soluble than sodium compounds.

_____ 6. Beryllium usually forms covalent bonds in its compounds.

_____ 7. All the alkaline-earth metals can be prepared by the electrolysis of their halides.

_____ 8. The reduction potentials of Ca, Sr, and Ba are about the same as their Group I counterparts K, Rb, and Cs.

_____ 9. All the alkali and alkaline earth metals react with water to form hydrogen.

_____10. Temporary hard water has the HCO_3^- ions removed.

_____11. The only important metallic element in Group IIIA is aluminum.

_____12. Anodized aluminum is made by oxidizing aluminum electrolytically.

_____13. The most stable oxidation state of the Group IVA metals is +4.

_____14. The Bi^{+3} ion shows little tendency to hydrolyze because of its large size.

_____15. The most important metalloids are boron and silicon.

Completion

16. Three characteristics of metallic elements are ______________________________, ______________________________, and ______________________________.

17. The alkali metals exist only in oxidation state ____________________ in compounds.

18. Magnesium is generally extracted from ______________________________.

19. Except for ____________________________ the alkaline earth metals form ionic compounds.

20. The chemical formula of lime is __________________, of slaked lime _____________, and of limestone __________________.

21. Ions responsible for hard water include ___________, ___________, and ___________.

22. Heating can remove _____________________ water hardness.

23. The lime-soda method for softening water consists of adding ___________________ to remove temporary hardness and _______________ to remove permanent hardness.

24. A very important base in industrial applications is ____________________.

25. In the Bayer process, impure _______________ is dissolved in _______________, from which ____________________ precipitates and is heated to form pure ________________.

26. In the Hall process _________________ is produced at the iron cathode while ________________ and _______________ are produced at the graphite anode.

27. Aluminum is oxidized easily but ____________________ protects it against attack by O_2.

28. Tin disease is the conversion of ________________ to ________________.

29. PbO_2 is a powerful ____________________ agent used in ____________________.

30. Boranes are ____________________ compounds that form ____________________ bonds.

Multiple Choice

31. Chemical properties of metals are related to:
(a) high density of solid state (b) ease of removal of electrons
(c) low chemical reactivity (d) body-centered-cubic structures

32. Alkali metals have which of the following properties?
(a) high densities (b) low conductivity
(c) soft metals (d) good oxidizing agents

33. The only alkali metal that forms the oxide on reaction with O_2 is:
(a) Li (b) Na
(c) K (d) Be

34. Alkaline earth metals do not show +1 ions because
(a) they have two electrons in the valence shell
(b) the first ionization energy is too high
(c) the +1 ion does not interact with anions or water molecules as strongly as the +2 ion with its higher charge density.
(d) the first and second ionization energies are about equal so both electrons come off in a cascade effect.

35. $BeCl_2$
(a) is covalent in the gas phase but ionic in the solid phase
(b) forms long chains of molecules in the solid state
(c) is a high melting solid
(d) forms nonlinear molecules in the gaseous state

36. Temporary water hardness
(a) can be removed by NaCl
(b) occurs only when SO_4^{2-} ions are present
(c) can be removed by allowing the water to stand quietly in the presence of CO_2
(d) can be removed by lime

37. Which of the following will remove permanent hardness from water?
(a) adding $Ca(OH)_2$ (b) adding NaCl
(c) adding washing soda (d) Permanent hardness cannot be removed. That is why it is called permanent.

38. The Bayer process is used to
(a) obtain aluminum from cryolite by electrolytic reduction
(b) make aspirin
(c) obtain magnesium from sea water
(d) purify bauxite

39. Cleansers containing lye (NaOH) dissolve or pit aluminum pans because
(a) the aluminum is anodized
(b) the soluble aluminate ion is formed
(c) the small aluminum ion hydrolyzes extensively in base
(d) the cleaners also contain chlorine bleach which forms soluble $AlCl_3$

40. Which of the following is not an allotrope of tin?
(a) rhombic tin (b) gray tin
(c) white tin (d) amorphous tin

41. Sn^{+2} is
(a) the stannous ion (b) the stannic ion
(c) the stannite ion (d) the stannate ion

42. $PbCl_2$ is soluble in

(a) water
(b) NaCl solution
(c) base
(d) sulfuric acid

43. Which of the following does not apply to bismuth?

(a) combusts in oxygen to give the oxide
(b) is a very dense metal with a dull metallic luster
(c) exists almost exclusively as the +3 ion in compounds
(d) has an amphoteric hydroxide

44. Which of the following does not apply to boron?

(a) is found in vitamin B_{12}
(b) is found in pyrex dishes
(c) occurs in nature as borax
(d) forms compounds deficient in electrons

45. Silicates containing some three bridge oxygens and some two bridge oxygens form a series of minerals which includes

(a) talc
(b) mica
(c) asbestos
(d) sand

Chapter 22

THE TRANSITION METALS

CHAPTER OVERVIEW

The elements between groups IIA and IIIA in the periodic table comprise the transition metals. These metals have several unique properties and characteristics and many similarities. Their ionization energies, electronegativities, and ionic radii show very little variation throughout the series. The availability of *d* orbitals allows complex hybridization which leads to a wide variety of geometries in the complex ions formed. We will investigate the nature of bonding and geometry in these compounds and see how the electronic structure is related to geometry and to the intense colors observed in transition metal compounds.

22-1 Electronic configurations

Recall from Sections 6-1 and 7-2 how *d* electrons are added to build transition metals in the Aufbau process. Note the irregular structures of chromium and copper associated with half-filled or filled *d* shells. This irregularity also occurs in fifth- and sixth-period elements and in the *f* shell of the inner transition series elements, the lanthanides and actinides.

22-2 General properties

The transition metals have properties generally associated with metals. Their hardness, density, conductivity, and chemical reactivity vary greatly and they show a wide range of oxidation states (Table 22-3 in the text). Note the "Consider This" section in the text explaining why the 4*s* electrons are ionized first even though the 3*d* electrons are added last in the Aufbau process.

22-3 Complex ions: general structure and nomenclature

The concepts and terms involved in the study of complex ions were introduced in Sections 12-2 and 16-3 and it would be a good idea to review those section now. The geometry of coordination numbers 2, 4, and 8 will be studied in conjunction with bonding and structure. Become familiar with the nomenclature rules so the names become an aid to your study rather than a stumbling block. Considerable help with nomenclature can be found in Appendix C in the text.

22-4 Bonding in complexes

There are three theories that describe the bonding in complex ions.

1. Hybrid-orbital theory

Review Section 19-2 to recall how atomic orbitals combine to form an equal number of equivalent hybrid orbitals. The geometry of the compound depends on the type of hybridization (see text Table 19-1).

Valence-bond, hybrid-orbital theory successfully predicts the geometry of complex ions but fails to predict whether an inner-orbital or outer-orbital complex will result in certain cases. This difference determines the spectral and magnetic properties of many complex ions, so the valence-bond, hybrid-orbital theory is inadequate for explaining the color and magnetic properties of some complex ions.

2. *Crystal-field theory*

The crystal-field model of bonding in complex ions considers the effect of electrostatic forces of the ligand on the *d* orbitals of the central metal ion. The energy level of these *d* orbitals are split into a set of higher energy orbitals and a second set of lower energy orbitals. These resulting orbitals are labeled e_g and t_{2g}. The energy difference between e_g and t_{2g} orbitals is called the ligand-field splitting energy and denoted by Δ_o or Δ_t. The nature of *d*-orbital splitting is shown ion Figure 22-5 in the text for octahedral geometry and in Figure 22-9 for tetrahedral geometry. Note that in octahedral geometry e_g orbitals have higher energies than t_{2g}, but in tetrahedral geometry the reverse is true.

The type of ligand determines the strength of the ligand field which fixes the magnitude of Δ. For weak-field ligands, the *d*-orbital splitting is small and electrons occupy any *d* orbital so there is maximum unpairing and the complex is of high electron spin. Strong-field ligands cause more *d*-orbital splitting, so electrons pair in lower energy orbitals to give low-spin complexes. The magnitude of Δ is also correlated with the wavelengths of the colors observed in complex ions. Crystal-field theory successfully predicts the geometry, magnetic properties, and color of complex ions. The spectrochemical series arranges ligands in order of their ability to cause splitting of *d* orbitals on the central metal ion.

3. *Molecular-orbital theory*

The application of molecular-orbital theory to complex ion bonding is called ligand-field theory. Molecular-orbital theory was discussed in Section 19-3 of the text. Molecular orbitals are formed by the combination of hybridized orbitals on the central ion with ligand orbitals. A bonding and an antibonding orbital result from each combination of orbitals on the central ion with orbitals of a ligand. The *d* orbitals on the central ion that are not engaged in bonding have no change in energy and are nonbonding orbitals. Energy levels and electron distributions in these orbitals are shown in Figure 22-11 in the text. The nonbonding t_{2g} orbitials are the d_{xy}, d_{xz}, and d_{yz} orbitals, while the e_g and $e_g{}^*$ orbitals result from the d_{z^2} and $d_{x^2-y^2}$ orbitals.

Ligand-field theory leads to the same geometric prediction as the valence-bond theory and is quite successful in predicting magnetic properties, but it is unable to explain color differences caused by different ligands on a central ion.

22-5 The stereochemistry of complex ions

Square-planar complex ions with at least two different ligands can form *cis-trans* isomers, or stereoisomers. In *cis* isomers identical ligands are adjacent or next to each other, while in *trans* isomers they are opposite or across the ion from each other.

Tetrahedral complex ions with four different ligands can exist in two structures which are mirror images of each other. These are called optical isomers or enantiomers. Examine Figure 22-12 in the text closely to see how these isomers are different.

Cis-trans isomers for octahedral complexes having the general formula MA_4B_2 are shown in text Figure 22-14a. Isomers of octahedral complexes of type MA_3B_3 are shown in Figure 22-14b. The presence of chelating agents can result in optical isomers of octahedral complexes as shown in text Figure 22-16.

22-6 Descriptive chemistry of selected transition elements

The maximum oxidation number for groups IIIB to VIIB is the same as the group number. Most of the elements in these groups have several oxidation numbers and all elements in the first transition series except Sc have a +2 oxidation number. For Ti and V the maximum oxidation number is also the most stable state, but lower oxidation states become more stable moving from left to right across the series.

Most of the first-series transition metals are strong and hard and resist corrosion, so they find important uses in alloys. The many oxidation states allow them to serve as oxidizing and reducing agents, and the ease with which electrons can be promoted to higher energy levels makes them important catalysts. Unlike the representative elements, similarities among members of horizontal periods in the transition elements are more noticeable than similarities in the vertical groups.

Some important aspects of the descriptive chemistry you should study include the redox reactions of chromium and manganese, especially $Cr_2O_7^{2-}$ and MnO_4^-; the chemical reactions occurring in blast furnaces in steel metallurgy; the mechanism and prevention of iron corrosion; and the complex ions of iron, cobalt, and nickel.

The platinum metals have very similar properties and are chemically quite unreactive. Copper, silver, and gold all have the same outer electronic configuration but have different stable oxidation states: Cu^{2+}, Ag^+, and Au^{3+}. They are excellent electrical conductors and quite unreactive chemically. The chemical reactions of silver in photography should be understood.

Zinc, cadmium, and mercury have +2 oxidation states; +1 is also common for mercury. These elements are quite reactive chemically compared to the group IB metals. Zinc and cadmium have very similar physical and chemical properties and both are used as coatings to prevent oxidation of iron.

Mercury is the only transition metal which is liquid at ordinary temperatures. It dissolves other metals to form alloys called amalgams. Dimethyl mercury and Hg^{2+} compounds are very toxic, making mercury a serious contaminant in the environment.

LEARNING OBJECTIVES

As a result of studying Chapter 22, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 357 of this *Study Guide*.

22-1 Electronic configurations

1. Tell what is distinctive about the electronic configuration of the transition metals compared to the representative elements. (Text Probs. 22-1, 22-2) (Self Test 3, 5)
2. Give the electronic configurations of the first-series transition metals and explain the irregularities in the Aufbau process for chromium and copper. (Text Prob. 22-30) (Self Test 16, 31)

22-2 General properties

1. List the chemical and physical properties that are similar for the transition metals and those that are not. (Self Test 5, 32)
2. List the common and the maximum oxidation states for the first-series transition metals. (Text Table 22-3; Text Probs. 22-5, 22-19) (Self Test 2, 5, 17)

22-3 Complex ions: general structure and nomenclature

1. Name the geometries possible for coordination numbers 2, 4, and 6. (Text Prob. 22-38) (Self Test 4, 19, 22, 23)
2. Apply the rules for writing formulas and names of complex ions. (Text Probs. 22-7, 22-8, 22-32, 22-33) (Self Test 6, 20, 21)

22-4 Bonding in complexes

1. Describe bonding in complex ions according to hybrid-orbital theory.
2. Describe the splitting of *d* orbitals into e_g and t_{2g} orbitals with different energies as ligands approach the central ion according to crystal-field theory. (Text Figs. 22-5, 22-9; Text Probs. 22-10, 22-34 to 22-37) (Self Test 10)
3. Assign the ligand and central-ion electrons to bonding, nonbonding, and antibonding orbitals for complex ions of the first-series transition metals and identify the unpaired electrons. (Text Fig. 22-6; Text Probs 22-11, 22-13, 22-46) (Self Test 7, 24, 35, 36)
4. Correlate weak-field ligands and strong-field ligands of the spectrochemical series with their ability to split the *d* electrons on the central ion and the resulting magnitude of Δ. (Self Test 11 to 14, 25, 26)
5. Correlate the magnitude of Δ with high-spin or low-spin complexes and with the color of complex ions. (Self Test 9, 25)
6. Write the electron configurations of elements for which high- and low-electron-spin configurations are possible. (Self Test 13, 37, 38)
7. Correlate paramagnetic measurements with a high- or low-spin configuration and classify the ligands involved as strong- or weak-field ligands. (Text Example 22-1)
8. Describe the formation of molecular orbitals in complex ions according to ligand-field theory. (Text Figs. 22-10, 22-11; Text Probs. 22-12, 22-39)
9. List the advantages of the crystal-field theory over hybrid-orbital and molecular-orbital theories. (Text Prob. 22-9) (Self Test 9, 34)

22-5 The stereochemistry of complex ions

1. List the types of isomers possible in square-planar, tetrahedral, and octahedral geometries. (Text Probs. 22-14, 22-15) (Self Test 8, 15, 27, 39)
2. Sketch *cis-trans* isomers in square-planar structures. (Text Prob. 22-17) (Self Test 15)
3. Sketch structures showing *cis-trans* and optical isomerism in octahedral complexes. (Text Figs. 22-14, 22-16; Text Probs. 22-18, 22-47) (Self Test 28)

22-6 Descriptive chemistry of selected transition elements

1. Explain what is meant by the lanthanide contraction and list its effects on the properties of the second- and third-series transition metals. (Text Prob. 22-3) (Self Test 1)
2. Write equations showing the use of $Cr_2O_7^{2-}$ and MnO_4^- in oxidation-reduction reactions. (Text Probs. 22-20e, 22-23b,c,h, 22-42) (Self Test 40, 41)
3. Write equations for the reactions occurring in a blast furnace. (Text Prob. 22-24) (Self Test 42)
4. Write electrochemical equations showing the corrosion of iron. (Text Prob. 22-20f) (Self Test 43)
5. List ways of preventing the corrosion of transition metals, especially iron. (Text Prob . 22-21)
6. Identify the groups of transition metals whose reactions and properties are very similar. (Text Prob. 22-26)
7. Describe the use of silver in photography. (Text Prob. 22-28) (Self Test 44)
8. Be familiar with the properties and reactions of transition metals. (Text Probs. 22-20, 22-23, 22-41, 22-47, 22-48) (Self Test 18, 40)
9. Write reactions showing the formation and decomposition of complex ions of first-series transition metals. (Text Probs. 22-23d,e, 22-43, 22-44)
10. Explain what is meant by ferromagnetism and list the elements that are ferromagnetic. (Text Prob. 22-25) (Self Test 30)

KEY TERMS

22-1 Electronic configurations

Actinide: A member of the 14 elements following actinium in the periodic table.

Inner transition series: The actinides or lanthanides.

Lanthanide: A member of the series of 14 elements following lanthanum in the periodic table.

22-2 General properties

Conductivity: The ability to transmit heat or electrical energy.

Hardness: The quality of being hard as measured by the ability to scratch or be scratched by another substance.

Luster: A measure of the light reflecting quality of a substance.

Noble metals: Transition elements which are poorer reducing agents than hydrogen.

Pyrophoric iron: Finely divided iron which bursts into flame when exposed to air.

Reflectivity: Ability to reflect light or sound.

22-3 Complex ions: general structure and nomenclature

Complex: An ion or molecule which consists of a central atom or ion surrounded by some peripheral ligands bonded to it.

Coordinate covalent bond: A covalent bond in which both shared electrons are donated by one of the bonded atoms.

Coordination chemistry: The study of formation and properties of complex ions.

Coordination number: The number of bonds to atoms, ions, or molecules surrounding a central atom or ion in a complex. Same as ligancy.

Ligancy: Same as coordination number.

Ligand: An atom, molecule, or ion bonded to the central atom in a complex.

22-4 Bonding in complexes

Crystal-field splitting energy: The energy difference between t_{2g} and e_g orbitals.

Crystal-field theory: A model useful in accounting for the properties of complexes based on the interaction of the electric field of ligands with the *d* orbitals of the central atom.

Diamagnetism: The weak interaction of electrons with a magnetic field. Diamagnetism occurs in all substances whether or not unpaired electrons are present.

High-spin complex: A complex with several unpaired electrons. High-spin complexes are associated with weak-field ligands.

Ligand-field theory: The application of molecular-orbital theory to complexes.

Low-spin complex: A complex with very few unpaired electrons. Low-spin complexes are associated with strong-field ligands.

Paramagnetism: Interaction with a magnetic field caused by unpaired electrons.

Spectrochemical series: A listing of ligands in order of their ability to cause *d*-orbital splitting in a complex.

Spin-forbidden: Electronic transitions to an excited state is highly unlikely if the transition results in a change in the number of unpaired electrons in a substance.

Strong-field ligand: Ligand with a strong electrostatic field which causes a high crystal-field splitting of the t_{2g} and e_g orbitals.

Weak-field ligand: Ligand with a weak electrostatic field which results in a small crystal-field splitting of the t_{2g} and e_g orbitals.

22-5 The stereochemistry of complex ions

Asymmetric: A compound with a chiral center.

Chelate: A complex in which the ligands are polydentate.

Chiral: A complex consisting of four different ligands bonded to a central atom.

***Cis* isomer:** Any isomer in which two identical atoms or groups are adjacent to each other or on the same side of a structure.

Enantiomer: Two structures that are mirror images of each other, but not identical.

Facial (fac) isomer: An arrangement of an octahedral complex in which one kind of ligand occupies three adjacent positions.

Labile: A ligand which can be replaced in a complex.

Meridional (mer) isomer: An arrangement of an octahedral complex in which the same type ligands occupy three positions in a plane with the central atom.

Multidentate: Ligands that bond to the central atom at more than one point. Same as polydentate.

Polarimeter: An instrument which measures the rotation of polarized light by a substance.

Polydentate: Same as multidentate.

Stereochemistry: The study of the spacial geometries of molecules and polyatomic ions.

Stereoisomer: Molecules or ions differing only in the spacial arrangements of their atoms.

***Trans* isomer:** An isomer in which two identical groups are located on opposite sides of a structure.

22-6 Descriptive chemistry of selected transition elements

Amalgam: An alloy containing mercury.

Blister copper: The product of roasting of copper ore. It is called blister copper because it contains many bubbles of sulfur dioxide.

Cast iron: An alloy of iron, carbon, and silicon that has a low enough melting point to be easily cast.

Cathodic protection: Preventing the oxidative corrosion of a metal by forcing it to be a cathode by using an electric voltage which opposes the normal electrolytic voltage.

Cementite: Fe_3C

Electrorefining: The final electrolytic process in the purification of a metal in metallurgy.

Galvanize: Coating a metal, usually iron or steel, with zinc to protect form oxidation.

Iron triad: The elements iron, cobalt, and nickel.

Lanthanide contraction: The gradual decrease in atomic radii of the lanthanide elements with increasing atomic number.

Mild steel: A low carbon, relatively soft steel which can easily be rolled into sheet form.

Pig iron: The impure iron produced by a blast furnace. The large blocks of this product are known as "pigs."

Polynuclear complex: A complex with two or more central atoms bridged by bidentate ligands.

Rust: The product of corrosion of iron, generally a hydrous iron(III) oxide.

Slag: The waste product containing mostly silicates from a smelting process.

Smelting: The reduction of an ore to the metal by a process involving melting.

Stainless steel: An alloy of iron, carbon, and chromium, often containing nickel or manganese, which is highly resistant to corrosion.

SELF TEST

True or False

_____ 1. The size of most transition metal atoms is about equal.

_____ 2. Transition metals show a wide range of oxidation states.

_____ 3. The *d* electrons added last to transition metals in the Aufbau process are the first to ionize.

_____ 4. The coordination number is equal to the number of bonds formed by the central atom in a complex ion.

_____ 5. The stable oxidation state gradually increases from left to right in a transition series.

_____ 6. Complex ions are named by writing the name of the ligands first, followed by the central atom name.

_____ 7. Ligands may be either neutral molecules or charged ions.

_____ 8. d^2sp^3 hybrid orbitals give square planar geometry.

_____ 9. The ligand field theory successfully predicts the color variations of complex ions.

_____10. In crystal field theory the *d* orbitals on the central atom are designated t_{2g} and are nonbonding orbitals in the octahedral geometry.

_____11. Weak-field ligands cause less splitting of *d* orbitals on the central atom.

_____12. F^- is a strong field ligand because it strongly repels the *d* electrons of the central atom.

_____13. High- and low-spin configurations are possible for all first-series transition metals.

_____14. Weak-field ligands give a low-spin configuration.

_____15. Stereoisomers are possible in both square-planar and tetrahedral geometries.

Completion

16. The first-series transition metals are filling the __________ subshell in the Aufbau process.

17. All first-series transition elements except scandium are known in _________ oxidation state.

18. The majority of transition elements are chemically ____________ (active, inactive).

19. Coordination number of 6 gives ______________ geometry and has ___________ or _____________ hybridization.

20. The correct name for $[Co(NH_3)_2Cl_4]^-$ is ______________________________.

21. The formula for diamminediaquadibromochromium(III) is __________________.

22. The most common coordination numbers in complex ions are __________________.

23. The coordination number of Co in $[CoCl_2(H_2O)en]^+$ is ___________________.

24. In crystal-field theory nonbonding *d* orbitals are designated ______________________.

25. The energy difference between the *d*-orbital subsets is called the ________________ and designated by __________________.

26. In a d^5 first-transition series ion such as ______________, the five *d* electrons spread out among all *d* orbitals in a ___________ (weak, strong) -ligand field such as one caused by __________ (Cl^-, NH_3) to form a ___________ (high, low) -spin complex ion.

27. The square-planar compound MA_2B_2 has __________ isomers while the tetrahedral configuration of the same formula has _________ isomers.

28. When ___________ different ligands are bonded to the central atom, the central atom is said to be _________________ and the structure is said to be _______________. The structures are called ____________________ or ______________________.

29. Ligands that bond to the central metal ion at more than one point are called __________ or ___________________.

30. The transition elements which are ferromagnetic are ___________________.

Multiple Choice

31. Which of the following transition elements has only one valence electron?
(a) Sc (b) La (c) Fe (d) Cu

32. Which of the following properties shows the most uniformity through the transition metals?
(a) density (b) size (c) hardness (d) melting point

33. The hybridization involved in $CoCl_3(NH_3)_3$ is
(a) sp^3 (b) d^2sp (c) d^2sp^3
(d) no hybridization is involved since it is a neutral compound and not a complex ion

34. The hybrid-orbital model of bonding in complex ions
(a) correctly predicts the geometry of all complex ions
(b) is combined with MO theory to give the crystal-field theory
(c) correctly predicts the geometry and spectral properties of complex ions
(d) divides the *d* orbitals into t_{2g} and e_g subsets

35. The three *d* orbitals with equal energy in crystal field theory are designated
(a) σ (b) t_{2g} (c) e_g (d) Δ

36. Electrons from the central ion occupy
(a) nonbonding or t_{2g} orbitals (b) antibonding or e_g orbitals
(c) empty hybrid orbitals (d) orbitals shared with the ligand electrons

37. The number of unpaired electrons when Cr^{2+} is combined in a strong-field ligand complex is
(a) 1 (b) 2 (c) 3 (d) 4

38. The number of unpaired electrons when Cr^{2+} is combined in a weak-field ligand complex is
(a) 1 (b) 2 (c) 3 (d) 4

39. The number of possible isomers of $[NiCl_4(NH_3)_2]^{2-}$ is

(a) 1 (b) 2 (c) 3 (d) 4

40. The dichromate ion
(a) is the dimer of $HCrO_4^-$
(b) reduces H_2O_2 in acidic solution but oxidizes it in basic solution
(c) can be reduced by zinc to Cr^{2+}
(d) all of the above

41. When MnO_4^- is used as an oxidizing agent
(a) the reducing agent is added to the MnO_4^-
(b) MnO_4^- is added to the reducing agent
(c) the reducing agent is added to acidified MnO_4^-
(d) the order of addition of reagents does not matter if the solution is basic

42. The reduction of iron ore in a blast furnace can be best represented by the reaction
(a) $2\ C + Fe_3O_4 \rightarrow 3\ Fe + 2\ CO_2$
(b) $4\ CO + Fe_3O_4 \rightarrow 3\ Fe + 4\ CO_2$
(c) $4\ H_2 + Fe_3O_4 \rightarrow 3\ Fe + 4\ H_2O$
(d) $4\ Ca + Fe_3O_4 \rightarrow 3\ Fe + 4\ CaO$

43. The cathode reaction in the rusting of iron may be represented as
(a) $Fe \rightarrow Fe^{2+} + 2\,e^-$
(b) $Fe \rightarrow Fe^{3+} + 3\,e^-$
(c) $O_2 + 4\,H^+ + e^- \rightarrow 2\,H_2O$
(d) $Fe^{3+} + 3\,H_2O \rightarrow Fe_2O_3 + 6\,H^+$

44. Silver is widely used in photography because
(a) its complex ions are highly colored
(b) the amount of silver oxidized is proportional to the intensity of light striking the film
(c) the reduced silver is easily dissolved by hypo or $Na_2S_2O_3$
(d) Ag^+ has a low reduction potential and forms soluble complex ions

45. Amalgams are alloys of
(a) Ag (b) Mn (c) Hg (d) Au

Chapter 23

ORGANIC CHEMISTRY

CHAPTER OVERVIEW

In Chapters 20 and 21 we saw how the first member of each group of representative elements has properties and reactivity different from the remaining members of the group. Carbon shows this departure from group behavior most strongly. It has a strong tendency to form covalent bonds with other carbon atoms to form compounds with chains of carbon atoms in various configurations. This chapter concerns organic chemistry, which is the chemistry of compounds containing carbon, hydrogen, and other elements, most commonly oxygen and nitrogen. The study of organic chemistry has been organized and simplified by classifying compounds into groups that depend on the functional group attached to the carbon chain. A functional group is an atom or group of atoms that gives special chemical properties to the organic compound. The common functional groups are listed in Table 23-6 in the text, and it is essential that you learn their names and structures.

The many different structures in Table 23-1 to 23-5 show the need for a systematic system of nomenclature in organic chemistry. The text discusses the nomenclature of each functional group and this may be the most important material to learn to help you organize the large amount of material presented in the chapter. The IUPAC names are designed to describe the exact structure of a molecule, so once you learn the terms used, you should be able to construct the chemical formula of complicated organic molecules from the name and devise correct names when the structural formula is given. Appendix C-3 in the text gives many examples of the nomenclature of organic compounds. The type of bonding and hybridization on carbon determines the structure and many properties of organic compounds. You should review Section 19-2 on hybrid orbitals and observe how the orientation of hybrid orbitals determines the shapes of molecules and leads to the occurrence of different types of isomers.

23-1 Saturated hydrocarbons

Keep in mind that carbon forms four covalent bonds in organic compounds. In saturated hydrocarbons the carbon skeleton is saturated with hydrogen atoms so that each carbon has four single bonds either to other carbon atoms or to hydrogen. Saturated hydrocarbons are called alkanes, or cycloalkanes if the carbon chain forms a closed ring. The names of the first ten straight-chain or normal hydrocarbons should be learned (Table 23-1 in the text). Names of cycloalkanes follow automatically from those of the normal alkanes. Short carbon chains are often attached to, or branch from, longer chains. These branching groups are called alkyl groups. The names of short-chain alkyl groups, especially those with one, two, or three carbon atoms, are often used in chemical nomenclature. You need to recognize these groups and their names.

Notice the different kinds of structural formulas that are used in organic chemistry. Figure 23-1 in the text shows structural formulas and three-dimensional models of simple alkanes. Compare the information conveyed by three-dimensional models, full structural formulas, condensed structural formulas, and carbon skeleton formulas. Chemists tend to use as many shortcuts as possible when writing structures so carbon skeleton formulas are very common, but you should be aware that they do not show the complete compound because hydrogen atoms are often omitted for clarity.

When using the IUPAC nomenclature system be careful as you identify the longest carbon chain. Often a structure is not written to appear as a "straight" chain. The locator numbers and chain orientation may be arranged in several different ways on paper and still represent the same spatial configuration. Note especially the example of 2-methylbutane (Examples 23-1 to 23-3 in the text) in this respect.

Molecules with four or more carbon atoms have more than one way of bonding the carbon atoms together and thus form isomers. The best way to visualize the spatial arrangement of carbon chains and the formation of isomers is by using ball-and-stick models. Styrofoam balls, gum drops, or marshmallows and toothpicks can be used to make models if you do not have access to a molecular model kit. You will find these models a valuable aid in visualizing organic bonding and structures.

The properties and reactions of alkanes are discussed in this section.

23-2 Unsaturated hydrocarbons

Hydrocarbons with at least one double bond are called alkenes. If they have at least one triple bond they are called alkynes. Suffixes *-ane*, *-ene*, and *-yne* are used to indicate alkanes, alkenes, and alkynes, respectively.

Cis-trans or geometrical isomerism is possible in alkenes. Study Table 23-4 in the text to see a comparison of *cis-trans* isomers and their names. The *cis* isomer has identical groups on the same side of the double bond while the *trans* isomer has identical groups on opposite sides of (across) the double bond.

Become familiar with the names and structures of the simple alkenes and alkynes in Table 23-4 and 23-5 in the text. Reactions and properties of unsaturated hydrocarbons are discussed in this section.

23-3 Aromatic hydrocarbons

The chemistry of aromatic hydrocarbons is the chemistry of benzene and its related compounds. Become familiar with the peculiarities of the structure of benzene shown in Figure 23-3 in the text and with its shorthand structural formula. The delocalized electrons and bond angles give it special stability and it forms the basic structure of most other aromatic compounds.

23-4 Functional groups

Learn the structures and names of the functional groups in Table 23-6 in the text.

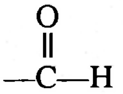
23-5 Alcohols

Alcohols contain the —OH functional group. Both IUPAC and common names of alcohols (listed in Table 23-7 in the text) are used frequently. Become familiar with the preparation, properties, and reactions of the low-molecular-weight alcohols and with the use and meaning of the terms *primary*, *secondary*, and *tertiary* in alcohol nomenclature. The most important reactions of alcohols are dehydration and oxidation.

23-6 Ethers

Ethers contain the functional group —O— and have the general formula ROR'. Become familiar with the common names and structures of the ethers given in Table 23-9 in the text. Ethers are generally quite unreactive.

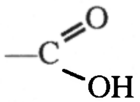
23-7 Aldehydes

Aldehydes are prepared by the oxidation of primary alcohols. They contain the functional group  $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ and can be easily oxidized to carboxylic acids. Become familiar with the IUPAC and common names and the structures of the aldehydes listed in Table 23-10 in the text.

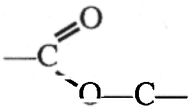
23-8 Ketones

Ketones are closely related to aldehydes. They are prepared by the oxidation of secondary alcohols, so the double-bonded oxygen is not on a carbon atom at the end of the chain as it is for aldehydes. Become familiar with the IUPAC and common names and the structures of the simple ketones listed in Table 23-11 in the text.

23-9 Carboxylic acids

Carboxylic acids contain the functional group  . This functional group may appear to be a combination of an alcohol and an aldehyde, but its properties and reactions are very different from them. The names and formulas of some common carboxylic acids are given in Table 23-12. You should become familiar with them. They participate in typical acid-base reactions.

23-10 Esters

Esters contain the functional group  and are prepared by the reaction of carboxylic acids with alcohols. Know the names and structures of the esters in Table 23-13 in the text. You should be able to give the name and structure of the carboxylic acid and alcohol from which each ester is derived. Note the unique properties and varied uses of esters. The most important reaction of esters is their hydrolysis (splitting into the parent acid and alcohol).

23-11 Amines

Amines result when hydrogen atoms in NH_3 are replaced by organic groups. They are sometimes called organic bases, and they react with acids in a manner similar to ammonia. The names and structures of some simple amines are given in Table 23-14 in the text.

23-12 Enantiomerism in organic compounds

Carbon atoms bonded to four different groups are called asymmetric. Compounds with asymmetric carbon atoms form isomers which are mirror images; these are called enantiomers. These isomers rotate a beam of polarized light as it passes through them. Enantiomers are designated (+) if they rotate light in a right-hand direction or (–) if they rotate it to the left.

23-13 Carbohydrates and proteins

Carbohydrates are aldehydes or ketones which also contain several alcohol groups. Glucose and fructose are common examples of simple carbohydrates called monosaccharides or simple sugars. Glucose and fructose can link together to form a disaccharide called sucrose (common table sugar). Many monosaccharide units can link together to form polysaccharides called starch or cellulose depending on how the monosaccharides are linked. Human beings can break the starch linkages and thus can digest starch, but cannot break the cellulose linkages.

Proteins are polymers of amino acids. Amino acids are molecules having both carboxylic acid and amine functional groups. The link between amino acids is called a peptide link, so small proteins are often called peptides. Hemoglobin, insulin, hormones, and many enzymes are naturally occurring proteins.

LEARNING OBJECTIVES

As a result of studying Chapter 23, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 370 of this *Study Guide.*

23-1 Saturated hydrocarbons

1. Understand the unique nature of carbon among all the elements. (Text Probs. 23-1, 23-2, 23-3) (Self Test 1)
2. Apply the hybridization concepts of Section 19-2 to predict the bonding and geometry of simple hydrocarbons. (Text Fig. 23-2; Text Probs. 23-4, 23-11, 23-14, 23-38, 23-39, 23-43, 23-50, 23-51) (Self Test 5, 31)
3. Draw Lewis structures for simple organic compounds. (Text Prob. 23-4) (Self Test 2, 3)
4. Give the IUPAC names for hydrocarbons whose parent compounds have up to six carbon atoms when given the structural formula, and draw structural formulas when given the names. (Text Tables 23-1 to 23-3; Text Appendix C-3; Text Examples 23-1 to 23-3; Text Probs. 23-5, 23-8, 23-40) (Self Test 4, 16, 34)
5. Draw structural formulas for all the isomers of butane, pentane, and hexane. (Text Example 23-4; Text Probs. 23-6, 23-37, 23-41) (Self Test 19, 32, 33)
6. Write equations for ring-opening reactions of cycloalkanes and substitution reactions of alkanes. (Text Probs. 23-9, 23-10)

23-2 Unsaturated hydrocarbons

1. Give the IUPAC name for all alkenes and alkynes through hexene and hexyne when given the structural formula, and draw structural formulas when given the names. (Text Tables 23-4, 23-5; Text App. C-3; Text Example 23-5; Text Probs. 23-12 to 23-14, 23-42, 23-59) (Self Test 6, 17, 18)
2. Draw structural formulas for *cis-trans* isomers. (Text Probs. 23-7, 23-26) (Self Test 39)
3. Write equations for addition of hydrogen halides to double or triple carbon bonds. (Text Prob. 23-15) (Self Test 20)

23-3 Aromatic hydrocarbons

1. Use Fig. 23-3 in the text to explain the bonding in benzene according to MO theory and draw Lewis structures to explain resonance in benzene and related compounds. (Text Probs. 23-16, 23-18) (Self Test 7)

2. Write IUPAC names of benzene derivatives given the structural formula or the ortho-meta-para system name. Draw the structural formula given the name in either system. (Text Probs. 23-17, 23-19) (Self Test 8, 21, 22, 35)
3. Draw structural formulas of isomers of the alkylbenzenes. (Text Prob. 23-17) (Self Test 8)

23-4 Functional groups

1. Write the names and structures of functional groups in Table 23-6 in the text. (Text Prob 23-48)

23-5 Alcohols

1. Write the IUPAC and common names of simple alcohols and draw the structural formulas when given the names. (Text Table 23-7; Text Probs. 23-20, 23-23b,g) (Self Test 9, 24)
2. Write equations for the preparation and oxidation of simple primary and secondary alcohols. (Text Probs. 23-21, 23-44) (Self Test 10)
3. Explain the different solubilities and boiling points of simple alcohols on the basis of hydrogen bonding. (Text Table 23-8; Text Prob. 23-24)

23-6 Ethers

1. Write the common names of simple ethers and draw the structural formulas when given the names. (Text Table 23-9; Text Prob 23-22) (Self Test 11)

23-7 Aldehydes

1. Give the IUPAC and common names of simple aldehydes and draw the structural formulas when given the names. (Text Table 23-10; Text Prob. 23-23i) (Self Test 12)
2. Write a chemical equation showing the oxidation of primary alcohols to aldehydes. (Text Prob. 23-52)

23-8 Ketones

1. Write the IUPAC and common names of simple ketones and draw the structural formulas when given the names. (Text Table 23-11; Text Prob. 23-23a,e,h) (Self Test 12)
2. Write a chemical reaction showing the oxidation of secondary alcohols to ketones. (Self Test 25, 36)

23-9 Carboxylic acids

1. Write the IUPAC and common names for simple carboxylic acids and draw the structural formulas when given the names. (Text Table 23-12; Text Prob. 23-23d,j)
2. Relate the strength of carboxylic acids to their structure. (Text Table 23-12; Text Probs. 23-25, 23-28, 23-49) (Self Test 13)
3. Write chemical equations for reactions of carboxylic acids with inorganic bases and alcohols. (Text Probs. 23-45, 23-46) (Self Test 26)

23-10 Esters

1. Write the IUPAC and common names for simple esters and draw structural formulas when given the names. (Text Table 23-13; Text Prob. 23-23f) (Self Test 26, 37)
2. Know the general properties and uses of simple esters. (Self Test 23)

23-11 Amines

1. Write the common names of simple amines and draw structural formulas when given the names. (Text Table 23-14; Text Prob. 23-23c,k) (Self Test 38)
2. Classify amines as primary, secondary, or tertiary. (Text Prob. 23-27) (Self Test 27)

23-12 Enantiomerism in organic compounds

1. Draw structures that show how optical isomerism arises in compounds with asymmetric carbon atoms. (Text Probs. 23-29, 23-30, 23-34) (Self Test 15, 29, 42, 45)

23-13 Carbohydrates and proteins

1. Draw the acyclic structure of a simple sugar. (Text Prob. 23-32) (Self Test 43)
2. Show the relation between mono-, di-, and polysaccharides. (Text Probs. 23-31, 23-54)
3. Explain the differences between cellulose and starch. (Text Prob. 23-33) (Self Test 44)
4. Name the functional groups present in amino acids and explain the special properties resulting from a basic and an acidic site in the same molecule. (Text Prob. 23-55)
5. Describe the peptide link that joins amino acids to form peptides and proteins. (Text Probs. 23-36, 23-56) (Self Test 30)

KEY TERMS

23-1 Saturated hydrocarbons

Alkane: A saturated hydrocarbon with general formula C_nH_{2n+2}.

Alkyl group: A hydrocarbon group consisting of an alkane molecule less one of its hydrogen atoms.

Branched chain: A hydrocarbon in which one or more carbon atoms is bonded to three or four different carbon atoms.

Condensed structural formula: A formula which lists successive carbon atoms, each followed immediately by the atoms bonded to it.

Cycloalkane: A cyclic hydrocarbon with general formula C_nH_{2n}.

Hydrocarbon: A compound containing only carbon and hydrogen.

Locator number: Numbers which give the position of a functional group or branch on a hydrocarbon chain.

Marsh gas: A common name for methane.

Normal alkane: A saturated hydrocarbon with no branching of the carbon chain.

Saturated hydrocarbon: A hydrocarbon in which all carbon-carbon bonds are single bonds.

Skeletal isomer: Hydrocarbons which have the same molecular formula but different branching of their carbon chains.

Straight-chain: Carbon chains without branching.

23-2 Unsaturated hydrocarbons

Addition reaction: A reaction in which one molecule adds to another with no loss of atoms from either.

Alkene: An unsaturated hydrocarbon containing a carbon-carbon double bond with general formula C_nH_{2n}.

Alkyne: An unsaturated hydrocarbon containing a carbon-carbon triple bond with general formula C_nH_{2n-2}.

***Cis* isomer:** Any isomer in which two identical atoms or groups are adjacent to each other or on the same side of a structure.

Electrophile: An atom or group of atoms which appears to seek electrons in its reactions.

Electrophylic addition: A reaction in which a molecule is added to double-bonded carbon atoms.

Elimination reaction: A reaction in which atoms or groups on adjacent atoms are removed to leave a double or triple bond between the atoms.

Markovnikov's rule: Hydrogen adds to the carbon of the double bond that is already bonded to the most hydrogen atoms.

***Trans* isomer:** Any isomer in which two identical groups are located on opposite sides of a structure.

Unsaturated hydrocarbon: A hydrocarbon with one or more multiple bonds.

23-3 Aromatic hydrocarbons

Aromatic hydrocarbon: A hydrocarbon with a benzene ring.

Catalytic reforming: A process occurring in the refining of petroleum in which straight-chain hydrocarbons are converted to aromatics using an appropriate catalyst.

Delocalized orbital: An orbital which extends over more than two atoms.

Meta–: m–. A prefix indicating groups on the 1 and 3 positions of a benzene ring.

Ortho–: o–. A prefix indicating groups on adjacent carbon atoms of a benzene ring.

Para–: p–. A prefix indicating groups on the 1 and 4 positions of a benzene ring.

Platforming: Catalytic reforming with a platinum catalyst.

23-4 Functional groups

Derivative: The compound resulting when a hydrogen on a hydrocarbon is replaced with a functional group.

Functional group: A group of atoms, often containing oxygen or nitrogen, which confers characteristic properties on the molecule.

23-5 Alcohols

Alcohol: An organic compound with the functional group —OH.

Dehydrogenation: The removal of hydrogen atoms from a compound.

Diol: A compound with two —OH functional groups.

Gasohol: A mixture of gasoline plus methyl alcohol or ethyl alcohol.

Grain alcohol: A common name for ethyl alcohol.

Nucleophile: An electron-rich atom or group of atoms which seeks to share its electrons with a relatively positive atom.

Nucleophilic substitution: The reaction occurring when one nucleophile replaces another nucleophile bonded to a compound.

Polyol: A compound with two or more —OH functional groups.

Primary: The position of a functional group bonded to a carbon atom which is in turn bonded to one other carbon atom.

Residue: A general term referring to the hydrocarbon part of a molecule.

Secondary: The position of a functional group bonded to a carbon atom which is bonded to two other carbon atoms.

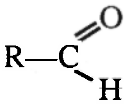
Tertiary: The position of a functional group bonded to a carbon atom which is bonded to three other carbon atoms.

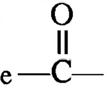
Wood alcohol: A common name for methyl alcohol.

23-6 Ethers

Ether: An organic compound with general formula R—O—R.

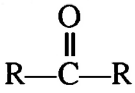
23-7 Aldehydes

Aldehyde: An organic compound with general formula  .

Carbonyl: The  $-\overset{\displaystyle O}{\overset{\|}{C}}-$ functional group.

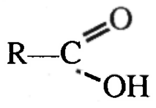
23-8 Ketones

Grignard reagent: A compound with general formula RMgBr used to add alkyl groups to organic compounds.

Ketone: An organic compound with general formula  $R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R$.

23-9 Carboxylic acids

Carboxylate ion: The anion of a carboxylic acid.

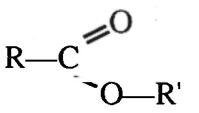
Carboxylic acid: An organic compound with general formula  .

Dicarboxylic acid: An organic compound with two carboxylic acid groups.

Difunctional: An organic compound with two different functional groups.

23-10 Esters

Emulsify: The dispersion of immiscible liquids into each other in droplets larger than colloidal size.

Ester: An organic compound with general formula  .

Esterification: The formation of an ester from a carboxylic acid and an alcohol.

Fat: A solid or semisolid ester of glycerol and long-chain carboxylic acids.

Fatty acid: Long-chain carboxylic acids.

Glyceride: A liquid or solid ester of glycerol.

Hydrogenation: The addition of hydrogen atoms to double-bonded carbon atoms. The double bond is eliminated in the process.

Hydrophilic: A polar compound which dissolves in water. Water-bonding.

Hydrophobic: A nonpolar compound which is insoluble in water. Water-fearing.

Oil: A liquid ester of glycerol and fatty acids.

Saponification: The hydrolysis of a fat or oil to form glycerol and a soap.

Soap: The sodium or potassium salt of a fatty acid.

23-11 Amines

Amine: An organic compound with an $\text{—}NH_2$ functional group.

23-12 Enantiomerism in organic compounds

Asymmetric: A compound with a chiral center.

Chiral: A molecule that cannot be superimposed on its mirror image.

Dextrorotatory: Molecules which rotate a plane of polarized light to the right.

Enantiomer: One of a pair of optical isomers.

Levorotatory: Molecules which rotate a plane of polarized light to the left.

Stereoisomer: Molecules or polyatomic ions with the same atoms and the same bonds but differing in the geometrical orientations of the atoms and bonds.

23-13 Carbohydrates and proteins

Amino acid: A carboxylic acid with an amine group on a noncarboxyl carbon atom.

Carbohydrate: An aldehyde or ketone which is a polyol.

Cellulose: A polysaccharide of glucose units combined by β linkage.

Disaccharide: A molecule consisting of two monosaccharides linked together.

Helix: A spiral or corkscrew-like structure found in proteins.

Hormone: Relatively small proteins important to the biological activities of cells.

Invert sugar: A mixture of glucose and fructose formed by the hydrolysis of sucrose.

Ketohexose: A six-carbon monosaccharide with a ketone group.

Monosaccharide: A five- or six-carbon sugar molecule which cannot be broken down to a simpler sugar by hydrolysis.

Peptide: Small protein-like molecules consisting of two or more amino acids bonded together by peptide links.

Peptide link: The combination of two amino acids when the amine group of one amino acid reacts with the carboxyl group of the other.

Polysaccharide: A combination of two or more monosaccharides. A complex carbohydrate.

Protein: Complex combinations of amino acids bonded together in a specific sequence by peptide links.

Quaternary structure: The geometry associated with the combination of several protein molecules to form a large unit.

Secondary structure: The geometry associated with the folding or bending of a protein.

Starch: A digestible polysaccharide of glucose units combined by α linkages.

Sugar: Any mono or disaccharide. Often sugar refers to the specific disaccharide, sucrose.

Tertiary structure: The three-dimensional shape into which a protein α-helix is bent.

SELF TEST

True or False

_____ 1. The main reason there are so many organic compounds is that carbon atoms form long chains held together by strong covalent bonds.

_____ 2. Carbon always bonds to four other atoms in organic compounds.

_____ 3. Alkanes are straight-chain hydrocarbons.

_____ 4. Propane and isopropane are isomers.

_____ 5. Rotation about a carbon-carbon double bond is not possible.

_____ 6. Acetylene is an alkene.

_____ 7. The π electrons in benzene are localized between two adjacent carbon atoms to form a system of alternating double and single bonds.

_____ 8. There are three isomers of dimethylbenzene.

_____ 9. Isopropyl alcohol is a primary alcohol.

_____10. Primary alcohols cannot be oxidized to ketones.

_____11. Ethers are isomers of alcohols.

_____12. Acetone is the ketone of acetic acid.

_____13. The acid strength of simple carboxylic acids are all about equal.

_____14. Saponification is the reverse reaction of esterification.

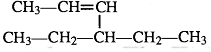
_____15. An asymmetric carbon atom always results in two enantiomers which have chiral centers and rotate polarized light in opposite directions.

Completion

16. The IUPAC name for isobutane is ______________________________

17. The structural formula for 3,5-dimethyl-4-ethyl-3-isopropyl-1-hexyne is __________

18. The IUPAC name for



$CH_3—CH_2—\overset{\overset{\displaystyle CH_3—CH{=}CH}{|}}{CH}—CH_2—CH_3$

is _______________

19. There are ___________ isomers of dichlorobutane.

20. The product of addition of HCl to propene is ______________________.

21. Another name for methylbenzene is __________________________

22. The IUPAC name for m-dimethylbenzene is ___________________________

23. Alcohols and carboxylic acids react to form ___________________________________

24. The IUPAC name for a secondary alcohol with four carbon atoms is ______________

25. Isopropyl alcohol may be oxidized to give a __________________ whose IUPAC name is _________________________ and whose common name is _________________.

26. The IUPAC name of the product of reaction between acetic acid and n-propyl alcohol is ____________________________. Its common name is _____________________.

27. Isopropyl amine is a ______________ (primary, secondary, tertiary) amine.

28. Nylon 66 is a _________________ polymer.

29. Enantiomers arise in compounds that have a (an) __________________ carbon atom.

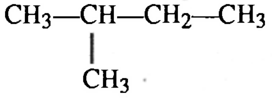
30. Proteins contain _________________links.

Multiple Choice

31. The class of hydrocarbons that has bonding involving sp^2 hybridization on carbon is
(a) alkane (b) alkene (c) alkyne (d) cycloalkane

32. Which of the following is not an isomer of the others?

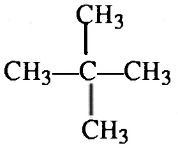
(a)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

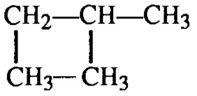
(b) $CH_3-CH_2-CH_2-CH_2-CH_3$

(c)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

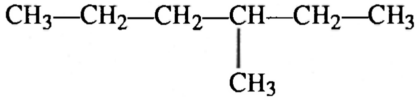
(d)



$\underset{\displaystyle CH_3}{\underset{|}{CH_2}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

33. The number of possible isomers of $C_5H_{11}Cl$ is
(a) 3 (b) 5 (c) 7 (d) 8

34. The IUPAC name for

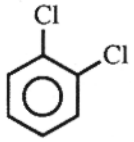


$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$ is

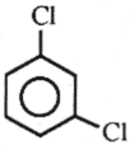
(a) 4-ethylpentane (b) 4-methylhexane
(c) 3-methylhexane (d) all of the above are correct

35. The correct structure for o-dichlorobenzene is

(a)

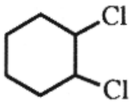


(b)



(c)

(d)



36. Oxidation of a secondary alcohol produces
(a) a primary alcohol (b) an aldehyde
(c) a ketone (d) an ester

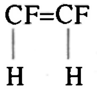
37. The ether which is an isomer of ethanol is
(a) methyl ether (b) methyl ethyl ether
(c) ethyl ether (d) ethers are not isomers of alcohols

38. Which of the following functional groups must contain a nitrogen atom?
(a) esters (b) saccharides
(c) aromatic hydrocarbons (d) amines

39. Which of the following can exist in *cis-trans* isomers?
(a) 1-butene (b) 2-methyl-1-butene
(c) 2,3-dimethyl-2-butene (d) 2-methyl-2-butene

40. Secondary amines react with nitrous acid to form
(a) nitrosamines (b) ammonium nitrites
(c) peptide links (d) amino acids

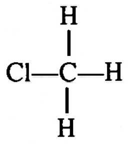
41. The polymer teflon has the formula $(\text{—CF}_2\text{—CF}_2\text{—})_n$. The monomer which polymerizes to produce teflon is
(a) $\text{—CF}_2\text{—}$ (b) $CF_2\text{—}CF_2$ (c) $CF_2{=}CF_2$ (d)



$\begin{array}{cc} CF= & CF \\ | & | \\ H & H \end{array}$

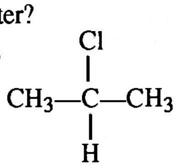
42. Which of the following has a chiral center?

(a)



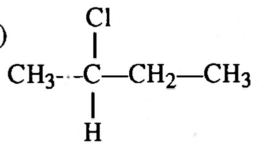
$\begin{array}{ccc} & H & \\ & | & \\ Cl— & C & —H \\ & | & \\ & H & \end{array}$

(b)



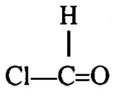
$\begin{array}{ccc} & Cl & \\ & | & \\ CH_3— & C & —CH_3 \\ & | & \\ & H & \end{array}$

(c)



$\begin{array}{ccc} & Cl & \\ & | & \\ CH_3— & C & —CH_2—CH_3 \\ & | & \\ & H & \end{array}$

(d)

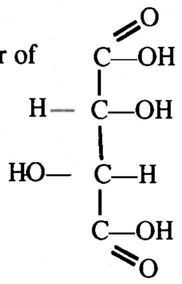


$\begin{array}{cc} & H \\ & | \\ Cl— & C{=}O \end{array}$

43. Glucose is
(a) a starch (b) an isomer of fructose (c) an aldehyde (d) a disaccharide

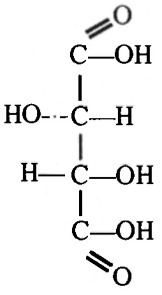
44. A starch is
(a) an enantiomer of cellulose (b) the cyclic form of sucrose
(c) invert sugar (d) a polymer of glucose units

45. The enantiomer of

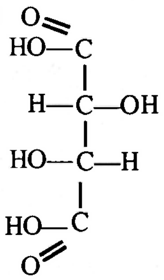


is

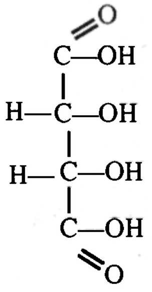
(a)



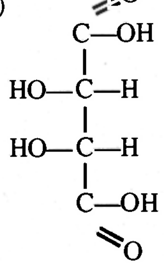
(b)



(c)



(d)



Chapter 24

NUCLEAR PROCESSES

CHAPTER OVERVIEW

Up to this point we have studied reactions involving the electrons in outer orbitals around the nuclei of atoms. The nucleus of an atom is not affected by these chemical interactions, but it is capable of undergoing changes called nuclear reactions or nuclear transformations in processes quite different from ordinary chemical reactions.

We have already covered considerable information about the nucleus and its properties in our study of atomic structure. Recall the properties of subatomic particles found in the nuclei and the types of radioactivity emanating from atoms discussed in Section 5-2. In Section 5-3, we found that isotopes are atoms of the same element that have different numbers of neutrons in the nucleus and we used atomic symbols to distinguish those isotopes. In this chapter we will enlarge upon these concepts and consider the important aspects of nuclear processes.

24-1 Radioactivity

Recall from Section 5-2 our discussion of types of radioactivity: the alpha, beta, and gamma rays. All three types of radioactivity emanate from nuclei of atoms undergoing nuclear disintegration. These processes can be described by equations much like chemical equations. The isotope symbols showing mass number and atomic number (see Section 5-3) are used in equations for nuclear processes. There are two distinct types of radioactivity: natural and artificial. This section deals only with natural radioactivity; artificial radioactivity is discussed in Section 24-3.

The most common type of natural radioactivity is the ordered decay of naturally occurring, unstable nuclei called the radioactive decay series. Three different natural decay series are known. One of these starts with $^{238}_{92}U$ and is shown in Fig. 24-2 in the text. Each step in this series is represented by a nuclear equation. You should be able to write equations of this type given sufficient information about the decay process.

24-2 The kinetics of nuclear decay

All radioactive decay processes follow first-order kinetics. The first-order equations developed in Section 13-2 apply directly to nuclear processes and can be used to calculate the time necessary for a given amount of decay to occur or the amount of material remaining after a given time. Each radioactive isotope has a characteristic half-life, and decay rates of different processes are often compared through values of half-lives of the isotopes. Half-lives vary from a fraction of a second to billions of years. The kinetics of decay of natural radioactive isotopes can be used to determine the age of substances containing the isotope. Uranium dating is used for minerals and carbon dating for artifacts containing carbon.

24-3 Nuclear reactions

Artificial or induced radioactivity results from the bombardment of nuclei with subatomic particles. The products of these bombardment processes are usually radioactive and undergo nuclear decay. Figure 24-3 in the text shows a diagram of a cyclotron used to bombard target nuclei with protons. All the elements with atomic numbers greater than 92 (beyond uranium) are artificial. They were produced by bombardment techniques and are all radioactive.

24-4 Nuclear stability

Figure 24-4 in the text can be used to determine whether or not a given isotope is radioactive. If the isotope lies outside the belt of stability it will decay spontaneously toward the stable region. Note how the neutron/proton ratio for stable nuclei increases as the atomic number increases.

24-5 Fission, fusion, and nuclear binding energy

Mass is not conserved in nuclear reactions. Spontaneous nuclear reactions always involve the loss of mass and the production of large amounts of energy. The decrease in mass can be determined by the difference between the mass of products and the mass of reactants, and the energy equivalent of this mass loss can be determined by Einstein's equation: $E = mc^2$. The mass of an atomic nucleus is always less than the mass of the constituent neutrons and protons. The energy equivalent of this mass defect or mass loss is called the binding energy of the nucleus. The highest binding energies per nucleon are found in elements of intermediate atomic number, as shown in Fig. 24-6 in the text. Moving toward the center from either end of this plot results in the formation of more stable nuclei accompanied by the release of energy. Therefore, the fusion of light nuclei into heavier ones and the fission of heavy nuclei into lighter ones both result in the release of energy. Nuclear fission, used in present nuclear reactors, is based on moving to the left on this plot. Nuclear fusion is based on moving to the right.

When a $^{235}_{92}U$ nucleus is bombarded by a neutron with the right kinetic energy, it undergoes fission to form two lighter nuclei, free neutrons, and energy. The free neutrons cause other $^{235}_{92}U$ atoms to fission, resulting in a chain reaction. Uncontrolled chain reactions produce nuclear explosions or atomic bombs, but by controlling the concentration of fissionable $^{235}_{92}U$ and absorbing excess neutrons, the rate of the fission process is slowed and energy is released under controlled conditions. Figure 24-7 in the text shows a diagram of a nuclear reactor which uses this process. In the uncontrolled process the fission fragments produce radioactive fallout from the explosion; in the controlled process they form highly radioactive waste materials.

Fusion of ^3_1H and ^2_1H has been proposed as an almost unlimited source of energy without the serious waste-disposal problems associated with fission-type reactors. The technological problems of developing fusion power are not solved and practical use of nuclear fusion is still many years in the future.

24-6 Chemical applications of radioactivity

We have already discussed the use of radioactivity for determining the age of minerals and objects containing carbon and for power generation. This section mentions other uses in chemical research, in medicine, and as tracers for following changes in almost any kind of process.

KEY EQUATIONS

24-2 The kinetics of nuclear decay

The decay of a radioactive isotope is given by

$$\ln \frac{N}{N_0} = -kt$$

where N = number of parent nuclei at time t
N_0 = number of parent nuclei at time $t = 0$
k = first-order rate constant
t = time since initial concentration N_0 was observed

The half-life is related to the rate constant by

$$t_{1/2} = \frac{0.693}{k}$$

where $t_{1/2}$ = half-life of the isotope
k = first-order rate constant

24-5 Fission, fusion, and nuclear binding energy

The Einstein relationship gives the energy equivalent of a quantity of mass

$$E = mc^2$$

where E = energy, J
m = mass, kg
c = speed of light = 2.998×10^8 m s^{-1}

LEARNING OBJECTIVES

As a result of studying Chapter 24, you should be able to write the definition and give an example illustrating the use of each key term and do the following. The list of key terms is found on page 386 of this *Study Guide*.

24-1 Radioactivity

1. List the three main types of radioactivity and give their symbols. (Text Probs. 24-2, 24-12) (Self Test 1, 4, 16)
2. Write nuclear equations for natural radioactive decay by alpha or beta emission. (Text Example 24-1; Text Probs. 24-8, 24-9, 24-13, 24-30, 24-32) (New Skills Examples 1, 2; Self Test 2, 3, 17, 26, 31 to 33, 37)
3. Identify the type of radioactive decay given the parent and daughter isotopes. (Text Example 24-2; Text Probs. 24-4, 24-7) (Self Test 2, 19, 22, 34)
4. Describe three methods for detecting radioactivity. (Self Test 18)

24-2 The kinetics of nuclear decay

1. Calculate the amount of a radioactive isotope remaining after a given time or the time required for a given amount to decay given the rate constant for decay or the half-life. (Text Examples 24-3, 24-4; Text Probs. 24-14 to 24-16, 24-33) (New Skills Example 3; Self Test 5, 6, 20, 35)
2. Use uranium, potassium-argon, and carbon dating calculations to determine the age of an object. (Text Examples 24-5, 24-6; Text Probs. 24-17, 24-18, 24-34) (Self Test 7, 21, 36, 43)

24-3 Nuclear reactions

1. Write nuclear equations for the transmutation of elements by nuclear bombardment. (Text Probs. 24-28, 24-29, 24-31) (Self Test 8, 32)

24-4 Nuclear stability

1. Write nuclear equations for radioactive decay by neutron or positron emission and for electron capture. (Text Probs. 24-3, 24-5, 24-10, 24-11) (Self Test 23, 26, 27, 32, 38)
2. Use the belt of stability in Fig. 24-4 in the text to predict whether or not a nucleus is unstable and the type of decay likely for unstable nuclei. (Text Probs. 24-19 to 24-21) (Self Test 9 to 11, 24, 25, 29, 39, 40)
3. Write nuclear reactions typical of the fission process for $^{235}_{92}U$. (Text Prob. 24-22) (Self Test 27)

24-5 Fission, fusion, and nuclear binding energy

1. Calculate the binding energy of a given isotope. (Text Probs. 24-23, 24-35) (New Skills Example 4; Self Test 12, 28, 41, 42)
2. Describe the $^{235}_{92}U$ chain reaction and construction of an atomic bomb and a nuclear power plant and list the basic differences in their construction and energy release. (Text Prob. 24-24) (Self Test 13, 30)
3. List some problems that have not yet been solved in the development of controlled fusion reactions. (Self Test 14)
4. Calculate the energy released in nuclear processes. (Text Probs. 24-36, 24-38) (New Skills Example 5; Self Test 41, 42)

24-6 Chemical applications of radioactivity

1. Describe four uses of radioactivity or radioactive isotopes. (Text Probs. 24-25 to 24-27, 24-39) (Self Test 15, 45)

NEW SKILLS

24-1 Radioactivity

Nuclear equations

We can write equations for nuclear processes in the same general manner as for chemical reactions. The isotope symbol is always used in nuclear equations and care must be taken to balance the total mass numbers and atomic numbers for products and reactants.

• EXAMPLE 1

Problem: Write a nuclear equation for the decay of cobalt-60 by beta emission to nickel-60.

Solution: The isotope symbols for the particles are: cobalt-60, $^{60}_{27}\text{Co}$; nickel-60, $^{60}_{28}\text{Ni}$; and a beta particle, $^{0}_{-1}e$. The nuclear equation is

$$^{60}_{27}\text{Co} \rightarrow {}^{0}_{-1}e^{-} + {}^{60}_{28}\text{Ni} \quad \bullet$$

Parallel Problem: Write a nuclear equation showing electron capture by beryllium.
Ans: $^{7}_{4}\text{Be} + {}^{0}_{-1}e^{-} \rightarrow {}^{7}_{3}\text{Li}$

• EXAMPLE 2

Problem: Write a nuclear equation for the alpha decay of radium-226.

Solution: The daughter isotope produced by the decay is not identified, but we can determine its mass number and atomic number from the information given because the totals of the mass numbers and atomic numbers remain constant during any nuclear process. The nuclear equation is

$$^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\text{He} + \ ?$$

The mass numbers of the helium nucleus and the daughter isotope must total 226 and their atomic numbers must total 88. Therefore, the daughter isotope has mass number $226 - 4 = 222$ and atomic number $88 - 2 = 86$, so it must be $^{222}_{86}\text{Rn}$. The completed equation is

$$^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn} \quad \bullet$$

Parallel Problem: Write a nuclear equation for the decay of carbon-11 by positron emission.
Ans: $^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}e^{+}$

Examples 24-1 and 24-2 in the text are similar problems.

24-2 The kinetics of nuclear decay

Actually there are no *new* skills in this section, only the application of familiar first-order kinetics to nuclear decay processes. We will work two examples illustrating these applications.

1. Using the first-order rate law to determine the amount of a radioactive species remaining after a given time

• EXAMPLE 3

Problem: Sodium-24 is injected into the bloodstream of patients suspected of having an obstruction in their circulatory system. The amount of radioactivity detected in parts of the body affected by the obstruction indicates the quantity of blood reaching that area and helps locate the obstruction. Sodium-24 undergoes beta decay with a half-life of 15.0 h. How long could a hospital keep a sample of Sodium-24 before it loses 90% of its radioactivity?

Solution: Ten percent of the Sodium-24 will be left after this time. The first-order decay rate gives the fraction of radioactive isotope left as a function of time.

$$\ln \frac{N}{N_0} = -kt$$

where $\frac{N}{N_0}$ = fraction of ${}^{24}_{11}\text{Na}$ remaining = 0.10

k = rate constant = $\frac{0.693}{t_{1/2}} = \frac{0.693}{15.0\ \text{h}} = 4.62 \times 10^{-2}\ \text{h}^{-1}$

t = time for 90% of ${}^{24}_{11}\text{Na}$ to decay

Substituting these values into the rate equation gives

$$\ln 0.10 = -(4.62 \times 10^{-2})t$$

$$t = 49.8\ \text{h} \quad \bullet$$

Parallel Problem: Strontium-90 is a hazardous isotope produced in the fission of uranium. A 5.000 gram sample of strontium-90 decays to only 0.393 g in ten years. What is the half-life of strontium-90?
Ans: 28.8 years

Example 24-3 in the text illustrates the calculation of the amount of a nuclide remaining after a given time period of decay.

2. *Use of radioactivity in determining the age of artifacts*

There are several methods for determining the age of an artifact by radioactivity. The best known of these is carbon dating or radiocarbon dating. Carbon-14 is radioactive and exists in a constant ratio with the more abundant isotope, carbon-12, in all living plants or animals. After death there is no more input of carbon so the carbon-14 decays and the ${}^{14}_{6}\text{C}/{}^{12}_{6}\text{C}$ ratio decreases. Measurements of this ratio can be used in the first-order decay rate equation to determine the time elapsed since the artifact was living.

Example 24-5 in the text illustrates the use of the ${}^{238}_{92}\text{U}/{}^{206}_{82}\text{Pb}$ ratio in dating and Text Example 24-6 shows an application of radiocarbon dating.

24-5 Fission, fusion, and nuclear binding energy

1. *Calculation of binding energy*

The mass of a nucleus is always less than the mass of the protons and neutrons in that nucleus. This difference in mass is called the mass loss or mass defect of the nuclide. Its energy equivalent is the binding energy of the nucleus.

• EXAMPLE 4

Problem: Calculate the nuclear binding energy of a helium-4 nucleus. The mass of a helium-4 nucleus is 4.00150 amu, of a proton 1.00728 amu, and of a neutron 1.00866 amu.

Solution: Helium-4 contains two protons and two neutrons. We would expect its mass to be

$$\begin{array}{lcl} \text{Mass of 2 protons} = & 2(1.00728\text{ amu}) = & 2.01456\text{ amu} \\ \text{Mass of 2 neutrons} = & \underline{2(1.00866\text{ amu}) =} & \underline{2.01732\text{ amu}} \\ \text{Total mass of nucleons} & = & 4.03188\text{ amu} \end{array}$$

The actual mass of the nucleus, 4.00150 amu, is less than the mass of the nucleons.

Mass of nucleons	4.03188 amu
Mass of nucleus	4.00150 amu
Mass loss	0.03038 amu

We use the Einstein relationship to calculate the energy equivalent to this mass loss

$$E = mc^2$$

where E = energy, J
m = mass, kg
c = speed of light = 2.998×10^8 m s^{-1}

It is most convenient to convert the mass loss to kilograms before substituting into the Einstein relationship.

$$\text{Mass loss} = 0.03038\text{ amu}\,\frac{1\text{ g}}{6.023 \times 10^{23}\text{ amu}}\,\frac{10^{-3}\text{ kg}}{\text{g}} = 5.044 \times 10^{-29}\text{ kg}$$

The Einstein relationship becomes

$$E = (5.044 \times 10^{-29}\text{ kg})(2.998 \times 10^8\text{ m s}^{-1})^2 = 4.534 \times 10^{-12}\text{ kg m}^2\text{ s}^{-2}$$

$$\text{or } 4.534 \times 10^{-12}\text{ J}$$

Binding energies are usually expressed per nucleon. There are four nucleons in a helium-4 nucleus, so the binding energy per nucleon is

$$\frac{4.534 \times 10^{-12}\text{ J}}{4\text{ nucleons}} = 1.133 \times 10^{-12}\text{ J nucleon}^{-1}$$ •

Parallel Problem: Calculate the nuclear binding energy in kilojoules per mole of carbon–12.
Ans: 8.60×10^9 kJ/mol

Figure 24-6 in the text shows how nuclear binding energy varies for the elements. The highest binding energies are found in elements with intermediate atomic numbers and these are the most stable nuclei.

2. *Calculation of energy released in fission or fusion processes*

• EXAMPLE 5

Problem: A fusion reaction that has been producing energy since the dawn of time remains virtually untapped to this day. The sun releases energy according to the overall process.

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{1}e^{+}$$

Calculate the energy released when 1 mol of helium nuclei is formed by this process. The mass of a proton is 1.00728 amu, of an alpha particle 4.00150 amu, and of a positron 0.000549 amu.

Solution: The energy released is the energy equivalent of the mass loss for the reaction. We can determine this mass loss as follows

$$\text{Mass of } 4\,{}^{1}_{1}\mathrm{H} = 4(1.00728) = 4.02912 \text{ amu}$$

$$\text{Mass of } {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{1}e^{+} = 4.00150 + 2(0.000549) = 4.01248$$

$$\text{Mass loss} = 4.02912 - 4.01248 = 0.01664 \text{ amu}$$

The energy equivalent of this mass loss is

$$E = mc^2 = 0.01664 \text{ amu} \frac{1 \text{ g}}{6.023 \times 10^{23} \text{ amu}} \frac{10^{-3} \text{ kg}}{\text{g}} (2.998 \times 10^{8} \text{ m s}^{-1})^2$$

$$= 2.483 \times 10^{-12} \text{ J per He nucleus}$$

$$2.483 \times 10^{-12} \text{ J (He nucleus)}^{-1}(6.023 \times 10^{23} \text{ He nuclei mol}^{-1}) = 1.500 \times 10^{12} \text{ J mol}^{-1}$$ •

Parallel Problem: Calculate the energy in kilojoules per mole that is released during the fusion of deuterium by the reaction

$$2\,{}^{2}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He}$$

The mass of a deuteron is 2.01355 amu and the mass of helium 4 is 4.00150 amu.
Ans: 2.30×10^{9} kJ/mol

This text works an example showing the calculation of the energy released in a fission process.

KEY TERMS

24-1 Radioactivity

Alpha particle: α. A radioactive emission consisting of two protons and two neutrons. A ${}^{4}_{2}\mathrm{He}$ nucleus.

Beta ray: β^{-}. A radioactive emission consisting of a high-energy electrons.

Bubble chamber: A device for revealing the path of a subatomic particle as a trail of tiny bubbles in liquid hydrogen.

Cloud chamber: A device for revealing the path of a subatomic particle as a visible trail of droplets condensed from a supersaturated vapor.

Daughter nuclide: The nuclide remaining after a radioactive decay takes place.

Electron capture: Radioactive decay in which an electron around an atom, usually from the K shell, is captured by a nucleus.

Gamma ray: γ. High-energy electromagnetic radiation emitted from a nucleus.

Geiger-Mueller counter: A device for detecting the emissions of radioactive decay by counting the ions produced by the radiation as it collides with argon atoms inside a tube.

K capture: Same as electron capture.

Natural radioactivity: The decay or decomposition of nuclei of atoms found in nature.

Nuclear disintegration: Same as radioactive decay.

Nuclear equation: A representation of radioactive decay showing the parent and daughter nuclides and radioactive emissions.

Parent nuclide: An unstable nucleus undergoing radioactive decay.

Radioactive decay: The decomposition of unstable nuclei. Samed as nuclear disintegration.

Radioactive decay series: The sequence of radioactive decay of an unstable nuclide leading to a final stable nucleus such as lead.

Radioactivity: The emissions from the decay or decomposition of unstable nuclei of atoms.

Scintillation counter: A sensitive device for detecting radioactive emissions by measuring the flashes of light given off by a crystal of an alkali-metal chloride when high-energy radiation hits it. The flash of light is detected by a photomultiplier and the signal is amplified and counted electronically.

Spark chamber: A device for revealing the path of a subatomic particle as a trail of spark discharges between a set of thin electrodes.

24-2 The kinetics of nuclear decay

Carbon dating: A method of determining the age of specimen containing carbon by comparing the ratio of $^{14}_{6}C$ to $^{12}_{6}C$ in the specimen to that found in the present environment.

Radiochemical dating: A method of determining the age of samples by comparing the amount of some radioactive isotope in the sample to the amount of that isotope found in a sample of known age and using first-order kinetics to determine the time needed to account for the difference in amounts of isotope.

Uranium dating: A method for dating geologic samples by calculating the time necessary to produce the lead content of the sample assuming the lead is formed by the natural decay sequence starting with uranium.

24-3 Nuclear reactions

Artificial radioactivity: Radioactivity from a nuclide which was produced by a nuclear bombardment process. Same as induced radioactivity.

Compound nucleus: A very unstable nucleus formed by nuclear bombardment.

Cyclotron: A device for accelerating charged subatomic particles to very high velocities using high-frequency alternating electrical fields in an evacuated circular chamber. The high-velocity particles are directed at some target.

Dee: One–half of a cyclotron.

Deuteron: The nucleus of a $^{2}_{1}H$ atom.

Induced radioactivity: Same as artificial radioactivity.

Linear accelerator: A device for accelerating charged particles along a linear path by exerting an electrical force on the particle as it travels on the linear path.

Neutron emission: Radioactive decay in which a neutron is emitted from the nucleus of the decaying atom.

Nuclear bombardment: A process of converting an isotope into a different element by the impact of a high-energy particle. The particle is absorbed by a nucleus which becomes unstable in the process.

Positron: $^{0}_{1}e^{+}$. A particle with the same mass as an electron but carries a unit positive charge.

Positron emission: Radioactive decay resulting in the emission of a positron from the nucleus of the decaying atom.

Synchroton: A device for accelerating charged particles to very high velocities by means of a combination of a high-frequency electric field and a low-frequency magnetic field.

Transmutation: The conversion of atoms of one element into atoms of a different element. Transmutation is accomplished by nuclear bombardment.

Transuranium element: An element with an atomic number greater than 92 (uranium).

24-4 Nuclear stability:

Belt of stability: The range of stable nuclei on a plot of neutron-to-proton ratio for all isotopes of the elements.

Induced nuclear fission: The absorption of a thermal neutron by certain transuranium atoms with the resulting splitting into two fragments plus excess neutrons.

Spontaneous nuclear fission: A mode of radioactive decay in which certain transuranium nuclides split into two fragments plus excess neutrons.

Thermal neutron: An emitted neutron which has lost much of its kinetic energy.

24-5 Fission, fusion, and nuclear binding energy

Chain reaction: A series of nuclear fission reactions in which the neutrons emitted by one fission initiate the fission of additional nuclei in a very rapid stepwise process.

Critical mass: The mass of a radioactive nuclide necessary to just sustain a chain reaction.

Fusion reaction: The combining of two low atomic mass nuclides into a heavier nuclide accompanied by a release of energy. Same as nuclear fusion.

Nuclear binding energy: The energy released if a nucleus were formed from its component protons and neutrons.

Nuclear explosion: The rapid fission of many nuclei and the resulting release of a very large quantity of energy.

Nuclear fusion: Same as fusion reaction.

Nuclear reactor: A device for carrying out controlled nuclear fission and converting the energy produced to useful work or electricity.

24-6 Chemical applications of radioactivity

Isotope dilution analysis: Determination of the distribution of a radioactive tracer between two parts of a system as an aid in analyzing the chemical distribution of similar nonradioactive species.

Neutron activation analysis: A sensitive technique for chemical analysis in which a sample receives neutron bombardment followed by analysis of the radioactive isotopes formed during the bombardment.

Neutron diffraction: The scattering of neutrons by atomic nuclei. Useful for determining the position of very low atomic mass nuclei such as hydrogen in crystal structures.

Radioactive tracer: A chemical containing a radioactive atom enabling the tracking of a complex reaction by measuring the radiation from the tracer.

SELF TEST

True or False

_____ 1. Radioactivity is the spontaneous emission of radiation from the nucleus of an atom.

_____ 2. Lead-210 decays to bismuth-210 by alpha emission.

_____ 3. Beta emission leaves the mass number of a nucleus unchanged.

_____ 4. An alpha particle is essentially a fast-moving helium nucleus.

_____ 5. All nuclear processes follow first-order kinetics.

_____ 6. Half-life is a measure of the stability of a nuclide.

_____ 7. The ratio of carbon to uranium can be used to determine the age of ancient relics.

_____ 8. Transuranium elements can be produced only by bombardment techniques.

_____ 9. Nuclei that lie below the belt of stability undergo beta decay.

_____10. The most common method of decay for nuclei that have a high neutron to proton ratio is neutron emission.

_____11. Nuclei with more than 83 protons are unstable no matter how many neutrons are present.

_____12. Binding energy is a measure of the stability of a nucleus.

_____13. The fission of uranium-235 can give a chain reaction to produce a nuclear explosion or can power a nuclear reactor.

_____14. Nuclear fusion offers an essentially unlimited supply of energy.

_____15. Radioactive isotopes are too dangerous to be of much use in chemical research.

Completion

16. The three most common types of radioactive emissions are ____________________, ____________________, and ____________________.

17. ____________________ emissions are usually not shown in nuclear equations since both the ______________ and the ______________ of the radioactive nuclide remain constant.

18. ________________ counters and ______________ counters are used to detect radioactivity.

19. The ordered sequence of natural decay of unstable nuclei is called a ______________.

20. The rate constant for the decay of Sn-110 is 0.173 hr^{-1}; its half-life is ____________.

21. Uranium dating is based on a measurement of the ______________ ratio.

22. Radioactivity of nuclei formed by bombardment techniques is called ______________.

23. A positron is a particle which has the same ________________ as an electron but has a ________________ charge.

24. When the number of neutrons is plotted against the number of protons for nonradioactive nuclei a region called the ____________________ is formed.

25. The neutron to proton ratio is approximately ________________ for light nuclei and gradually ______________ (increases, decreases) for heavier nuclei.

26. Beta decay _____________ (increases, decreases) the atomic number and ________ (increases, decreases) the neutron to proton ratio.

27. _____________ can be induced when a $^{235}_{92}$U nucleus captures a ______________.

28. The difference between the mass of a nucleus and the mass of __________________ and __________________ that are contained in the nucleus is the ____________. The energy equivalence of this mass difference is called the __________________.

29. Nuclei which are __________ (low, high, intermediate) in atomic number have high binding energies and therefore are _________ (more, less) stable.

30. The quantity of fissionable material capable of sustaining a chain reaction is called a ____________________.

Multiple Choice

31. Which of the following isotopes results form the beta decay of $^{234}_{90}Th$?
(a) $^{234}_{91}Pa$ (b) $^{234}_{89}Ac$ (c) $^{235}_{90}Th$ (d) $^{233}_{90}Th$

32. Which of the following nuclear equations is not balanced correctly?
(a) $^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$
(b) $^{76}_{36}Kr + ^{0}_{-1}e^{-} \rightarrow ^{76}_{35}Br$
(c) $^{209}_{83}Bi + ^{2}_{1}H \rightarrow ^{210}_{84}Po + ^{1}_{0}n$
(d) $^{30}_{14}Si \rightarrow ^{30}_{15}P + ^{0}_{1}e^{+}$

33. The type of decay involved when $^{65}_{35}Br$ decays into $^{65}_{34}Se$ is
(a) alpha decay (b) beta decay (c) positron decay
(d) neutron emission

34. The natural radioactive decay series for $^{226}_{88}Ra$ is by successive emission of five alpha particles and four beta particles. At the end of this series the nucleus has mass and atomic numbers of
(a) 216, 79 (b) 206, 72 (c) 210, 83 (d) 206, 82

35. The half-life of cobalt-60 is 5.0 years. How much of a 1.00-gram sample of this nuclide will remain after 7 years?
(a) 0.0063 g (b) 0.286 g (c) 0.378 g (d) 0.422 g

36. A scroll of parchment is claimed to be a Dead Sea Scroll, but archaeologists suspect it is not authentic. Radiocarbon data shows the parchment to have a $^{14}_{6}C/^{12}_{6}C$ ratio of 0.950. How old is the parchment?
(a) 420 yr. (b) 1890 yr. (c) 8110 yr. (d) 24,500 yr.

37. When a nucleus undergoes alpha decay the mass number
(a) does not change (b) decreases by one
(c) decreases by two (d) decreases by four

38. When a nucleus undergoes neutron emission it
(a) does not change atomic number
(b) increases its atomic number by one
(c) decreases its atomic number of one
(d) splits into different fragments

39. Nuclei with neutron to proton ratios lying above the belt of stability undergo
(a) alpha decay (b) beta decay
(c) positron emission (d) electron capture

40. Nuclei with neutron to proton ratios lying below the belt of stability undergo
(a) alpha decay (b) beta decay
(c) neutron emission (d) positron emission

41. What is the loss in mass during the formation of a $^{12}_{6}C$ nucleus? (Mass of $^{12}_{6}C$ is 11.99671 amu, mass of neutron is 1.00867 amu, and mass of a proton is 1.00728 amu.)
(a) 0.00834 amu (b) 0.09899 amu
(c) 1.643×10^{-22} kg (d) none of the above

42. What is the binding energy of a $^{12}_{6}C$ nucleus? (Use the data in problem 41, the speed of light is 2.998×10^{8} ms^{-1}.)
(a) 1.231×10^{-12} J nucleon^{-1} (b) 1.037×10^{-13} J nucleon^{-1}
(c) 4.926×10^{-20} J nucleon^{-1} (d) 4.151×10^{-21} J nucleon^{-1}

43. An advantage of uranium dating for minerals over carbon dating is
(a) it is more accurate (b) it is faster
(c) it can be used for older objects (d) it is less expensive

44. The process which produces energy in the sun is
(a) nuclear fission (b) nuclear fusion
(c) radioactive decay (d) nuclear bombardment

45. Small amounts of radioactive isotopes used for following changes in many kinds of processes are known as
(a) exchangers (b) scintillators (c) tracers (d) counters

ANSWERS TO SELF TESTS

CHAPTER 1
PRELIMINARIES AND PREMISES

1 True: This is the first step in the scientific method.
2 False: Science terms often have several meanings. Some may be quite ambiguous. It takes considerable effort to learn the meanings of these terms.
3 True: This will soon become apparent.
4 True
5 False: Na and Cl are chemical symbols for sodium and chlorine. NaCl is the chemical formula for sodium chloride.
6 True: This is the law of conservation of mass.
7 False: Heat is energy in transit.
8 True
9 True
10 True: This is the law of constant composition.
11 False: The SI unit for volume is cubic meter.
12 True: Not the conventional units, but still a measure of mass per unit volume.
13 True
14 False: Units must be consistent when applying unit factors. Grams cannot be converted to grams volume^{-1}.
15 False: There are four significant figures in 45.70.
16 hypothesis
17 scientific law
18 homogeneous
19 homogeneous
20 compound
21 work
22 heat
23 joule
24 potential energy
25 kinetic energy
26 3.70×10^{-4}
27 4.0×10^{-10}
28 $1\ \text{L}/10^3\ \text{mL}$
29 $10^3\ \text{g}/1\ \text{kg}$
30 kilogram
31 (c)
32 (d) Combustion of natural gas is a chemical change.
33 (c) The sugar simply dissolves, it does not change its chemical composition.
34 (d) Kinetic energy is energy of motion.
35 (c)
36 (d)
37 (d) 65.8 This number has the correct number of significant figures and the correct round-off. The answer is in kilograms.

$$145\ \text{lb} \times \frac{454\ \text{g}}{1\ \text{lb}} \times \frac{1\ \text{kg}}{1000\text{g}} = 65.8\ \text{kg}$$

38 (a) $$1\ \text{mi} \times \frac{5280\ \text{ft}}{1\ \text{mi}} \times \frac{12\ \text{in}}{1\ \text{ft}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{1\ \text{m}}{100\ \text{cm}} \times \frac{1\ \text{km}}{1000\text{m}} = 1.61\ \text{km}$$

39 (c) $\frac{55\ \text{mi}}{1\ \text{hr}} \times \frac{1.61\ \text{km}}{1\ \text{mi}} = 88\ \text{km hr}^{-1}$

40 (d)

41 (c) volume $= 55.0\ \text{g} \times \frac{1\ \text{cm}^3}{7.86\ \text{g}} = 7.00\ \text{cm}^3$

42 (c) $\%\ \text{sodium} = \frac{\text{g sodium}}{\text{g sodium chloride}} \times 100 - \frac{23.0}{58.4} \times 100 = 39.4\%$

43 (a) $50.0\ \text{g sulfur} \times \frac{60.0\ \text{g oxygen}}{40.0\ \text{g sulfur}} = 75.0\ \text{g oxygen}$

44 (c) $^\circ\text{C} = \frac{5}{9}(^\circ\text{F} - 32) = \frac{5}{9}(72 - 32) = 22^\circ\text{C}$

45 (d) $4.7\ \text{g hydrogen} \times \frac{88.9\ \text{g oxygen}}{11.1\ \text{g hydrogen}} = 37.6\ \text{g oxygen}$

CHAPTER 2
FORMULAS, EQUATIONS, AND STOICHIOMETRY

1 True
2 True: It also signifies the mass contained in Avogadro's number of particles of a substance.
3 True
4 False: The number of moles of individual elements in the reactants must equal the number of moles of that element in the products. This relation does not ordinarily hold for total moles of reactants compared to total moles of products.
5 False: There are two atoms of oxygen in each molecule of oxygen.
6 True
7 False: There are 8 mol of oxygen atoms in 1 mol of $Ba_3(PO_4)_2$.
8 True: Although only in a two-dimensional sense.
9 False: There are 12 mol of oxygen atoms in 2 mol of $Ba(NO_3)_2$.
10 False: The correct name for Na_2S is sodium sulfide.
11 True
12 False: The correct name is magnesium chloride.
13 False: The correct name is potassium nitrate.
14 False: One mole of H_2 contains 6.02×10^{23} hydrogen molecules or $2(6.02 \times 10^{23})$ hydrogen atoms.
15 True
16 9.9×10^{23} atoms

$$28\ \text{g NH}_3 \times \frac{1\ \text{mol N}}{17.0\ \text{g NH}_3} \times \frac{6.02 \times 10^{23}\ \text{N atoms}}{1\ \text{mol N}} = 9.9 \times 10^{23}\ \text{N atoms}$$

17 0.50 mol $14\ \text{g N}_2 \times \frac{1\ \text{mol N}_2}{28.0\ \text{g N}_2} = 0.50\ \text{mol N}_2$

18 $342\ \text{g mol}^{-1}$

19 22.0 g

$$3.01 \times 10^{23} \text{ molecules } CO_2 \times \frac{1 \text{ mol } CO_2}{6.02 \times 10^{23} \text{ molecules } CO_2} \times \frac{44.0 \text{ g } CO_2}{1 \text{ mol } CO_2} = 22.0 \text{ g } CO_2$$

20 224 g $3.00 \text{ mol KCl} \times \frac{74.5 \text{ g KCl}}{1 \text{ mol KCl}} = 224 \text{ g KCl}$

21 371 g

$$3.00 \times 10^{22} \text{ molecules KCl} \times \frac{1 \text{ mol KCl}}{6.02 \times 10^{23} \text{ molecules KCl}} \times \frac{74.5 \text{ g KCl}}{1 \text{ mol KCl}} = 371 \text{ g KCl}$$

22 0.0869 mol

$$8.34 \text{ g S} \times \frac{1 \text{ mol S}}{32.0 \text{ g S}} \times \frac{1 \text{ mol } Al_2(SO_4)_3}{3 \text{ mol S}} = 0.0869 \text{ mol } Al_2(SO_4)_3$$

23 29.0% Basis for calculation: 1 mol K_2S

$$\% \text{ S} = \frac{32.0 \text{ g S}}{(32.0 + 78.2) \text{ g } K_2S} \times 100 = 29.0\% \text{ S}$$

24 98.0 g mol^{-1}
25 limiting reagent
26 solvent, solute
27 neutralization
28 lithium phosphide
29 calcium phosphate
30 ClF_3
31 (c) Hydrogen does not exist as molecules in H_2O.
32 (c)
33 (c)
34 (a) Basis for calculation: 1 mol SO_2

$$\% \text{ S} = \frac{32.0 \text{ g S}}{(32.0 + 32.0) \text{ g } SO_2} \times 100 = 50.0\% \text{ } SO_2$$

35 (c) $Ca(OH)_2 + 2\,HNO_3 \rightarrow Ca(NO_3)_2 + 2\,H_2O$

$$\text{mol } HNO_3 = \frac{0.250 \text{ mol } HNO_3}{1 \text{ L}} \times 0.030 \text{ L} = 7.5 \times 10^{-3} \text{ mol } HNO_3$$

$$\text{mol } Ca(OH)_2 = 7.5 \times 10^{-3} \text{ mol } HNO_3 \times \frac{1 \text{ mol } Ca(OH)_2}{2 \text{ mol } HNO_3} = 3.75 \times 10^{-3} \text{ mol } Ca(OH)_2$$

$$\text{Vol } Ca(OH)_2 = \frac{\text{mol } Ca(OH)_2}{\text{M } Ca(OH)_2} = \frac{3.75 \times 10^{-3} \text{ mol}}{0.100 \text{ mol L}^{-1}} = 3.75 \times 10^{-2} \text{ L}$$

36 (a)

$$10 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2} \times \frac{2 \text{ mol O}}{1 \text{ mol } CO_2} \times \frac{6.02 \times 10^{23} \text{ atoms O}}{1 \text{ mol O}} = 2.7 \times 10^{23} \text{ atoms O}$$

37 (c)
38 (d) Atomic masses of X and Y are needed to determine the empirical formula.

39 (c) $M = \frac{1.00 \text{ mol}}{0.100 \text{ L}} = 10.0 \text{ mol L}^{-1}$

40 (d) $M = \dfrac{24\text{ g NaOH}/40.0\text{ g mol}^{-1}}{0.400\text{ L}} = 1.5\text{ mol L}^{-1}$

41 (b) Solution A: $M_A = \dfrac{20.0\text{ g NaOH}/40.0\text{ g mol}^{-1}}{0.500\text{ L}} = 1.00\text{ mol L}^{-1}$

Solution B: $M_B = \dfrac{M_A V_A}{V_B} = 1.00\,M \times \dfrac{100\text{ mL}}{200\text{ mL}} = 0.500\text{ mol L}^{-1}$

42 (d)
43 (c)

44 (d) Basis for calculation: 100 g of compound

$$\text{mol Mn} = \frac{49.08\text{ g Mn}}{54.94\text{ g Mn mol}^{-1}} = 0.8933\text{ mol Mn}$$

$$\text{mol F} = \frac{50.92}{19.00} = 2.68$$

$$\frac{2.68\text{ mol F}}{0.8933\text{ mol Mn}} = 3.000\text{ mol F per mol Mn}$$

The empirical formula is MnF_3

45 (c) $\text{mol NaCl} = \dfrac{3.54\text{ g}}{58.4\text{ g mol}^{-1}} = 0.0606\text{ mol}$

$$M = \frac{0.0606\text{ mol}}{0.500\text{ L}} = 0.121\text{ M}$$

CHAPTER 3
THERMOCHEMISTRY

1 True
2 True: This is the first law of thermodynamics.
3 False: Specific heat is always per gram or per mole; heat capacity may refer to any given amount of mass.
4 True
5 True: Heat and work depend on the path by which a process occurs.
6 True
7 True
8 True
9 False: $\Delta E = q + w = -2.00\text{ J} + (-1.7\text{ J}) = -3.7\text{ J}$
10 True
11 True
12 True
13 True
14 False: The comparison should be made using heats of combustion per gram.
15 True
16 positive
17 volume
18 constant pressure
19 negative
20 ΔH
21 both
22 $\Delta E = q + w$
23 $\text{J mol}^{-1}\,{}^{\circ}\text{C}^{-1}$
24 calorimeter
25 thermochemical equation
26 its elements in their standard state

27 zero

28 ΔE

29 The enthalpy of reaction depends only on the chemical nature of the reactants and products and is independent of the path or number of steps in the reaction.

30 $\Delta H^{o}_{Rxn} = \sum (\Delta H^{o}_{f})_{\text{products}} - \sum (\Delta H^{o}_{f})_{\text{reactants}}$

31 (b)

32 (a)

33 (c) $q = nC\Delta t = \dfrac{50\ \text{g}}{18\ \text{g mol}^{-1}} \times 75.3\ \text{J mol}^{-1}\ °\text{C}^{-1} \times 10°\text{C} = 2090\ \text{J}$

34 (d) $q_{Rxn} = -\left[75.3\ \text{J mol}^{-1}\ °\text{C}^{-1}\left(\dfrac{1020\ \text{g}}{18\ \text{g mol}^{-1}}\right) + 1163\ \text{J}\ °\text{C}\right] 5.32°\text{C}$

$= -28.9\ \text{kJ}$

molar $q_{Rxn} = \dfrac{-28.9\ \text{kJ}}{0.500\ \text{g}/16\ \text{g mol}^{-1}} = -925\ \text{kJ mol}^{-1}$

35 (c) $q = nC\Delta t = 20\ \text{g} \times 4.18\ \text{J g}^{-1}\ °\text{C}^{-1} \times 10°\text{C} = 836\ \text{J}$

36 (d) $4\ PCl_3(g) \rightarrow P_4(s) + 6\ Cl_2(g)$ $\quad \Delta H = +1084\ \text{kJ}$

$\underline{P_4(s) + 10\ Cl_2(g) \rightarrow 4\ PCl_5(g)}$ $\quad \Delta H = -1528\ \text{kJ}$

$4\ PCl_3(g) + 4\ Cl_2(g) \rightarrow 4\ PCl_5(g)$ $\quad \Delta H = -444\ \text{kJ}$

$PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ $\quad \Delta H = -111\ \text{kJ}$

37 (a) $2[C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)]$ $\quad \Delta H^{o} = 2(131.3)\text{kJ}$

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ $\quad \Delta H^{o} = -41.2\ \text{kJ}$

$\underline{CO(g) + 3\ H_2(g) \rightarrow CH_4(g) + H_2O(g)}$ $\quad \Delta H^{o} = -206.1\ \text{kJ})$

$2\ C(s) + 2\ H_2O(g) \rightarrow CH_4(g) + CO_2(g)$ $\quad \Delta H^{o} = 15.3\ \text{kJ}$

38 (b)

39 (a) and (b)

40 (c) Since the water absorbs its molar heat of vaporization during this process, $q = 40.7\ \text{kJ mol}^{-1}$. Work involved in expanding the vapor against the atmosphere is

$w = -P\ \Delta V = -P\ (V_{vapor} - V_{liquid}) \cong -P\ V_{vapor}$

$V_{vapor} = \dfrac{nRT}{P} = \dfrac{1.00\ \text{mol}(0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1})(373\ \text{K})}{1\ \text{atm}} = 30.6\ \text{L}$

$w = -1.00\ \text{atm}(30.6\ \text{L}) \times 101.2\ \text{J (L atm)}^{-1} = -3100\ \text{J}$

$\Delta E = q + w = 40.7\ \text{kJ} - 3.1\ \text{kJ} = 37.6\ \text{kJ}$

41 (a) The formation reaction for SO_3 is

$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$

This can be obtained from the given equations by algebraically adding them as follows:

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\quad \Delta H = -296.8\ \text{kJ mol}^{-1}$

$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$ $\quad \Delta H = -98.9\ \text{kJ mol}^{-1}$

$S(s) + SO_2(g) + \frac{3}{2}O_2(g) \rightarrow SO_2(g) + SO_3(g)$ $\quad \Delta H = -395.7\ \text{kJ mol}^{-1}$

The net result is $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$. Hess's law says that adding the ΔH's of the given reactions in the same manner as the reactions themselves will give ΔH for the net reaction.

42 (a) $$\begin{aligned}\Delta H^{\circ}_{\text{reaction}} &= \Sigma(\Delta H^{\circ}_{f})_{\text{products}} - \Sigma(\Delta H^{\circ}_{f})_{\text{reactants}}\\ &= [2(\Delta H^{\circ}_{f})_{CO_2} + 2(\Delta H^{\circ}_{f})_{H_2O}] - [(\Delta H^{\circ}_{f})_{C_2H_4} + 3(\Delta H^{\circ}_{f})_{O_2}]\\ &= [2(-393.5\ \text{kJ}) + 2(-285.8\ \text{kJ})] - [52.3\ \text{kJ} + 3(0\ \text{kJ})]\\ &= -1359\ \text{kJ} - 52.3\ \text{kJ} = -1411\ \text{kJ}\end{aligned}$$

If your answer was (c) or (d) you forget to multiply the standard enthalpies of formation by the number of moles of each component indicated by the stoichiometric coefficients. Be sure you keep the signs straight.

43 (d)
44 (d)
45 (d) $C = \dfrac{q}{n\Delta t} = \dfrac{1.400\ \text{J}}{\dfrac{2.00\ \text{g}}{200.6\ \text{g mol}^{-1}} \times 2.00^{\circ}\text{C}} = 70.2\ \text{J mol}^{-1}\ {}^{\circ}\text{C}^{-1}$

CHAPTER 4
GASES

1 False: PV = constant only if the temperature remains unchanged.
2 False: The number of molecules or moles does not change as the pressure changes.
3 True: This is Charles' law.
4 True
5 True
6 True: From Dalton's law.
7 True: Gay-Lussac's law of combining volumes.
8 True: Graham's law says the gas with the lower molecular mass diffuses faster.
9 True
10 False: The total pressure is the sum of the partial pressures.
11 False: $P_{\text{final}} = 2.0\ \text{atm} \times \dfrac{473\ \text{K}}{373\ \text{K}} = 2.5\ \text{atm}$
12 False: Pressure is inversely proportional to volume.
13 False: Moles per liter is the same for all ideal gases but grams per liter depends on the molecular mass.
14 True
15 True for real gases. Ideal gases maintain constant temperature during free expansion.
16 $PV = nRT$
17 unit area
18 kelvin
19 increases
20 decreases
21 less
22 partial pressure
23 molar masses or densities
24 0.0821 L atm mol^{-1} K^{-1}
25 molar mass $= \dfrac{32.0\ \text{g}}{11.2\ \text{L}} \times \dfrac{22.4\ \text{L}}{1\ \text{mol}} = 64\ \text{g mol}^{-1}$
26 transition
27 helium
28 effusion
29 diffusion
30 $4.00\ \text{L} \times \dfrac{353\ \text{K}}{273\ \text{K}} = 5.17\ \text{L}$
31 (b) $8.0\ \text{L} \times \dfrac{60\ \text{kPa}}{80\ \text{kPa}} = 6.0\ \text{L}$

32 (d) $8.0 \text{ L} \times \frac{546 \text{ K}}{273 \text{ K}} = 16 \text{ L}$

33 (c) The gas increases in temperature; therefore the volume will increase and the temperature ratio must be greater than 1 and expressed in kelvins, 423/373. The gas decreases in pressure; therefore the volume will increase and the pressure ratio must be greater than 1, 90/50.

34 (b) Final volume changes by 1/2 for pressure change and by 4 for temperature change. Net change is 1/2 x 4 = 2 times the original volume.

35 (a) The temperature and mass of gas do not change, but the volume increases by a factor of 2 because of the pressure change. Since density = mass per unit volume, the density must decrease by a factor of 2 as the volume increases.

36 (c) $\text{Density at STP} = \frac{\text{molecular mass in g mol}^{-1}}{22.4 \text{ L mol}^{-1}} = \text{g L}^{-1}$

37 (a) $\text{mol } H_2 = 1000 \text{ kg } NH_3 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } NH_3}{17.0 \text{ g } NH_3} \times \frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3}$

$= 8.82 \times 10^4 \text{ mol } H_2$

$\text{liters } H_2 = 8.82 \times 10^4 \text{ mol } H_2 \times 22.4 \text{ L mol}^{-1} = 1.98 \times 10^6 \text{ L}$

38 (b)

39 (c) Density is directly proportional to molar mass for gases.

40 (c)

41 (b)

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

$$P = \frac{2.00 \text{ mol } (0.082 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.00 \text{ L} - (2.00 \text{ mol})(0.0371 \text{ L mol}^{-1})} - \frac{(2.00 \text{ mol})^2(4.17 \text{ L}^2 \text{ atm mol}^{-2})}{(1.00 \text{ L})^2}$$

$= 36.1 \text{ atm}$

43 (b) The densities of the possible gases at STP are:

H_2: $\frac{2 \text{ g mol}^{-1}}{22.4 \text{ L mol}^{-1}} = 0.089 \text{ g L}^{-1}$ O_2: $\frac{32 \text{ g mol}^{-1}}{22.4 \text{ L mol}^{-1}} = 1.43 \text{ g L}^{-1}$

CH_4: $\frac{16 \text{ g mol}^{-1}}{22.4 \text{ L mol}^{-1}} = 0.714 \text{ g L}^{-1}$ SO_2: $\frac{64 \text{ g mol}^{-1}}{22.4 \text{ L mol}^{-1}} = 2.86 \text{ g L}^{-1}$

O_2 has the same density as the unidentified gas and is the best choice.

44 (b) Using Graham's law of effusion

$$\frac{\text{Rate}_{\text{He}}}{\text{Rate}_{\text{g}}} = \frac{\sqrt{MM_g}}{\sqrt{MM_{\text{He}}}}$$

Since the rate for He is 2 times the rate of the unidentified gas

$$\frac{2}{1} = \frac{\sqrt{MM_g}}{\sqrt{4}}$$

$$\sqrt{MM_g} = 2 \times 2 = 4$$

$$MM_g = 16 \text{ g mol}^{-1}$$

The molecular mass is close to that of CH_4

45 (b) The balanced equation is

$$CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(g)}$$

Since the gases are measured under the same conditions

$$L\ O_2 = 10\ L\ CH_4 \times \frac{2\ L\ O_2}{1\ L\ CH_4} = 20\ L\ O_2$$

CHAPTER 5
THE ATOM

1 False: Dalton proposed that different elements have different properties because their atoms are different.
2 True: This shows that electrons carry a negative charge.
3 True
4 True: Removal of an electron leaves an excess of positive charge on the atom.
5 True
6 True
7 False: The number of protons plus neutrons.
8 False: There are 24 protons and 28 neutrons.
9 False: Isotopes of a given element differ in mass.
10 True
11 True
12 False: It has 62 neutrons and 48 protons.
13 True
14 True
15 False: The correlation is good only for the hydrogen atom.
16 electrons
17 negative
18 nucleus, electrons
19 atomic
20 proton, neutron, electron
21 neutrons
22 number, isotopes
23 mass number
24 mass spectrometry
25 cycles per second
26 quantized
27 the speed of light, $3.0 \times 10^8\ ms^{-1}$ in a vacuum
28 continuous
29 Bohr atom
30 line
31 (d) This idea came from Rutherford.
32 (c)
33 (c) Thomson measured the charge to mass ratio of an electron.
34 (d)
35 (a)
36 (a)
37 (b) Both the stationary electron and the orbiting electron would collapse into the nucleus according to classical physics.
38 (a) 27.185 megahertz = 2.7185×10^7 hertz

$$\lambda = \frac{c}{\upsilon} = \frac{3.00 \times 10^8\ m\ sec^{-1}}{2.7185 \times 10^7\ sec^{-1}}$$

$$\lambda = 11.0\ m$$

39 (d) ^{14}N has mass number = 14, which is the highest.
40 (a) ^{28}Si and ^{29}P have 14 neutrons each.
41 (b) Both have 6 neutrons.
42 (c) ^{10}B and ^{11}B are isotopes of boron.
43 (a) The atomic number of beryllium is 4, so it has 4 protons in its nucleus and a total nuclear charge of +4.

44 (b) There is 93.0% ^{39}K and 7.0% ^{41}K. The atomic mass of K is the sum of the contributions of ^{39}K and ^{41}K.

Contribution of ^{39}K = 0.930 (38.96) = 36.2
Contribution of ^{41}K = 0.070 (40.96) = 2.87
Total mass of K = 39.1
Atomic mass of K = 39.1

45 (d) The Rydberg equation is used to calculate the wavelength.

$$\frac{1}{\lambda} = 1.10 \times 10^{-2}\ \text{nm}^{-1}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

$$\frac{1}{\lambda} = 1.10 \times 10^{-2}\ \text{nm}^{-1}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$= 11.10 \times 10^{-2}\ \text{nm}^{-1}\ (0.250 - 0.0625) = 2.06 \times 10^{-3}\ \text{nm}^{-1}$$

$$\lambda = \frac{1}{2.06 \times 10^{-3}}\ \text{nm} = 485\ \text{nm}$$

CHAPTER 6
ELECTRONS

1 False: Read the first page of the text chapter again if you missed this question.
2 True: Two electrons are the maximum allowed in any orbital.
3 False: Paired electrons have antiparallel spins.
4 False: The energy of sublevels can shift depending on the number of electrons present. Half-filled or filled *f* subshells can alter the order of filling. See Table 6-1 in the text, especially elements Cr, Nb, Pd, and Gd.
5 True: See Fig. 6-9 in the text.
6 True: There are one 3*s*, three 3*p*, and five 3*d* orbitals in the third energy level, for a total of nine orbitals. Each orbital holds two electrons.
7 True: Each contains 5 orbitals.
8 True
9 True
10 True
11 True
12 False: See Figures 6-4 or 6-5 in the text. The lower-energy 4*s* orbital fills before the higher-energy 3*d* orbitals
13 True: $m_l = -l \ldots 0 \ldots +l$
14 False: The *d* sublevel has 5 orbitals.
15 True
16 0.121 nm

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{kg m s}^{-1}}{9.11 \times 10^{31}\ \text{kg}\ (6.00 \times 10^{6}\ \text{ms}^{-1})} = 1.21 \times 10^{-10}\ \text{m}$$

or 0.121 nm
17 lead (Pb)
18 4, 16. (Subshells are 4*s*, 4*p*, 4*d*, and 4*f*. There are one 4*s*, three 4*p*, five 4*d*, and seven 4*f* orbitals.)
19 magnetic
20 2, 2, 2, 2
21 $1s^22s^22p^63s^23p^63d^24s^2$ or $[\text{Ar}]3d^24s^2$
22 4 (Minimum value of *l* is 3, so $n - 1 = 3$ or $n = 4$ is the minimum value of *n*)
23 5
24 3
25 2, 4
26 probability

27 13 ($n = 3$ designates the third shell, $l = 1$ designates a p orbital; $m_l = -1$ designates the first p orbital; and $m_s = -\frac{1}{2}$ designates the first electron in the orbital, so the last electron was $3p_x$.)
28 Spins
29 one (See Table 6-4 in the text)
30 seven. ($l = 3$ refers to f orbitals)
31 (d) $2n^2 = 2(5)^2 = 50$
32 (d) Cr has five $3d$ and one $4s$ electrons that are unpaired.
33 (b) Aufbau filling order is $4s$, then $3d$.
34 (c)
35 (d)
36 (d)
37 (d)
38 (c) In the Aufbau procedure the $5s$ subshell fills first.
39 (c) For $l = 2$, the possible values of m_l are –2, –1, 0, 1, and 2, for a total of five values.
40 (c) One electron in $4s$ and three electrons in $3d$ is not a ground-state configuration. Answer (d) contains a half-filled $3d$ subshell, so the filling order is altered. This is the configuration of ${}_{24}\text{Cr}$.
41 (a) The mass of a proton in SI units is

$$m = 1 \text{ amu} \times \frac{1 \text{ g}}{6.02 \times 10^{23} \text{ amu}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 1.66 \times 10^{-27} \text{ kg}$$

The velocity of the proton is

$$v = 3.00 \times \frac{10^8 \text{ m s}^{-1}}{1000} = 3.00 \times 10^5 \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{1.66 \times 10^{-27} \text{ kg } (3.00 \times 10^5 \text{ m s}^{-1})} = 1.33 \times 10^{-12} \text{ m}$$

42 (a)
43 (c) For element 18, the last electron is the sixth electron in the $3p$ subshell. For the $3p$ subshell $n = 3$ and $l = 1$. The sixth electron in the subshell would have $m_l = -1$ and $m_s = -\frac{1}{2}$. See Table 6-4 and add one more electron)
44 (c) In answers (b) and (d) l has an unallowed value, in answer (a) the value of m_l is not allowed.
45 (b) The last electron in Ga is in a $4p$ orbital so $n = 4$, $l = 1$.

CHAPTER 7
CHEMICAL PERIODICITY

1 True
2 True
3 False: The atomic radius increases from top to bottom in a group.
4 False: Both chemical and physical properties follow the periodic law.
5 True
6 False: Group IA elements are the alkali metals, group IIA are the alkaline-earth elements.
7 True
8 True
9 True
10 False: Horizontal rows on the periodic table are periods.
11 True
12 False: Iron(III) chloride or ferric chloride.
13 True

14 True
15 False: Gallium is a metal.
16 groups or columns
17 electron affinity
18 transition metals
19 less
20 smaller
21 group number
22 cerium
23 metalloids or semimetals
24 one
25 seven
26 three or four
27 lanthanide and actinide
28 lanthanides and actinides
29 copper(I) fluoride or cuprous fluoride
30 $Mg(OH)_2 \rightarrow Mg^{2+} + 2\,OH^-$
31 (b)
32 (c)
33 (c) Atoms are largest at the left of a given period and sizes increase going down a group.
34 (b) Ionization energy is highest at the left of a given period and at the top of a group.
35 (d)
36 (b) Electron affinity shows the same trend as ionization energy in question 34.
37 (c)
38 (c)
39 (d)
40 (d)
41 (a) Mg is in the same group.
42 (c)
43 (c) Electron affinity is highest in the upper left corner of the periodic table, except for the noble gases, which have a completed valence shell.
44 (c)
45 (c)

CHAPTER 8
CHEMICAL BONDING

1 False: Atoms tend to achieve completed *s* and *p* orbitals in the outside shell.
2 False: Covalent bonds often have polar character from unequal sharing of the electron pair.
3 False: Metals such as sodium lose electrons to form positive ions.
4 True
5 False: Al_2S_3
6 True
7 True
8 False: Lewis structures for ionic compounds are represented as
$2\,Na^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:^{2-}$
9 False: The symmetrical structure of the molecule cancels any polar effect of the Si—H bond
10 False: They occupy orbitals of one atom only and are not engaged in bonding.
11 True

12 False: (See Prob. 8-16 in the text) Electron affinity is the energy released when an isolated atom gains another electron. Electronegativity is the tendency of a bonded atom to gain another electron.
13 True
14 True
15 True
16 Al → $Al^{3+} + 3\,e^-$ Aluminum is in group IIIA, so it loses three electrons.
17 X_3Y_2 X has +2 charge, Y has –3 charge.
18 six
19 $[\mathrm{Mg}]^{2+} + 2[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^-$
20 $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}-\overset{\cdot\cdot}{\underset{|}{\mathrm{N}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$

$:\underset{\cdot\cdot}{\mathrm{Cl}}:$

21 eight. Seven valence electrons from the chlorine atom plus one electron gained in the formation of the chloride ion.
22 $[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:]^{2-}$
23 electronegativity
24 ionic
25 covalent bond
26 polar covalent
27 sulfur: zero, (6 – 6 = 0), oxygen: –1, (6 – 7 = –1)
28 Rb < K < Na
29 trigonal pyramidal. NH_3 has a steric number of 4 and one lone pair of electrons. See Table 8-7 in the text.
30 upper right
31 (b)
32 (c)
33 (c) Do not forget the two electrons for the ionic charge.
34 (d) There are two double bonds.
35 (a)
36 (c) Cs and F have the greatest difference in electronegativity.
37 (b) S has four electrons as its share of four shared pairs. Formal charge = 6 – 4 = +2.
38 (c) Structure C obeys the octet rule, but the formal charge on oxygen is +2, which is not consistent with a group VIA element, so the structure is not allowed. Note also that oxygen has four bonds in structure C.
39 (d) NH_3 is the only one that has a plane dividing the center of positive and negative charge.
40 (d) Repulsion between bonding pairs is weak and can be neglected.
41 (d) SiH_4 is analogous to CH_4, H_2O is bent, NH_3 is pyramidal, and C_2H_2 is linear.
42 (d) The Lewis structure for 22 valence electrons is $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:\overset{\cdot\cdot\,\cdot}{\underset{\cdot\cdot}{\mathrm{Xe}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$
where Xe has 10 electrons in its valence shell. There are two bonding pairs and three nonbonding pairs on Xe, so the steric number is 5.
43 (c) There are eight total valence electrons so the Lewis structure is
$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Se}}}:\mathrm{H}$ giving two lone pairs on Se.
44 (d) Oxygen with single bond: Formal charge = 6 – 7 = –1, oxygen with double bond: Formal charge = 6 – 6 = 0.
45 (c) 12 electrons around Xe

CHAPTER 9
SOLIDS

1 True
2 True: One particle at each of eight corners belongs to eight different cells, so each cell has one net particle for the corners. There is also one particle in each of six faces that belongs to two unit cells, so each cell has three net particles in the faces. The total is four particles per cell.
3 True
4 True
5 False: Van der Waals forces are much weaker than electrostatic attractions in ionic bonds.
6 False: There are two atoms per unit cell in body-centered cubic structure.
7 False: Face-centered cubic (also called cubic close-packed) is the most densely packed type.
8 True: Perfect crystals are very difficult to grow.
9 True: Which means they also have high melting points.
10 True
11 True
12 True: That is why they are called tetrahedral holes.
13 True
14 True
15 False: This would make an n-type semiconductor.
16 amorphous solids or supercooled liquids
17 spacing of planes of atoms
18 unit cell
19 packing efficiency
20 ionic, molecular, covalent, and metallic
21 dipole-dipole forces and London or dispersion forces
22 poor
23 low
24 lattice defects
25 two
26 semiconductors
27 hexagonal close-packed, cubic close-packed or face-centered cubic
28 tetrahedral and octahedral
29 lattice interstitial
30 lattice vacancies
31 (b)
32 (c)
33 (d) See Figure 9-17b in the text.
34 (c) The Bragg relation gives

$$n\lambda = 2d \sin \theta$$

Since $n = 1$, $\lambda = 1.54$ nm, and $\sin \theta = \sin 35^\circ 30' = 0.581$

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{1(1.54 \text{ nm})}{2(0.581)} = 1.32 \text{ nm}$$

35 (c) There are twice as many tetrahedral holes as spheres in the unit cell of a close-packed structure.

36 (b) Mass of unit cell

$$\text{Mass of unit cell} = \frac{\text{atomic mass}}{N_{\text{Avogadro}}} \times \text{ atoms (unit cell)}^{-1}$$

$$= \frac{184 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ atoms mol}^{-1}} \times \frac{2 \text{ atoms}}{\text{unit cell}}$$

$$= 6.11 \times 10^{-22} \text{ g (unit cell)}^{-1}$$

$$\text{Volume of unit cell} = \text{g (unit cell)}^{-1} \frac{1}{\text{g cm}^{-3}} = \frac{\text{cm}^3}{\text{unit cell}}$$

$$= 6.11 \times 10^{-22} \text{ g (unit cell)}^{-1} \frac{1}{19.3 \text{ g cm}^{-3}}$$
$$= 3.16 \times 10^{-23} \text{ cm}^3$$

$$3.16 \times 10^{-23} \text{ cm}^3 \left(\frac{10^7 \text{nm}}{1 \text{ cm}}\right)^3 = 3.16 \times 10^{-2} \text{ nm}^3$$

37 (b) The length of an edge of the unit cell is
$$l = (0.0316 \text{ nm}^3)^{1/3} = 0.316 \text{ nm}$$
In a body-centered structure atoms touch along the diagonal of the cell through the body-centered atom (see Fig. 9-15b in the text). The cell diagonal forms a right triangle with an edge of the cell and the diagonal of the face of the cell. The cell diagonal forms the hypotenuse of this triangle so
$$\overline{(\text{CD})}^2 = l^2 + d^2$$
where $\overline{\text{CD}}$ = length of cell diagonal
d = length of face diagonal
l = length of cell edge
We have already shown in Example 1 in the *Study Guide* that
$$d^2 = 2l^2$$
so
$$\overline{(\text{CD})}^2 = l^2 + 2l^2 = 3l^2$$
In the body-centered cell $\overline{(\text{CD})} = 4r$ where r is the radius of the atoms touching along the cell diagonal
$$(4r)^2 = 3l^2$$
$$r = \frac{\sqrt{3}}{4} l = \frac{\sqrt{3}}{4}(0.316 \text{ nm}) = 0.137 \text{ nm}$$

38 (b) Some metallic solids have low melting points, but all molecular solids do. Weak van der Waals forces result in low melting points.
39 (a) $\Delta H_{\text{lat}} = \Delta H_{\text{form}} - (\Delta H_{\text{subl}} + \Delta H_{\text{ion}} + \Delta H_{\text{diss}}/2 + \Delta H_{\text{e.a.}})$
$= -612 - (155 + 520 + 79/2 - 333) = -994 \text{ kJ mol}^{-1}$
See *Study Guide* Example 4.
40 (c)
41 (d)
42 (b)
43 (e)
44 (c) Each of the corner atoms touches the center atom.
45 (b) Each atom is surrounded by 6 nearest neighbors at the corners of an octahedron.

CHAPTER 10
LIQUIDS AND CHANGES OF STATE

1 False: Boiling points decrease as pressure decreases.
2 False: Melting point and freezing point are the same.
3 True
4 False: Vapor pressure is a function of temperature but not of external pressure.
5 True
6 True
7 True
8 False: The slope is equal to $-\Delta H_{\text{vap}}/R$, so it is different for each liquid.

9 True: Temperature remains constant during melting, so kinetic energy does not change. The increase in energy is an increase in potential energy only.
10 False: Solid and gas phases can exist in equilibrium at temperatures below the triple point.
11 True
12 False: One atmosphere of pressure is below the triple point, so sublimation to the gas phase occurs.
13 False: This statement is true only at the boiling point; at other conditions of pressure and temperature the temperature will increase as heat is added.
14 False: If the density of the liquid is greater than that of the solid the mixture will contract. This occurs with water.
15 True
16 boiling chips
17 melting point
18 liquid
19 decreases
20 normal boiling point
21 condensation
22 vapor pressure
23 less
24 evolution
25 lower
26 two
27 surface tension
28 critical pressure
29 melting point or freezing point
30 decreases
31 (c)
32 (b)
33 (d)
34 (a)
35 (b)
36 (b)
37 (d) This is the basic relation of the Clausius-Clapeyron equation.

38 (d) $\ln \frac{P_1}{P_2} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\begin{aligned} P_1 &= 1 \text{ atm} \\ P_2 &= ? \\ T_1 &= 273 - 162^\circ\text{C} = 111 \text{ K} \\ T_2 &= 273 + 25^\circ\text{C} = 298 \text{ K} \\ \Delta H_{vap} &= 8{,}200 \text{ J mol}^{-1} \\ R &= 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\ln \frac{1 \text{ atm}}{P_2} = \frac{-8200 \text{ J mol}^{-1}}{8.31 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{111 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\ln \frac{1 \text{ atm}}{P_2} = -5.58$$

$$\frac{1}{P_2} = e^{-5.58} = 3.80 \times 10^{-3}$$

$$P_2 = \frac{1}{3.80 \times 10^{-3}} = 263 \text{ atm}$$

39 (b)

$$\ln\frac{P_1}{P_2} = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

P_1 = 1 atm

P_2 = 3.70 atm

T_1 = ?

T_2 = 273 + 25°C = 298 K

ΔH_{vap} = 11,200 J mol^{-1}

R = 8.31 J mol^{-1} K^{-1}

$$\ln\left(\frac{1\text{ atm}}{3.70\text{ atm}}\right) = \frac{-11{,}200\text{ J mol}^{-1}}{8.31\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{T_1}-\frac{1}{298\text{ K}}\right)$$

$$-1.308 = -1348\left(\frac{1}{T_1} - 3.356 \times 10^{-3}\right)$$

$$\frac{1}{T_1} = \frac{-1.308}{-1348} + 3.356 \times 10^{-3} = 4.33 \times 10^{-3}$$

$$T_1 = 231\text{ K} \quad \text{or} \quad -42^\circ\text{C}$$

40 (c)
41 (d)
42 (c)
43 (b)
44 (d)
45 (c)

$$\ln\frac{P_1}{P_2} = \frac{-\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

P_1 = 1 atm

P_2 = ?

T_1 = 273 − 42.1°C = 231 K

T_2 = 273 + 25°C = 298 K

ΔH_{vap} = 11,200 J mol^{-1}

R = 8.31 J mol^{-1} K^{-1}

$$\ln\frac{1\text{ atm}}{P_2} = \frac{-11{,}200\text{ J mol}^{-1}}{8.31\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{231\text{ K}}-\frac{1}{298\text{ K}}\right)$$

$$\ln\frac{1}{P_2} = -1.312$$

$$\frac{1}{P_2} = e^{-1.312} = 0.269$$

$$P_2 = \frac{1}{0.269} = 3.71\text{ atm}$$

CHAPTER 11
SOLUTIONS

1 False: Homogeneous mixtures have their own unique properties.
2 False: Molality, mole fraction, and molarity are always consistent in a given solvent system.
3 False: Hydrogen bonding increases the solubility of compounds containing hydrogen bonded to N, O, or F in aqueous solutions.
4 True: This is Henry's law.
5 False: The percent by mass is 50% but the mole fractions are different because there are different numbers of moles of each.

6 True: Where the volume of the solute is negligible.

7 True: $\Delta H_{soln} = \Delta H_{hyd} - \Delta H_{lat}$. ΔH_{hyd} is negative, while ΔH_{lat} is positive, so if $\Delta H_{hyd} > \Delta H_{lat}$, ΔH_{soln} will be negative.

8 False: ΔH_{soln} must be positive for solubility to increase with temperature.

9 False: The solubility of gases increases as temperature decreases, so the solution becomes unsaturated.

10 True: The strong interactions between unlike molecules reduces their escaping tendency and hence their vapor pressure is below that predicted by Raoult's law for ideal behavior.

11 True

12 False: The Δt of -1.855°C would be correct if the $MgCl_2$ did not dissociate into ions. However, since $MgCl_2$ produces three moles of ions for every mole of $MgCl_2$, the actual Δt will be $3\,(-1.855) = -5.56$°C.

13 False: The "like dissolves like" rule predicts that only polar solutes are soluble in water, which is polar.

14 True

15 False: Osmotic pressure is only a function of the molarity of the solute and temperature.

16 homogeneous

17 like

18 decreases

19 $K_f = 1.855\text{°C m}^{-1}$

20 Bases

21 mole fraction

22 solute–solvent, solvent–solvent, solute–solute

23 moles, kilogram

24 vapor-pressure lowering, freezing-point depression, boiling-point elevation, and osmotic pressure

25 70

26 100.52°C

27 salts or strong electrolytes

28 H_3O^+

29 $3(0.45) = 1.35\ M$

30 colligative properties

31 (d) $$n\ MgF_2 = \frac{50.0\text{ g}}{62.3\text{ g mol}^{-1}} = 0.802\text{ mol}$$
$$n\ H_2O = 11.1\text{ mol}$$
$$X_{MgF_2} = \frac{0.802\text{ mol}}{0.802\text{ mol} + 11.1\text{ mol}} = 0.0674$$

32 (d) $\text{mol\%} = X_{MgF_2}(100) = 0.0674(100) = 6.74\%$

33 (a) $$m = \frac{\text{mol } MgF_2}{\text{kg } H_2O} = \frac{0.802\text{ mol}}{0.200\text{ kg}} = 4.01\ m$$

34 (b) $$V = \frac{\text{g}}{\text{density}} = \frac{200\text{ g} + 50.0\text{ g}}{1.070\text{ g cm}^{-3}} = 234\text{ cm}^3 \quad \text{or} \quad 234\text{ mL}$$
$$M = \frac{\text{mol}}{\text{liter}} = \frac{0.802\text{ mol}}{0.234\text{ L}} = 3.43\ M$$

35 (d) $$\text{Total mass of solution} = 100\text{ mL}(1.10\text{ g cm}^{-3})\left(\frac{1\text{ cm}^3}{1\text{ mL}}\right) = 110\text{ g}$$
$$\text{mass } H_2O = 110\text{ g} - 26.0\text{ g} = 84\text{ g}$$
$$m = \frac{26.0\text{ g NaCl}}{0.084\text{ kg } H_2O} \times \frac{1\text{ mol NaCl}}{58.4\text{ g NaCl}} = 5.30\ m$$

36 (b) $V_{conc} = V_{dil}\dfrac{M_{dil}}{M_{conc}} = 1.00\text{ L}\dfrac{0.250\ M}{6.00\ M} = 0.0416\text{ L} \quad \text{or} \quad 41.6\text{ mL}$

37 (d) $X_{O_2} = K_{O_2}P_{O_2} = 2.58 \times 10^{-5}\text{ atm}^{-1}\,(2.00\text{ atm}) = 5.16 \times 10^{-5}$

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} = \frac{n_{O_2}}{n_{O_2} + (1000\text{ g}/18\text{ g mol}^{-1})}$$

$$= \frac{n_{O_2}}{n_{O_2} + 55.6} = 5.16 \times 10^{-5}$$

$n_{O_2} = 2.87 \times 10^{-3}\text{ mol L}^{-1}$

$\text{g } O_2 = n_{O_2}(32\text{ g mol}^{-1})(2.00\text{ L}) = 2.87 \times 10^{-3}\text{ mol}(32\text{ g mol}^{-1})(2.00\text{ L}) = 0.198\text{ g}$

38 (b) $m = 2.000\text{ molal} = \dfrac{2.000\text{ mol solute}}{1.000\text{ kg } H_2O}$

$$X_{H_2O} = \frac{1000\text{ g}/18.02\text{ g mol}^{-1}}{2.000\text{ mol} + (1000\text{ g}/18.02\text{ g mol}^{-1})} = 0.9651$$

$P_{soln} = X_{H_2O}P^{o}_{H_2O} = 0.9651\ (42.18\text{ mmHg}) = 40.71\text{ mmHg}$

39 (c) $m_{\text{total ions}} = 2(m_{NaCl}) = 2(0.200\ m) = 0.400\ m$

$\Delta T_b = K_b m = 0.512^{\circ}\text{C } m^{-1}\ (0.400\ m) = 0.205^{\circ}\text{C}$

40 (c) $m_{toluene} = \dfrac{5.00\text{ g}/92\text{ g mol}^{-1}}{0.100\text{ kg benzene}} = 0.543\text{ m}$

$\Delta T_f = -K_f m = -(5.12^{\circ}\text{C } m^{-1})\ (0.543\ m) = -2.78^{\circ}\text{C}$

$T_f = 5.50 - 2.78 = 2.72^{\circ}\text{C}$

41 (d) The osmotic pressure required is

$$100\ m\ H_2O \times \frac{10^3\text{ mm}}{1\ m} \times \frac{1\text{ mmHg}}{13.55\text{ mmH}_2\text{O}} \times \frac{1\text{ atm}}{760\text{ mmHg}} = 9.71\text{ atm}$$

$$M = \frac{\pi}{RT} = \frac{9.71\text{ atm}}{(0.082\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})} = 0.397\ M$$

42 (d) $m = \dfrac{-\Delta T_f}{K_f} = \dfrac{-(-0.415^{\circ}\text{C})}{1.855^{\circ}\text{C } m^{-1}} = 0.224\ m$

$\text{Moles} = m(\text{kg solvent}) = 0.224\text{ mol kg}^{-1}\ (0.100\text{ kg}) = 0.0224\text{ mol}$

$\text{Molar mass} = \text{g mol}^{-1} = \dfrac{2.50\text{ g}}{0.0224\text{ mol}} = 112\text{ g mol}^{-1}$

43 (c) $n_2 = \dfrac{\pi V}{RT} = \dfrac{(0.0147\text{ atm})(1\text{ L})}{(0.082\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})} = 6.01 \times 10^{-4}\text{ mol}$

$\text{Molar mass} = \text{g mol}^{-1} = \dfrac{5.00\text{ g}}{6.01 \times 10^{-4}\text{ mol}} = 8320\text{ g mol}^{-1}$

44 (b) The freezing point of undissociated acetic acid would be

$\Delta T_f = -K_f m = -(1.855^{\circ}\text{C } m^{-1})(0.150\ m) = 0.278^{\circ}\text{C}$

$$\frac{m_{diss}}{m_{undiss}} = \frac{(\Delta T_f)_{diss}}{(\Delta T_f)_{undiss}} = \frac{-0.284}{-0.278} = 1.02$$

The acid is 2 percent dissociated. (See Text Example 11-13)

45 (b)

CHAPTER 12
AQUEOUS-SOLUTION REACTIONS

1 True
2 False: Acids are electron pair acceptors.
3 True: The protonated solvent is the strongest acid possible in any solvent system.
4 False: The salt formed may hydrolyze and make the solution either acidic or basic.
5 True
6 True: NH_2^- is the base ion in NH_3.
7 True
8 False: This is the net ionic reaction only when a strong acid and strong base react.
9 True: Alkali metal carbonates are soluble.
10 True
11 False: The correct net ionic equation is $Ag^+ + Cl^- \rightarrow AgCl(s)$.
12 True
13 True
14 True
15 True
16 aqueous
17 autodissociation
18 insoluble
19 insoluble
20 +3
21 +6
22 loses, increases
23 reduction
24 will: $SrCO_3$ is insoluble.
25 three
26 0.800 N
27 0.600 N
28 $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4(s)$
29 $1.5\ \text{mol L}^{-1}\ (2\ \text{equiv mol}^{-1})\ (3.0\ \text{L}) = 9.0\ \text{equiv.}$
30 NH_2^-, OH^-
31 (d)
32 (b)
33 (b)
34 (b)
35 (d) The coefficients are 2, 1, 3, 1, 6, 2, 8
36 (d) The coefficients are 6 H^+, 10, 2, 5, 2, 8 H_2O
37 (c)
38 (d)
39 (d)
40 (c)
41 (a) $N_{Ca(OH)_2} = 0.200\ M\ \dfrac{2\ \text{equiv}}{1\ \text{mol}} = 0.400\ N$

$N_{HNO_3} = M_{HNO_3} = 0.150\ N$

$V_{Ca(OH)_2} = V_{HNO_3} \times \dfrac{N_{HNO_3}}{N_{Ca(OH)_2}} = (25.0\ \text{mL})\ \dfrac{0.150\ N}{0.400} = 9.38\ \text{mL}$

42 (d) number of equivalents $= 3.0 \text{ mol} \times \frac{2 \text{ equiv}}{\text{mol}} = 6.0 \text{ equiv}$

43 (a) N in HNO_3 changes oxidation state from +5 to +2
$N = 3M = 3(2.00\,M) = 6.00\,N$

44 (c) In this reaction 1 mol Na_2CO_3 = 1 equiv Na_2CO_3, so equivalent mass = molecular mass = 106 g equiv^{-1}

45 (a) $V_{KMnO_4} = V_{AsH_3} \frac{N_{AsH_3}}{N_{KMnO_4}} = (30.0 \text{ mL}) \frac{0.250\,N}{0.200\,N} = 37.5 \text{ mL}$

Answers to redox equation balancing problems in Chapter 12. Answers are numerical coefficients of substances in same order as they appear in the given equation. Required H^+, OH^- or H_2O is indicated.

1 6, 10, 3, 10, 5
2 5, 2, 6, 5, 2, 2, 8
3 1, 2, 2, 1, 1
4 1, 10, 1, 3, 10, 5
5 2, 3, 24, 6, 1, 4, 15
6 5, 2, 16, 10, 2, 8
7 10, 8, 2, 5, 1, 2, 8
8 3, 8, 6, 1
9 3, 3, 6, 1
10 1, 4, 12, 2, 5, 1
11 8 H^+, 5, 1, 5, 1, 4 H_2O
12 4 H^+, 1, 2, 1, 1, 2 H_2O
13 10 H^+, 4, 1, 4, 1, 3 H_2O
14 3 H_2O, 6, 1, 1, 6, 6 H^+
15 6 H^+, 1, 2, 2, 2, 4 H_2O
16 6 H^+, 1, 6, 1, 3, 3 H_2O
17 6 H^+, 2, 5, 2, 5, 8 H_2O
18 6 OH^-, 3, 5, 1, 3 H_2O
19 10 OH^-, 2, 3, 6, 2, 8 H_2O
20 3 H_2O, 3 OH^-, 1, 3, 1
21 OH^-, 1, 1, 2, 1, H_2O
22 2, 3, 3, 2, 3 H_2O

CHAPTER 13
CHEMICAL KINETICS

1 False: It can, since the rate of production of products is related stoichiometrically to the rate of disappearance of reactants, even though the rate is not a function of product concentration. See New Skills 1–1:2.
2 True
3 False: Except for zero-order reactions, rate is a function of concentration of reactants.
4 False: Rate constant and rate are equal only if reactant concentrations are all unity, that is, one molar or one atmosphere.
5 True
6 True
7 True

8 False: A plot of the logarithm of concentration versus time is linear for a first-order reaction.
9 False: Only true for the elementary processes in a reaction mechanism.
10 True: See added comment on the meaning of mechanisms in Sec. 13-1 of the text.
11 False: A plot of ln *k* versus 1/*T* is linear.
12 True
13 True
14 True
15 False: Energy of activation is not a function of temperature.
16 reaction rate constant or rate constant
17 2.5, 2 or second
18 concentration of reactants, temperature, chemical nature of the reactants, and presence of a catalyst
19 instantaneous rate
20 $M\ s^{-1}$ or $\text{mol L}^{-1}\ s^{-1}$
21 Arrhenius plot, log *k* versus 1/*T*
22 the initial rate method and the graphical (linear plot) method
23 $t_{1/2} = 0.693/k$
24 zero
25 steric factor
26 rate-determining or rate-limiting step
27 activated complex or transition state
28 activation energy
29 homogeneous catalyst
30 alters
31 (a)
32 (c)
33 (d) doubling [A] increases the rate fourfold, doubling [B] increases the rate twofold $(2)^2(2)$ = eightfold total
34 (c)
35 (b)
36 (d)
37 (a)
38 (c)

39 (b) Rate = $k[A]^2$

$$k = \frac{\text{rate}}{[A]^2} = \frac{4.00 \times 10^{-3}\ M\ s^{-1}}{(0.500\ M)^2} = 1.60 \times 10^{-2}\ M^{-1}\ s^{-1}$$

$$\text{Rate} = 1.60 \times 10^{-2}\ M^{-1}\ s^{-1}\ (0.250\ M)^2 = 1.00 \times 10^{-3}\ M\ s^{-1}$$

40 (d) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{1.74 \times 10^{-3}\ s^{-1}} = 398\ s$

41 (b) $\ln[A] = -kt + \ln[A]_o$

$$k = \frac{1}{t}\ln\frac{[A]_o}{[A]} = \frac{1}{30\ \text{min}}\ln\frac{0.70}{0.25} = 0.0343\ \text{min}^{-1}$$

$$t = \frac{1}{k}\ln\frac{[A]_o}{[A]} = \frac{1}{0.0343\ \text{min}^{-1}}\ln\frac{0.35}{0.25} = 9.8\ \text{min}$$

42 (a) $k = 0.0343\ \text{min}^{-1}$

$$\begin{aligned} \ln[A] &= -kt + \ln[A]_o \\ &= -(0.0343\ \text{min}^{-1})(1\ \text{hr})(60\ \text{min}/1\ \text{hr}) + \ln 0.70 \\ &= -2.06 + (-0.357) = -2.42 \\ [A] &= 0.0892 \end{aligned}$$

43 (a)

44 (a) $$\ln\frac{k_2}{k_1} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{k_2}{5.44 \times 10^{-3}\ \text{s}^{-1}} = \frac{90{,}000\ \text{J mol}^{-1}}{8.31\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{298\ \text{K}} - \frac{1}{353\ \text{K}}\right) = 5.66$$

$$\frac{k_2}{5.44 \times 10^{-3}\ \text{s}^{-1}} = e^{5.66} = 287$$

$$k_2 = 287\ (5.44 \times 10^{-3}\ \text{s}^{-1}) = 1.56\ \text{s}^{-1}$$

45 (c) $$E = \frac{R\ \ln(k_2/k_1)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= \frac{8.31\ \text{J mol}^{-1}\ \text{K}^{-1}\ \ln\ (0.735\ \text{s}^{-1}/5.44 \times 10^{-3}\ \text{s}^{-1})}{1/298\ \text{K} - 1/353\ \text{K}}$$

$$= 78{,}000\ \text{J mol}^{-1}$$

CHAPTER 14
CHEMICAL EQUILIBRIUM

1 True
2 False: It involves a single phase which may contain many substances.
3 True
4 False: The forward and reverse rates are equal but not zero.
5 True: This is LeChâtelier's principle.
6 True
7 True: This is the law of chemical equilibrium.
8 False: It shifts to the right until Q becomes as large as K.
9 False: The relation holds for all reactions.
10 False: They apply to any system.
11 True
12 True
13 True: The concentrations of reacting substances are not affected by the presence of an inert gas.
14 True
15 False: True for an endothermic reaction.
16 right
17 left
18 right
19 right
20 zero
21 numerator
22 temperature
23 equilibrium constant
24 LeChâtelier's
25 very large
26 removal
27 mass-action expression
28 temperature and standard enthalpy of reaction

29 0.30 $$K_c = \frac{[C]^3}{[A][B]^2} = \frac{(2.0)^3}{(3.0)(3.0)^2} = 0.30$$

30 0.67 M $K_c = \frac{[C]^2}{[A][B]}$ $[A] = \frac{[C]^2}{K_c[B]} = \frac{(4.0)^2}{8.0(3.0)} = 0.67$

31 (c)
32 (c)
33 (c) $K' = 1/K$
34 (c) $\Delta n = 0$ so $K_p = K_c$
35 (a) $Q = \frac{[C]^2}{[A][B]} = \frac{(1.5)^2}{(2)(4)} = 0.28$
Since $Q > K$, the reaction will shift to the left.

36 (b)
37 (d)
38 (c)
39 (a) $\ln\frac{5.0}{(K_p)_2} = -\frac{125{,}000\ \text{J mol}^{-1}}{8.31\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{298\ \text{K}} - \frac{1}{373\ \text{K}}\right) = 10.15$

$(K_p)_2 = \frac{5.0}{e^{10.15}} = \frac{5.0}{2.56 \times 10^4} = 1.96 \times 10^{-4}$

40 (c) $K_c = \frac{[C]^2}{[A][B]^2} = \frac{(0.210)^2}{(0.250)(0.300)^2} = 1.96$

41 (c) $K_p = P_{CO_2} = 0.061$ atm

42 (b) $K_c = \frac{[A][B]}{[C]^2}$, let $x = [A] = [B]$

$8.50 = \frac{x^2}{(0.020)^2}$ $x = [8.50(0.020)^2]^{1/2} = 0.0580$

43 (c) $K_p = \frac{1}{P_A P_B}$ $P_A = \frac{1}{K_p P_B} = \frac{1}{3.00(0.750\ \text{atm})} = 0.444$ atm

44 (c) $K_c = \frac{[C]^2}{[A][B]}$

let x = mol L^{-1} of A and B produced during the reaction

	Initial Conc.	Change	Equilib. Conc.
A	0	x	x
B	0	x	x
C	2.00	$-2x$	$2.00 - 2x$

$$25 = \frac{(2.00 - 2x)^2}{x^2}$$

Take the square root of each side of the equation

$5 = \frac{2.00 - 2x}{x}$ $x = 0.29$

$[C] = 2.00 - 2x = 2.00 - 2(.29) = 1.42\ M$

45 (b) $K_c = \dfrac{[C]}{[A][B]}$

let x = mol L^{-1} of C produced during the reaction

	Initial Conc.	Change	Equilib. Conc.
A	1.00	$-\frac{x}{2}$	$1.00 - x/2$
B	2.00	$-\frac{x}{2}$	$2.00 - x/2$
C	0	x	x

$$3.00 \times 10^{-5} = \frac{x}{\left(1.00 - \frac{x}{2}\right)\left(2.00 - \frac{x}{2}\right)} \cong \frac{x}{(1.00)(2.00)}$$

$$x = [C] = 6.00 \times 10^{-5}$$

CHAPTER 15
AQUEOUS SOLUTIONS: ACID-BASE EQUILIBRIA

1 True: This is an example of the common-ion effect.
2 False: The percent dissociation decreases as the solution becomes more concentrated.
3 False: The $[H^+]$ has changed by 10^3, or 1000.
4 False: The pH is 11.
5 True
6 True
7 True
8 True
9 True
10 False: They form the weak base plus H^+.
11 True: Generally about 10^7 smaller.
12 True
13 True
14 False: See Example 15-20 in the text.
15 False: $[H^+]$ and $[H_3O^+]$ are equivalent expressions.
16 the cyanide ion, a common ion to HCN.
17 the acid, the equilibrium expression
18 3
19 11
20 anion or cation, weak acid or weak base
21 $K_w = K_h K_a$
22 weak acid, strong base
23 greater than
24 basic
25 greater than
26 55.5 mol L^{-1}
27 Brønsted–Lowry
28 greater than
29 acid-base indicator, titration
30 pH, composition
31 (c) $pH = -\log[H^+] = -\log(5.0 \times 10^{-5}) = 4.3$
$pOH = 14.00 - pH = 9.7$
32 (d) $CN^- + H_2O \rightarrow HCN + OH^-$

33 (c) a weak acid and its salt or conjugate base
34 (d)
35 (a)
36 (b) See Example 15-15 in the text

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+ \qquad K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Let x = amount of NH_4^+ hydrolyzed in moles per liter.

	Initial conc., mol L^{-1}	Change	Equilib. conc. mol L^{-1}
NH_4^+	0.10	$-x$	$0.10 - x \cong 0.10$
NH_3	0	$+x$	x
H_3O^+	0	$+x$	x

$$5.6 \times 10^{-10} = \frac{x^2}{0.10}$$
$$x = [H_3O^+] = 7.5 \times 10^{-6}$$
$$pH = -\log(7.5 \times 10^{-6}) = 5.1$$

37 (b) $[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}\ M$

38 (c) $[OH^-] = 2[Ba(OH)_2] = 2(0.010) = 0.020$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.020} = 5.0 \times 10^{-13}$$
$$pH = -\log[H^+] = -\log(5.0 \times 10^{-13}) = 12.3$$

39 (d) $pOH = 14.00 - 10.00 = 4.00$

$$[OH^-] = 10^{-pOH} = 10^{-4}\ M$$

40 (b) $K_h = \dfrac{K_w}{K_2} = \dfrac{1 \times 10^{-14}}{6.30 \times 10^{-8}} = 1.60 \times 10^{-7}$

41 (d) $[OH^-] = \dfrac{(0.100\ M)(0.040\ L) - (0.150\ M)(0.025\ L)}{0.040\ L + 0.025\ L} = 3.85 \times 10^{-3}\ M$

$$[H^+] = \frac{1.0 \times 10^{-14}}{3.85 \times 10^{-3}} = 2.6 \times 10^{-12}$$

42 (c) $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

Let x = the amount of NH_3 dissociated in moles per liter.

	Initial conc., mol L^{-1}	Change	Equilib. conc. mol L^{-1}
NH_3	0.05	$-x$	$0.05 - x$
NH_4^+	0.10	$+x$	$0.10 - x$
OH^-	0	$+x$	x

Neglecting x with respect to 0.05 and 0.10, and substituting into the dissociation expression, we obtain

$$1.8 \times 10^{-5} = \frac{(0.10)x}{0.05}$$

$$x = [OH^-] = 9.0 \times 10^{-6}\,M$$

43 (d)

44 (c) $pH = pK_a - \log \frac{[\text{acetic acid}]}{[\text{sodium acetate}]}$

$$= -\log (1.8 \times 10^{-5}) - 0 = 4.74$$

45 (b) $pH = pK_a - \log \frac{[HF]}{[NaF]}$

$pK_a = -\log (6.7 \times 10^{-4}) = 3.17 \qquad 4.00 = 3.17 - \log \frac{0.100}{[NaF]}$

$\log \frac{0.100}{[NaF]} = 0.83 \qquad [NaF] = \frac{0.100}{10^{0.83}} = \frac{0.100}{6.76} = 0.0148$

or 0.0148 mol NaF per liter of buffer

CHAPTER 16
AQUEOUS SOLUTIONS: SOLUBILITY AND COMPLEX-ION EQUILBRIA

1 False: K_{sp} is the solubility product constant. It is the product of the ions in solution raised to the proper power. The solubility of a compound is the moles per liter needed to make a saturated solution.
2 False: The ion product does not necessarily apply to a saturated solution.
3 True: See Examples 16-1 and 16-2 in the text.
4 True
5 True
6 False: The common-ion effect of Cl^- will reduce the solubility of AgCl.
7 False: For instance, the K_{sp} of AgCl and CaF_2 are equal, but their solubilities are quite different. Solubilities would be equal only when the number of ions from each compound is equal.
8 True
9 True
10 False: Only if the ion product exceeds K_{sp}.
11 True
12 True
13 True
14 True
15 True: H^+ reacts with S^{2-} to form HS^- and H_2S. If S^{2-} is reduced sufficiently by this reaction the ion product becomes less than K_{sp} and the compound dissolves.
16 $[Ca^{2+}][F^-]^2$
17 $K_{sp} = [Ca^{2+}][OH^-]^2$
18 $Al(OH)_{3(s)} \rightleftarrows Al^{3+} + 3\,OH^-$
19 decrease
20 increase
21 ion product, greater
22 ligands
23 stability or formation constant
24 amphoteric

25 $K_f = \dfrac{[Co(NH_3)_6{}^{3+}]}{[Co^{3+}][NH_3]^6}$

26 $Cu(NH_3)_4{}^{2+} \rightleftarrows Cu^{2+} + 4\ NH_3$

27 acid

28 NH_3 (forms soluble $Ag(NH_3)_2{}^+$)

29 pH

30 does not (see added comment at the end of the chapter in the text)

31 (a) $Ag_2CO_{3(s)} \rightleftarrows 2\ Ag^+ + CO_3{}^{2-}$

$K_{sp} = [Ag^+]^2[CO_3{}^{2-}]$

$[Ag_2CO_3]_{(aq)} = \dfrac{0.032\ g\ L^{-1}}{276\ g\ mol^{-1}} = 1.16 \times 10^{-4}\ M$

$[Ag^+] = 2(1.16 \times 10^{-4}\ M) = 2.32 \times 10^{-4}\ M$

$[CO_3{}^{2-}] = 1.16 \times 10^{-4}\ M$

$K_{sp} = (2.32 \times 10^{-4})^2(1.16 \times 10^{-4}) = 6.2 \times 10^{-12}$

32 (d)

33 (c) pOH = 14 − pH = 14 − 5.13 = 8.87

$[OH^-] = 10^{-pOH} = 10^{-8.87} = 1.35 \times 10^{-9}$

$[Fe(OH)_3] = \dfrac{[OH^-]}{3} = \dfrac{1.35 \times 10^{-9}}{3} = 4.5 \times 10^{-10}$

34 (c) $BaF_{2(s)} \rightleftarrows Ba^{2+} + 2\ F^-$

$[Ba^{2+}] = 7.5 \times 10^{-3}\ M$

$[F^-] = 2(7.5 \times 10^{-3}) = 1.5 \times 10^{-2}\ M$

$K_{sp} = [Ba^{2+}][F^-]^2 = (7.5 \times 10^{-3})(1.5 \times 10^{-2})^2$

$= 1.7 \times 10^{-6}$

35 (a) $Pb(IO_3)_2 \rightleftarrows Pb^{2+} + 2\ IO_3{}^-$

$K_{sp} = [Pb^{2+}][IO_3{}^-]^2$

$[Pb^{2+}] = M$

$[IO_3{}^-] = 2\ M$

$K_{sp} = M(2\ M)^2 = 4\ M^3$

36 (a)

37 (d) See Table 16-2 in the text.

38 (c) $AgI \rightleftarrows Ag^+ + I^-$

$K_{sp} = [Ag^+][I^-]$

$[I^-] = 0.028\ M$

$[Ag^+] = \dfrac{K_{sp}}{[I^-]} = \dfrac{8.5 \times 10^{-17}}{0.028} = 3.0 \times 10^{-15}$

solubility = $[Ag^+] = 3.0 \times 10^{-15}$ mol L^{-1}

39 (d) $Ag^+ + 2\ NH_3 \rightarrow Ag(NH_3)_2{}^+$

$K_f = \dfrac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$

40 (c) $Ag(NH_3)_2{}^+ \rightleftarrows Ag^+ + 2\ NH_3$

let $x = [Ag^+]$

$[Ag(NH_3)_2{}^+] = 0.10 - x \cong 0.10$

$[NH_3] = 0.50 - 2[Ag(NH_3)_2^+] = 0.50 - 2(0.10) = 0.30$

$K_{diss} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$

$[Ag^+] = \frac{K_{diss}[Ag(NH_3)_2^+]}{[NH_3]^2} = \frac{(5.9 \times 10^{-8})(0.10)}{(0.30)^2} = 6.6 \times 10^{-8}$

41 (d)

42 (b) $PbCl_2 \rightleftarrows Pb^{2+} + 2\ Cl^-$

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$[Pb^{2+}] = 0.010\ M$

$[Cl^-] = \left(\frac{K_{sp}}{[Pb^{2+}]}\right)^{1/2} = \left(\frac{1.6 \times 10^{-5}}{0.01}\right)^{1/2}$

$= 4.0 \times 10^{-2}\ M$

43 (a) $Fe(OH)_3 \rightleftarrows Fe^{3+} + 3\ OH^-$

$K_{sp} = [Fe^{3+}][OH^-]^3$

let $x = [Fe^{3+}]$

$3x = [OH^-]$

$1.1 \times 10^{-36} = x(3x)^3$

$x^4 = \frac{1.1 \times 10^{-36}}{27} = 4.07 \times 10^{-38}$

$x = 4.5 \times 10^{-10}$

$[OH^-] = 3x = 3(4.5 \times 10^{-10}) = 1.35 \times 10^{-9}$

$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.35 \times 10^{-9}} = 7.4 \times 10^{-6}$

$pH = -\log[H^+] = -\log(7.4 \times 10^{-6}) = 5.1$

44 (a) $Fe(OH)_2 \rightleftarrows Fe^{2+} + 2\ OH^-$

$K_{sp} = [Fe^{2+}][OH^-]^2$

$[OH^-] = \left(\frac{K_{sp}}{[Fe^{2+}]}\right)^{1/2} = \left(\frac{2 \times 10^{-15}}{0.020}\right)^{1/2} = 3.2 \times 10^{-7}\ M$

Enough NH_4^+ must be added to repress the dissociation of NH_3 so $[OH^-]$ is less than $3.2 \times 10^{-7}\ M$.

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$

$[NH_4^+] = \frac{K_b[NH_3]}{[OH^-]} = \frac{1.8 \times 10^{-5}\ (0.050)}{3.2 \times 10^{-7}} = 2.9\ M$

45 (c) $H_2S \rightleftarrows 2\ H^+ + S^{2-}$

$K = K_1K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = (1.1 \times 10^{-7})(1 \times 10^{-14}) = 1.1 \times 10^{-21}$

$[S^{2-}] = \frac{K[H_2S]}{[H^+]^2} = \frac{(1.1 \times 10^{-21})(0.10)}{(0.050)^2} = 4.4 \times 10^{-20}\ M$

$SnS \rightleftarrows Sn^{2+} + S^{2-}$

$$K_{sp} = [Sn^{2+}][S^{2-}] = 1 \times 10^{-26}$$

$$[Sn^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{1 \times 10^{-26}}{4.4 \times 10^{-20}} = 2.3 \times 10^{-7}\, M$$

CHAPTER 17
CHEMICAL THERMODYNAMICS

1 True: According to the convention described in Chapter 3, work done by the system is negative and the first law of thermodynamics, $\Delta E = q + w$, says ΔE decreases if w is negative.
2 False: The sign of ΔH is not a reliable indicator of spontaneity. Entropy changes may determine the sign of ΔG in certain cases.
3 True: For instance, in the universe.
4 False: A system tends toward a maximum in entropy.
5 True: $\Delta H = \Delta E + \Delta(PV)$. $\Delta(PV)$ is very small for condensed systems.
6 True
7 True
8 True
9 False: Entropy increases as a system changes from solid to liquid to gas.
10 True
11 True: These are statements of the first and second laws of thermodynamics.
12 False: Entropy decreases as matter becomes more ordered.
13 True: $\Delta G = \Delta H - T\Delta S$. If ΔH is positive and ΔS is negative then ΔG must be positive and the process is nonspontaneous.
14 True
15 True: The spontaneous change will continue until the available free energy has been removed and the system is no longer able to do work. At this point the system is at equilibrium.
16 $\Delta E = q + w$
17 zero
18 $w = -P_{ext}(V_2 - V_1)$
19 $Ca_{(s)} + C_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow CaCO_{3(s)}$
20 zero
21 $\Delta G = \Delta H - T\Delta S$
22 increases
23 higher
24 disordered
25 highest
26 work
27 positive
28 positive
29 spontaneous
30 entropy
31 (a) Since $\Delta E = 0, q = -w$ and the system must lose the acquired heat energy by doing an equal amount of work to maintain constant energy. (b) and (c) are incorrect because compressing the system or expanding into a vacuum would not dissipate the heat energy. (d) is incorrect because energy can only be conserved by balancing heat and work for the system.
32 (d) For expansion into a vacuum, $P_{ext} = 0$, $w = -P_{ext}\Delta V = 0$. Since the expansion is also at constant temperature, $\Delta E = C_v\Delta T = 0$ and $q = \Delta E - w = 0$. Therefore only (d) can be correct. Answers (b) and (c) are not consistent with the first law.
33 (c) The second law says the entropy of the universe must increase for any irreversible change, so (d) is incorrect. ΔS for the system (the growing plant) is negative since the reaction products (the plant) are more ordered than the reactants.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

must hold, so $\Delta S_{\text{surroundings}}$ must have a large enough positive value to make $\Delta S_{\text{universe}} > 0$.

34 (c) Since the water absorbs its molar heat of vaporization during this process, q = 40.7 kJ mol^{-1}. Work involved in expanding the vapor against the atmosphere is

$$w = -P\,\Delta V = -P(V_{\text{vapor}} - V_{\text{liquid}}) \cong -P\,V_{\text{vapor}}$$

$$V_{\text{vapor}} = \frac{nRT}{P} = \frac{1.00\text{ mol}(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(373\text{ K})}{1\text{ atm}} = 30.6\text{ L}$$

$$w = -1.00\text{ atm}(30.6\text{ L}) \times 101.2\text{ J(L atm)}^{-1} = -3100\text{ J}$$
$$\Delta E = q + w = 40.7\text{ kJ} - 3.1\text{ kJ} = 37.6\text{ kJ}$$

35 (b) $\Delta S = \dfrac{\Delta H_{\text{vap}}}{T} = \dfrac{(40{,}700\text{ J mol}^{-1})(2\text{ mol})}{373\text{ K}} = 218\text{ J K}^{-1}$

The entropy for any phase change can be calculated in a similar manner.

36 (d) $\Delta S^{\circ} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}} = 2S^{\circ}_{\text{NH}_3} - S^{\circ}_{\text{N}_2} - 3S^{\circ}_{\text{H}_2}$

$$= [2\text{ mol}(192.3\text{ J mol}^{-1}\text{ K}^{-1}) - [1\text{ mol}(191.5\text{ J mol}^{-1}\text{ K}^{-1}) + 3\text{ mol}(130.6\text{ J mol}^{-1}\text{ K}^{-1})] = -384.6\text{ J K}^{-1} - 583.3\text{ J K}^{-1}$$
$$= -198.7\text{ J K}^{-1}$$

Since the reaction is written for 2 mol of NH_3, ΔS°_f per mole of NH_3 is

$$\Delta S^{\circ}_f = \frac{-198.7\text{ J K}^{-1}}{2\text{ mol NH}_3} = -99.4\text{ J mol}^{-1}\text{ K}^{-1}$$

The negative value of ΔS°_f means the products are more ordered than the reactants.

Can you explain why from a molecular point of view? Note that ΔG°_f and ΔH°_f of

N_2 and H_2 are 0, while S° for the elements has a finite value. Why is this so?

37 (c) For the reaction

$$\Delta G^{\circ} = \Sigma(\Delta G^{\circ}_f)_{\text{products}} - \Sigma(\Delta G^{\circ}_f)_{\text{products}}$$

$$\Delta G\text{o} = (\Delta G^{\circ}_f)_{\text{CO}_2} + \frac{1}{2}(\Delta G^{\circ}_f)_{\text{N}_2} - (\Delta g^{\circ}_f)_{\text{CO}} - (\Delta G^{\circ}_f)_{\text{NO}}$$

$$= -394.4\text{ kJ} + 0 - (-137.2\text{ kJ}) - (86.6\text{ kJ}) = -343.8\text{ kJ}$$

Since ΔG is negative, the reaction is thermodynamically spontaneous. Many environmental problems might be solved with this reaction if the right catalyst were found to initiate it.

38 (b) The chemical reaction is $Ag_2O(s) \rightarrow 2\,Ag(s) + \frac{1}{2}O_2(g)$ for which ΔG° = +10.9 kJ and ΔH° = +30.5 kJ.

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} = \frac{30.5 - 10.9}{298} = 0.0658\text{ kJ K}^{-1}$$

$$T_{\Delta G = 0} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{30.5}{0.0658} = 463\text{ K} \quad \text{or} \quad 190^{\circ}\text{C}$$

This low temperature of decomposition explains why silver is not found in nature as the oxide.

39 (b) $Ag_2O(s) \rightarrow 2\ Ag(s) + \frac{1}{2}O_2(g)$

$$\Delta G^o = +10.9\ \text{kJ}$$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-10{,}900\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\ (298\ \text{K})} = -4.40$$

$$K_p = 1.2 \times 10^{-2}$$

If your answer was (c) you forgot to use the absolute temperature.

40 (c) $\Delta G = \Delta H - T\,\Delta S$. Since T is always positive:

1 If ΔH^o is negative and ΔS^o is positive, ΔG^o is always negative so the process is always spontaneous.

2 If ΔH^o is positive and ΔS^o is negative, ΔG^o is always positive so the process is always nonspontaneous.

3 and 4 If ΔH^o and ΔS^o are both positive or both negative, the sign of ΔG^o depends on their relative values and the temperature.

41 (d)
42 (c)
43 (a)
44 (c) Thermodynamics does not predict kinetics.
45 (b)

CHAPTER 18
ELECTROCHEMISTRY

1 True
2 True
3 True
4 False: The anode is given first.
5 False: The gas-ion electrode uses a gas in electrical contact with its ion in solution. The hydrogen electrode is an example.
6 True
7 False: always negative
8 False: Electrolysis of molten NaCl yields sodium and chlorine. Electrolysis of aqueous NaCl yields NaOH, H_2, and Cl_2.
9 False: $CuSO_4 \rightleftarrows Cu^{2+} + SO_4^{2-}$ There are two equivalents of Cu per mol, so two faradays are required per mol of Cu.
10 False: The standard hydrogen potential is zero because it was defined as zero to provide a convenient reference.
11 False: Stronger reducing agents than H_2 have positive reduction potentials; stronger oxidizing agents have negative reduction potentials.
12 True
13 False: The reducing agent is Na, not Na^+. (Reducing agents are on the right side of the equation.) Na^+ has already lost its valence electron so cannot act as a reducing agent. Na will reduce Mg^{2+} to Mg.
14 True: They depend on concentrations, but not on the quantities reacting.
15 True
16 physically separate the electrode compartments, provide electrical continuity through the cell, and reduce the liquid junction potential
17 $Zn_{(s)} \mid ZnSO_{4(aq)} \parallel CuSO_{4(aq)} \mid Cu_{(s)}$
18 Zn, Cu, Zn
19 metal-metal ion

20 $2\,H_2O \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$ or $4\,OH^-(aq) \rightarrow O_2(g) + 2\,H_2O + 4\,e^-$
21 positive
22 oxidation and reduction or anode and cathode
23 negatively, oxidized
24 sodium
25 the quantity of electricity used
26 faraday
27 ampere, second
28 right, bottom
29 nonspontaneous
30 $\Delta G = -nFE$
31 (a)
32 (b)
33 (d)
34 (c)
35 (a)
36 (d)
37 (c)
38 (a) $Fe^{3+} + 3\,e^- \rightarrow Fe$

One mol of Fe is 3 equivalents so the equivalent mass is

$$\frac{56\text{ g mol}^{-1}}{3\text{ equiv mol}^{-1}} = 19\text{ g equiv}^{-1}$$

39 (b) $Ni^{2+} + 2\,e^- \rightarrow Ni$

$$\text{equiv Ni} = \frac{0.10\text{ g }(2\text{ equiv mol}^{-1})}{(59\text{ g mol}^{-1})} = 0.0034\text{ equiv}$$

$$\text{amps} = \frac{\text{equiv}}{\text{s}}(9.65 \times 10^4\text{ coulomb equiv}^{-1})$$

$$= \frac{(0.0034\text{ equiv})(9.65 \times 10^4\text{ coulomb equiv}^{-1})}{(20\text{ min})(60\text{ s min}^{-1})} = 2.7\text{ amps}$$

40 (c)

41 (d) $E_{\text{cell}} = -(-0.14) + 0.34 = 0.48$

42 (c) The half reactions are

$6\,e^- + 2\,NO_3^- + 8\,H^+ \rightarrow 2\,NO + 4\,H_2O$
$3\,Cu \rightarrow 3\,Cu^{2+} + 6\,e^-$

43 (a) The half reactions are

$$\begin{array}{ll} Zn \rightarrow Zn^{2+} + 2\,e^- & E_{\text{oxid}} = +0.76 \\ 2\,H^+ + 2\,e^- \rightarrow H_2 & E_{\text{red}} = 0 \\ \hline 2\,H^+ + Zn \rightarrow Zn^{2+} + H_2 & E_{\text{cell}} = 0.76 \end{array}$$

The Nernst equation is

$$E = E^{\circ} - \frac{0.0257}{2}\ln\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$= 0.76 - \frac{0.0257}{2}\ln\frac{(0.50)(0.30)}{(0.020)^2}$$

$$= 0.68\text{ volts}$$

44 (d) $\ln K = \dfrac{nE^{\circ}}{0.0257} = \dfrac{2(0.76)}{0.0257} = 59.1$

$$K = e^{59.1} = 4.7 \times 10^{25}$$

45 (c)

CHAPTER 19
COVALENT BONDING

1 True
2 False: Molecular orbitals result from combinations of atomic orbitals. They completely replace the atomic orbitals, so atomic orbital overlap is not part of the MO theory.
3 False: Depending on the number of *p* orbitals used, *sp*, sp^2, or sp^3 hybrid orbitals can result.
4 True
5 True
6 False: A triple bond has one sigma and 2 pi bonds
7 True
8 True
9 False: The relative energy of σ_{2p} to π_{2p} depends on the total number of valence electrons and is different in N_2 and O_2.
10 True: B_2 has bond order of 1 while C_2 has bond order of 2.
11 True: Bond order of Be_2 is zero. The molecule has never been observed.
12 False: The higher the bond order, the shorter the bond, so they are inversely proportional.
13 True: The greater the overlap, the stronger the bond.
14 True: One valence electron in the σ_{2s} bonding orbital.
15 True
16 valence bond, molecular orbital
17 sigma
18 pi
19 sigma, pi
20 three
21 sp^2
22 tetrahedron
23 bonding
24 antibonding, *p*
25 sigma two *s* star
26 sigma
27 π^*_{2pz}
28 Three; CO has 10 electrons so is isoelectronic with N_2 and has the same configuration and bond order
29 unstable or does not exist
30 antibonding
31 (a)
32 (c)
33 (c) This is part of MO theory, not VB theory.
34 (a) *sp* hybrid orbitals give a linear molecule.
35 (c)
36 (b)
37 (b) NO^+ has 10 valence electrons, is isoelectronic with N_2, and has the same configuration. (See Table 19-2 in the text) There are two antibonding and eight bonding electrons.
38 (b) There is one sigma bond between each pair of bonded atoms. There are also two pi bonds between the carbon atoms.

39 (d) The configurations and bond orders are: NF (same as O_2 in text Table 19-2), BN (same as C_2 in text Table 19-2), BeC (same as B_2 in text Table 19-2), and He_2^+ $\sigma_{1s}^2\ \sigma_{1s}^*$ The bond order in He_2^+ is 1/2.

40 (b)

	Bonding e^-	Antibonding e^-	Bond order
O_2	8	4	2
O_2^+	8	3	5/2
O_2^-	8	5	3/2
O_2^{2-}	8	6	1

The highest bond order gives the shortest and strongest bond.

41 (c)
42 (b)
43 (d) XeF_4 has 4 bonding electron pairs and 2 lone pairs, so it has an octahedral arrangement which requires d^2sp^3 hybridization on the Xe. The molecular geometry is square planar because the two lone pairs occupy two lobes of the octahedron but are not counted in the molecular geometry; hence all atoms are in the same plane with the four fluorine atoms at the corners of a square.

44 (e)
45 (e)

CHAPTER 20
THE NONMETALS

1 False: stannous
2 True
3 False: *ate* indicates a high oxidation state for an anion.
4 False: Bismuth oxide chloride. Bismuth hypochlorite would be $Bi(OCl)_3$.
5 False: Gold, silver, and platinum do not react with most acids. The reaction of HNO_3 with metals does not give H_2.
6 True
7 True
8 True
9 False: at 4°C.
10 False: HF is a weak acid.
11 True
12 False: There is very little hydrogen bonding in H_2S, so it has a low boiling point.
13 False: Thermal decomposition of NH_4NO_2 gives N_2.
14 True
15 True
16 $CuSO_4$, HNO_2, $NaBrO_3$, CaC_2, $HBrO_2$, MnO_4^-, $Al(HSO_4)_3$, Ag_2CO_3
17 copper(I) iodide, lead(II) hypochlorite, cobalt(III) phosphate, tin(IV) nitrite
18 hydrides
19 O_2 and O_3
20 $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$
21 I^-
22 $HClO_4$
23 F_2

24 $S + O_2 \rightarrow SO_2$
$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$
$H_2S_2O_7 + H_2O \rightarrow 2\ H_2SO_4$
25 N_2O
26 NH_3
27 phosphate rock [$Ca_3(PO_4)_2$], coke, and sand
28 diamond and graphite
29 bicarbonates or hydrogen carbonates and carbonates
30 Xenon plus oxygen or fluorine
31 (c)
32 (a)
33 (d)
34 (c)
35 (a)
36 (d)
37 (c)
38 (b)
39 (c)
40 (b)
41 (a)
42 (b)
43 (d)
44 (b)
45 (d)

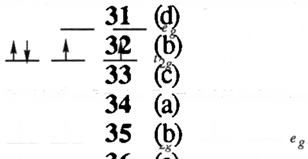
CHAPTER 21
THE REPRESENTATIVE METALS AND METALLOIDS

1 True
2 True: The small size of Li^+ causes strong hydrolysis.
3 True: See text for an explanation of this paradox.
4 False: Only Li forms the oxide. Na forms the peroxide. K, Rb, and Cs form superoxides.
5 True
6 True
7 True
8 True
9 False: Be does not.
10 False: HCO_3^- is present in temporary hard water.
11 True
12 True
13 False: +2 is a more stable state.
14 False: Bi^{+3} hydrolyzes strongly.
15 True
16 luster, good conductor, easily oxidized
17 +1
18 seawater
19 beryllium
20 CaO, $Ca(OH)_2$, $CaCO_3$
21 Ca^{2+}, Mg^{2+}, Fe^{3+}
22 temporary
23 $Ca(OH)_2$, Na_2CO_3

24 $Ca(OH)_2$
25 Al_2O_3, NaOH, $Al(OH)_3$, Al_2O_3
26 Al, O_2 and F_2
27 a tough layer of Al_2O_3
28 β-tin or white tin to α-tin or gray tin
29 oxidizing, lead storage cells
30 electron deficient, three center
31 (b)
32 (c)
33 (a)
34 (c)
35 (b)
36 (d)
37 (c)
38 (d)
39 (b)
40 (d)
41 (a)
42 (b)
43 (d)
44 (a)
45 (c)

CHAPTER 22
THE TRANSITION METALS

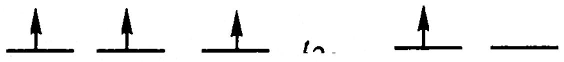
1 True
2 True
3 False: The ns^2 electrons are lost first in ionization.
4 True
5 False: It increases to the center of the series then decreases.
6 True
7 True
8 False: Octahedral.
9 False: Crystal-field theory does.
10 True
11 True
12 False: F^- is a weak-field ligand.
13 False: Only for d^4, d^5, d^6 and d^7 ions.
14 False: They give high-spin configurations.
15 False: Only in tetrahedral geometry.
16 3*d*
17 +2
18 inactive
19 octahedral, d^2sp^3 or sp^3d^2
20 diamminetetrachlorocobaltate(III) ion
21 $[CrBr_2(H_2O)_2(NH_3)_2]^+$
22 2, 4, 6
23 6
24 t_{2g}, $\overset{*}{e_g}$
25 ligand-field splitting energy, Δ
26 Fe^{3+}, weak, Cl^-, high
27 2, 1
28 4, assymmetric, chiral, optical isomers or enantiomers
29 polydentate or chelating agents



30 Fe, Co, Ni
31 (d)
32 (b)
33 (c)
34 (a)
35 (b)
36 (a)

37 (b) Cr^{2+} has d^4 configuration. The strong field d-orbital energy diagram is

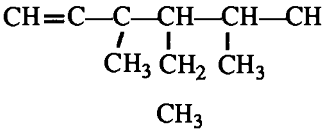
38 (d) Cr^{2+} had d^4 configuration. The weak-field d-orbital energy configuration is



39 (b) as *trans* forms
40 (d)
41 (b)
42 (b)
43 (c)
44 (d)
45 (c)

CHAPTER 23
ORGANIC CHEMISTRY

1 True
2 False: Carbon always forms four bonds in organic compounds but if double or triple bonds are formed it will bond to less than four atoms.
3 False: They may have branched chains.
4 False: There is no such compound as isopropane.
5 True
6 False: An alkyne.
7 False: The π electrons are delocalized.
8 True
9 False: It is a secondary alcohol.
10 True: They give aldehydes.
11 True
12 False: It is the ketone of propane.
13 True: Presence of another functional group may change the acid strength considerably.
14 True
15 True
16 2–methylpropane
$CH_3—CH_2—CH_3$

17


$CH{=}C—\underset{CH_3}{C}—\underset{CH_2}{CH}—\underset{CH_3}{CH}—CH$

CH_3

18 4-ethyl-2-hexene (the double bond is given the lower number)

19 nine
20 2-chloropropane (why not 1-chloropropane?)
21 toluene
22 1-3,dimethylbenzene
23 esters
24 2-butanol
25 ketone, 2-propanone, acetone
26 propyl ethanoate, n-propyl acetate
27 primary
28 condensation
29 asymmetric
30 peptide
31 (b)
32 (d)
33 (d)
34 (c)
35 (a)
36 (c)
37 (c)
38 (d)
39 (d)
40 (a)
41 (c)
42 (c)
43 (b)
44 (d)
45 (a)

CHAPTER 24
NUCLEAR PROCESSES

1 True
2 False: Alpha emission would reduce the mass number by 4 and the atomic number by 2.
3 True
4 True
5 True
6 True
7 False: $^{238}_{92}U/^{206}_{82}Pb$ and $^{14}_{6}C/^{12}_{6}C$ ratios are used.

8 True
9 False: Nuclei below the belt of stability have a low neutron to proton ratio; they increase this ratio by positron decay or electron capture.
10 False: Neutron emission is rare. These nuclei decay by beta emission.
11 True
12 True
13 True
14 True
15 False: Text Section 24-6 gives many common uses.
16 Alpha particles, beta particles, gamma rays
17 gamma, mass number, and atomic number
18 Geiger-Muller, scintillation
19 radioactive decay series
20 4 hours
21 $^{238}_{94}U/^{206}_{82}Pb$

22 artificial or induced radioactivity
23 mass, positive
24 belt of stability
25 one, increases
26 increases, decreases
27 fission, slow, or thermal neutron
28 neutrons and protons, loss in mass or mass defect, nuclear binding energy
29 intermediate, more
30 critical mass
31 (a)
32 (d)
33 (c)
34 (d)
35 (c) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.0\ \text{yr}} = 0.139\ \text{yr}^{-1}$

$\ln \frac{x}{1} = -(0.139\ \text{yr}^{-1})(7.0\ \text{yr}) = -0.973$

$x = e^{-0.973} = 0.378$

36 (a) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5670\ \text{yr}} = 1.22 \times 10^{-4}\ \text{yr}^{-1}$

$\ln 0.990 = -(1.22 \times 10^{-4}\ \text{yr}^{-1})t$

$t = 420$ years

37 (d)
38 (a)
39 (b)
40 (d)
41 (b) mass of 6 neutrons = 6(1.00867) = 6.05202 amu
mass of 6 protons = 6(1.00728) = <u>6.04368</u> amu
12.09570 amu
mass loss = 12.09570 − 11.99671 = 0.09899 amu

42 (a) $0.09899\ \text{amu} \left(\frac{1\ \text{g}}{6.023 \times 10^{23}\ \text{amu}}\right) \frac{10^{-3}\ \text{kg}}{\text{g}} = 1.643 \times 10^{-28}\ \text{kg}$

$E = mc^2 = (1.643 \times 10^{-28}\ \text{kg})(2.998 \times 10^{-8}\ \text{m s}^{-1})^2 = 1.477 \times 10^{-11}\ \text{J}$

or

$\frac{1.477 \times 10^{-11}\ \text{J}}{12\ \text{nucleons}} = 1.231 \times 10^{-12}\ \text{J nucleon}^{-1}$

43 (c)
44 (b)
45 (c)

UNITS, CONSTANTS, AND CONVERSION EQUATIONS (See also Appendix B)

SI BASE UNITS

Physical quantity	**Name of SI unit**	**Symbol**
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Luminous intensity	candela	cd
Amount of substance	mole	mol

SELECTED SI DERIVED UNITS

Physical quantity	**Unit**	**Symbol**	**Definition**	
Force	newton	N	m kg s^{-2}	
Pressure	pascal	Pa	N m^{-2}	= m^{-1} kg s^{-2}
Energy, work	joule	J	N m	= m^{2} kg s^{-2}
Power	watt	W	J s^{-1}	= m^{2} kg s^{-3}
Electric charge	coulomb	C	A s	
Electric potential, electromotive force	volt	V	J C^{-1}	= m^{2} kg s^{-3} A^{-1}
Frequency	hertz	Hz	s^{-1}	

METRIC PREFIXES

Multiple	10^{18}	10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{2}	10^{1}
Prefix	exa	peta	tera	giga	mega	kilo	hecto	deka
Symbol	E	P	T	G	M	K	h	da

Submultiple	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}
Prefix	deci	centi	milli	micro	nano	pico	femto	atto
Symbol	d	c	m	μ	n	p	f	a

PHYSICAL CONSTANTS

Constant	**Symbol**	**Numerical value**
Avogadro's number	N	6.022137×10^{23} mol^{-1}
Faraday's constant	$\mathscr{F}$	9.648531×10^{4} C mol^{-1}
Ideal-gas constant	R	8.31451 J K^{-1} mol^{-1} 8.31451 dm^3 kPa K^{-1} mol^{-1} 8.20578×10^{-2} L atm K^{-1} mol^{-1}
Planck's constant	h	6.626076×10^{-34} J s
Rydberg's constant	R	$1.097373153 \times 10^{7}$ m^{-}1
Molar volume of ideal gas, STP	V_m	22.4141 L mol^{-1}
Electron charge	e	$1.6021773 \times 10^{-19}$ C
Electron rest mass	m_e	9.109390×10^{-28} g 5.485799×10^{-4} amu
Neutron rest mass	m_n	1.674929×10^{-24} g 1.008665 amu
Proton rest mass	m_p	1.672623×10^{-24} g 1.007276 amu
Speed of light in a vacuum	c	2.99792458×10^{8} m s^{-1} (exactly)

CONVERSION EQUATIONS

Conversion	**Equation**
Energy	
Calories–joules	1 cal = 4.184 J (exactly)
Electronvolts–joules	1 ev = 1.602×10^{-19} J
Liter atmospheres–joules	1 L atm = 101.3 J
Length	
Ångstrom units–meters	1 Å = 10^{-10} m
Ångstrom units–nanometers	1 Å = 10^{-1} nm
Inches–centimeters	1 in = 2.54 cm (exactly)
Yards–meters	1 yd = 0.9144 m (exactly)
Volume	
Liters–cubic decimeters	1 L = 1 dm^3
Quarts (US)–liters	1 qt = 0.9464 L

Conversion	**Equation**
Mass	
Ounces (avoirdupois)–grams	1 oz = 28.35 g
Pounds (avoirdupois)–kilograms	1 lb = 0.4536 kg
Pressure	
Atmospheres–kilopascals	1 atm = 101.3 kPa
Atmospheres–millimeters of mercury	1 atm = 760.0 mmHg
Atmospheres–pascals	1 atm = 1.013×10^{5} Pa
Atmospheres–torr	1 atm = 760.0 Torr
Bars–pascals	1 bar = 10^{5} Pa