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Chemistry Concepts and Problems

A Self-Teaching Guide

Second Edition

Clifford C. Houk, Ph.D. Richard Post, M.A.



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Preface

In our years of teaching the fundamental concepts of chemistry to students with widely divergent backgrounds, levels of preparation, career goals, and motivation, the most frequently asked question by those students has been: "Do you have something that I can study on my own?" Followed immediately by: "I need some other review material" or "This is the first time I have encountered this stuff, so I need to start from scratch" or "It has been three years since my high school chemistry course. I need something to refresh my memory."

This book has been written to meet such needs. It can stand alone as a "first look" at chemistry or may be used as a supplement to any of the many excellent textbooks or methods of instruction currently in use. The material presumes no previous exposure to chemistry and requires only simple algebra.

There are no secrets. Each chapter includes an introductory statement, a list of objectives, and the main teaching section, which consists of frames of programmed material with constant practice exercises. Each chapter closes with a self-test. You can use this self-test to assess whether you have mastered the chapter well enough to continue and to identify weaknesses that require additional study.

The topics presented are usually covered early in a general introductory course. We have minimized "heavy" theoretical discussions, while emphasizing descriptive and practical concepts. There is enough theoretical explanation to provide a basis for understanding the material but not so much that you will get bogged down trying to work through the book.

CCH RP

January 1, 1996 Athens, Ohio

How to Use This Book

You can use *Chemistry: Concepts and Problems* as a self-instructional text requiring no chemistry background or as a supplementary text for any general chemistry course. Each chapter is divided into objectives, a programmed study section, a self-test, and test answers.

Objectives. By examining the chapter objectives, you can determine what information is contained in the chapter. If you already know the material, take the self-test at the end of the chapter. Review those questions you missed by checking the frame references given with the answer to each question.

Programmed study frames. The body of each chapter is divided into numbered frames. Each frame contains new information, a problem, or an example of a concept with one or more questions for you to answer. Answers for the questions in each frame are given below the questions. Cover the book's answers with your hand or a piece of paper. Try to answer each question yourself and then compare your answer with the printed answer. If your answer does not agree with the printed one, reread the frame and try to determine why. Each frame is built upon preceding frames. Therefore, if the material is new to you, go through the frames in sequence. Skipping ahead will cause you to miss important information or practice.

Self-test. The self-test at the end of each chapter will help you to determine if you have mastered the chapter material. After completing the chapter, take the test. Refer back to the chapter only if you need formulas or tables to answer specific questions. Compare your answers with those given immediately following the test. If your answers do not agree with the printed ones, review the appropriate frames cited after each answer.

The authors assume no prerequisites except simple high school algebra. However, each chapter builds upon the information provided in previous chapters, so we recommend that the chapters be covered in sequence.

This book has been used by thousands of students both with and without background in chemistry. They have successfully learned from it, and we hope that you will, too.

Although we have tried to make this book as useful as possible to the student, any suggestions for improving future revisions would be appreciated. Please address your comments to:

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Acknowledgments

We wish to thank all those students who used the first edition and took the time to write to us and to John Wiley & Sons, Inc., to express their gratitude for helping them understand chemistry and successfully complete a required chemistry course. They were high school, nursing school, junior college, technical school, and university students of all ages. It is because of them we have written this second edition.

We also wish to thank those faculty who thought enough of the book that they adopted it for classroom use or recommended it as a self-paced, "second opinion" study guide.

We wish to thank our editor, Judith McCarthy, and our publisher, John Wiley & Sons, Inc., for having the foresight and courage to publish a second edition after several successful printings. We also thank the Wiley editorial and production staffs for their very thorough editorial comments and enthusiastic encouragement during the preparation of this manuscript.

Finally, we wish to thank our families, who suffered through the preparation of the original manuscript and are still with us today to further enjoy the fruits of their earlier labors with minimal disruption of their current household routines.

_____1 Atomic Structure, Periodic Table, Electronic Structure

There is a *smallest* unit of substance. This smallest unit may be only a single atom or a group of atoms chemically joined together.

This chapter deals with the structure of the atom, which is the very backbone of chemistry. In this chapter we introduce the three basic subatomic particles in an atom, their arrangement in the atom, and the similarities of this arrangement revealed by the position of the elements in the periodic table. A clear understanding of this chapter will give you a sound basis for learning chemistry.

OBJECTIVES

After completing this chapter, you will be able to

- define, describe, or illustrate: proton, neutron, electron, atom, nucleus, atomic number, shell, orbital, subshell, alkali metal, noble gas, halogen, alkaline earth, period, group, family, oxide, ductile, malleable, metal, nonmetal, metalloid, and Bohr model of an atom;
- determine the numbers of protons, neutrons, and electrons in a neutral atom when given its mass number and atomic number;
- compare and contrast the three fundamental particles in an atom according to mass and charge;
- determine the maximum number of electrons any given shell can hold;
- determine the maximum number of orbitals in any given shell;
- write the electron configuration for any element;
- determine what element is represented when given its electron configuration;
- use the periodic table to locate different families of elements and determine whether an element is a metal, nonmetal, or metalloid.
- An atom, the smallest unit of an element, is composed primarily of three fundamental particles: electrons, protons, and neutrons. The combination of these par-

| Each element has a unique combination of protons and electrons in its atoms. The combination of electrons and protons in an atom of one element is different from that in an atom of any other element. Since each element has a known unique number of protons and electrons in its atoms, would it be possible to identify a element if you know the number of protons and electrons in its atoms? Answer: yes (if you could compare the number of electrons and protons in your unknown atom with a list of the electrons and protons in atoms of each known element) Protons are particles with a positive (plus) charge. Electrons are particles with negative (minus) charge. Unless otherwise stated, an atom is assumed to be neutrally with the positive and negative charges being equal. In any neutral atom, the number of electrons (having a negative charge) is always equal to the number of proton (having a positive charge). A boron atom contains five protons. We assume the atom to be neutral. Ho many electrons must it have? Answer: five An atom contains eight electrons. How many protons does it contain? Answer: eight Each element has a unique number of electrons and protons in its atoms. Since the number of electrons in a neutral atom is equal to the number of protons, do you think we can identify an element if we know just the number of protons in its atoms? Answer: yes (if we could compare the number of protons in an atom of the unknown element) | | n an atom is distinct for each element. An atom of the element radon is sed primarily of a specific combination of what three basic particles? |
|---|--|--|
| tons. Each atom of the same element has the same combination of protons at electrons. An atom of the element helium in outer space has (the same, a differer combination of electrons and protons as that of an atom of heliu on earth. **Answer:* the same** Each element has a unique combination of protons and electrons in its atoms. To combination of electrons and protons in an atom of one element is different fro that in an atom of any other element. Since each element has a known unique number of protons and electrons in its atoms, would it be possible to identify a element if you know the number of protons and electrons in its atoms? | Answer: | electrons, protons, neutrons (any order) |
| Each element has a unique combination of protons and electrons in its atoms. The combination of electrons and protons in an atom of one element is different from that in an atom of any other element. Since each element has a known unique number of protons and electrons in its atoms, would it be possible to identify a element if you know the number of protons and electrons in its atoms? | tons. E | ach atom of the same element has the same combination of protons and as. An atom of the element helium in outer space has (the same, a different) combination of electrons and protons as that of an atom of helium |
| combination of electrons and protons in an atom of one element is different fro that in an atom of any other element. Since each element has a known unique number of protons and electrons in its atoms, would it be possible to identify a element if you know the number of protons and electrons in its atoms? | Answer: | the same |
| Protons are particles with a positive (plus) charge. Electrons are particles with negative (minus) charge. Unless otherwise stated, an atom is assumed to be neutral with the positive and negative charges being equal. In any neutral atom, the nur ber of electrons (having a negative charge) is always equal to the number of proton (having a positive charge). A boron atom contains five protons. We assume the atom to be neutral. Ho many electrons must it have? Answer: five An atom contains eight electrons. How many protons does it contain? Answer: eight Each element has a unique number of electrons and protons in its atoms. Since the number of electrons in a neutral atom is equal to the number of protons, do you think we can identify an element if we know just the number of protons in its atoms? Answer: yes (if we could compare the number of protons in an atom of the unknown eleme | combin that in number | ation of electrons and protons in an atom of one element is different from an atom of any other element. Since each element has a known unique of protons and electrons in its atoms, would it be possible to identify an |
| negative (minus) charge. Unless otherwise stated, an atom is assumed to be neutral with the positive and negative charges being equal. In any neutral atom, the number of electrons (having a negative charge) is always equal to the number of proton (having a positive charge). A boron atom contains five protons. We assume the atom to be neutral. Ho many electrons must it have? Answer: five An atom contains eight electrons. How many protons does it contain? Answer: eight Each element has a unique number of electrons and protons in its atoms. Since the number of electrons in a neutral atom is equal to the number of protons, do yo think we can identify an element if we know just the number of protons in its atoms? Answer: yes (if we could compare the number of protons in an atom of the unknown eleme | | |
| An atom contains eight electrons. How many protons does it contain? Answer: eight Each element has a unique number of electrons and protons in its atoms. Since the number of electrons in a neutral atom is equal to the number of protons, do you think we can identify an element if we know just the number of protons in atoms? Answer: yes (if we could compare the number of protons in an atom of the unknown element) | negative with the ber of e (having A b | e (minus) charge. Unless otherwise stated, an atom is assumed to be neutral, e positive and negative charges being equal. In any neutral atom, the numlectrons (having a negative charge) is always equal to the number of protons a positive charge). oron atom contains five protons. We assume the atom to be neutral. How |
| Answer: eight Each element has a unique number of electrons and protons in its atoms. Since the number of electrons in a neutral atom is equal to the number of protons, do you think we can identify an element if we know just the number of protons in atoms? Answer: yes (if we could compare the number of protons in an atom of the unknown element) | Answer: | five |
| number of electrons in a neutral atom is equal to the number of protons, do you think we can identify an element if we know just the number of protons in it atoms? | | |
| | number think w | of electrons in a neutral atom is equal to the number of protons, do you we can identify an element if we know just the number of protons in its |
| with a list or table of the number of protons in atoms of every known element) | | yes (if we could compare the number of protons in an atom of the unknown element st or table of the number of protons in atoms of every known element) |

The periodic table is a very useful table describing the atoms of every known element. A complete periodic table is included in the Appendix of this book. Each box in the periodic table represents an element. The one- or two-letter symbol in each box is a shorthand notation used to represent a neutral atom of an element. The symbol "C" represents a neutral atom of the element carbon. The symbol "He" represents a neutral atom of the element helium.

The number of protons in an atom is listed above each symbol. (Ignore the number underneath the symbol for the time being.)



| | An atom of carbon has six protons. How many protons does an atom of helium have? |
|----|--|
| | Answer: two |
| | Note: The table of atomic weights, located in the Appendix along with the periodic table, lists all the elements alphabetically and gives the symbol for each. (Ignore the atomic weights for now.) You'll be using the periodic table and the table of atomic weights throughout this book. |
| 8 | The number of protons in an atom of an element is called its atomic number. What is the atomic number of the element helium (He)? |
| | Answer: 2 |
| 9 | The element zinc (Zn) has an atomic number of 30. How many protons does an atom of zinc contain? |
| | Answer: 30 |
| 10 | A neutral atom of zinc contains how many electrons? |
| | Answer: 30 (the same as the number of protons) |
| 11 | Using the periodic table, determine the number of electrons in a neutral atom of copper (Cu). |
| | Answer: 29 (the same as the number of protons) |
| | |

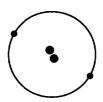
BOHR ATOMIC MODEL



A Danish physicist, Niels Bohr, came up with a model that pictured the atom with a nucleus of protons in the center and electrons spinning in an orbit around it (similar to the movement of the planets around the sun). The following Bohr model contains one orbiting electron and a nucleus of one proton.



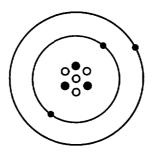
What is the atomic number of the element represented? _____ What element is represented? Answer: 1 (The atomic number equals the number of protons.); hydrogen (H). An electron always carries a negative charge. A proton carries a charge exactly 13 opposite that of the electron. A proton must therefore have a (negative, positive, neutral) _____ charge. Answer: positive An electron has very little mass when compared to a proton. It takes about 1836 14 electrons to equal the weight of just one proton. In a hydrogen atom consisting of just one proton and one electron, the greatest proportion by weight is accounted for by the (electron, proton) _____. Answer: proton (The proton accounts for about 99.95% of the weight of a hydrogen atom and the electron 0.05%.) The element helium (He), represented by the Bohr model below, has an atomic 15 number of _____.



Answer: 2

| The neutral atom of He contains now many protons? electrons? |
|--|
| Answer: two; two |
| The weight of an atom of helium is not totally accounted for by the protons and electrons. A third subatomic particle, the neutron, is responsible for the additional weight. The neutral atoms of all elements except the most common form of the element hydrogen have one or more neutrons in the nucleus of their atoms. The diagram below shows the neutrons in the corrected Bohr model of helium. Since a neutral atom contains equal numbers of negatively charged electrons and positively charged protons, what type of electrical charge do you think is possessed by a neutron? (negative, positive, no charge) |
| |
| Answer: no charge (The name neutron means a neutral particle.) |
| A neutron is slightly heavier than a proton. Of the primary fundamental particles in an atom: |
| (a) which is the lightest in weight? |
| (b) which is the heaviest? |
| (c) which is between the other two in weight? |
| Answer: (a) the electron; (b) the neutron; (c) the proton |
| In the Bohr model of a lithium atom shown on page 6, which subatomic particle(s is (are) represented by the circular orbits shown by the larger circles? |
| Answer: electrons; protons and neutrons |
| If the negative charge of an electron is represented by -1 , the charge on the protor would be $(-1, +1, neutral)$ and the charge on the neutron would be $(-1, +1, neutral)$. |
| |

Answer: +1; neutral



Neutrons can be found in all atoms of all elements except the most common form of the simplest element. Identify that element. (Hint: If you don't remember, reread frame 17.)

Answer: hydrogen

You have just learned the names, charges, and relative sizes of the fundamental particles that constitute an atom. You have also been shown one model representing the arrangement of these particles in an atom.

We have referred you to the periodic table and hinted that atoms with certain numbers of protons and electrons are located in a specific place in that table. You learned from your introduction to the periodic table that each atom is identified by some symbol.

We continue this chapter by looking more closely at the periodic table. You will be introduced to specific groups of elements and their physical and chemical properties as they relate to their location on the periodic table. We expand upon the use of symbols and the numbers of each particle in an atom as we prepare to study a second model of an atom.

PERIODIC TABLE

Look at the periodic table. An atom of each element is represented by a one- or two-letter symbol such as "C" for carbon and "Al" for aluminum. These symbols serve as shorthand notation for the elements. The shorthand symbol in each case indicates a neutral atom. The symbol "Ca" represents a neutral atom of the element calcium. Remembering the definition of a neutral atom, you know that Ca contains 20 protons and how many electrons?

Answer: 20 (A neutral atom contains an equal number of protons and electrons.)

The periodic table of the elements is made up of several rows and some columns. The rows are called **periods** and the columns are called **groups**. The groups are

| | included in which group? |
|----|--|
| | Answer: Group IIA |
| 24 | The elements Li, Be, B, C, N, O, F, and Ne are all members of a (group, period) |
| | Answer: period |
| 25 | Groups are often called families because the elements that make up the groups or families have similar chemical properties. Argon (Ar) is part of Group VIIIA. It is a rather unreactive gas. Since families or groups of elements have similar properties, would you expect krypton (Kr) to be a highly reactive gas? |
| | Answer: no (All of the elements in Group VIIIA are rather unreactive.) |
| 26 | Because all Group VIIIA elements are rather unreactive and are gaseous at room temperature, they have been named the noble gas family. An element in Group VIIIA may be generalized by its family name as a(n) gas. |
| | Answer: noble |
| 27 | Group IA on the left side of the chart is often called by the family name of alkali metals (with the exception of hydrogen). These elements can react vigorously with water to form strong alkaline solutions. If a friend told you that aluminum (Al) was an alkali metal would he be right or wrong? |
| | Answer: wrong (Aluminum is located in Group IIIA and the alkali metals are all located in Group IA.) |
| 28 | Group IIA elements are known as the alkaline earth metals because the oxides of these metals (chemical compounds of the metals and oxygen) form alkaline solutions in water. The element potassium (K) can be classified as a(n) (noble gas, alkaline earth, alkali metal) |
| | Answer: akali metal (Group IA) |
| 29 | The element Ba (barium) can be classified as a(n) (alkali metal, alkaline earth, noble gas) |
| | Answer: akaline earth (Group IIA) |
| 30 | An unknown element is placed in water. A vigorous reaction takes place, and the result is an alkaline solution. Of which family is the element probably a member? (alkaline earth, alkali metal, noble gas) |

Answer: alkali metal (Alkali metals react directly with water to form alkaline solutions. The oxides of alkaline earth elements react with water to form alkaline solutions.)

| 31 | The elements in Group VIIA are known as the halogens, which means "salt formers." Elements from the halogen family combine with metals to form compounds known as salts. Common table salt (NaCl) is made up of sodium (Na) and chlorine (Cl). These two elements (Na and Cl) are members of what families or groups? Na: |
|--------|---|
| | Answer: Group IA, the alkali metals (either answer is acceptable); Group VIIA, the halogens (either answer is acceptable). |
| 32 | Strontium (Sr) is an element in the family. Iodine (I) is an element in the family. |
| | Answer: alkaline earth; halogen |
| METALS | , NONMETALS, AND METALLOIDS |
| 33 | The periodic table can also be divided into just three classes of elements—the metals, the nonmetals, and the metalloids. In the periodic table, you may have noticed a steplike line. Elements to the left of this line can be classified as metals (with the exception of hydrogen). A friend informed you that the element Ti (titanium) is a metal. Is your friend correct? |
| | Answer: Yes, titanium can be classified as a metal. |
| 34 | Certain properties are characteristic of metals. Metals are usually malleable (can be beaten into fine sheets) and ductile (can be drawn into wires). Gold leaf is a very thin sheet of gold. In making gold leaf, we are using what common property of metals? |
| | Answer: the property of malleability |
| 35 | Besides being malleable and ductile, metals are also good conductors of heat and electricity. Copper is useful in making electrical wiring. What two metallic properties would be useful in electrical wiring? |
| | Answer: The metal is a conductor of electricity and it is ductile (can be drawn into fine wires) |

| 36 | (with the exception of mercury, which is liquid at room temperature). Metal cooking utensils take advantage of what two properties of metal? (conducts electricity, conducts heat, ductile, solid) |
|----|---|
| | Answer: Metal conducts heat and is solid. |
| 37 | Nonmetals are located on the right side of the steplike line in the periodic table. Which of the following families of elements are classified as nonmetals? (halogens, alkaline earths, noble gases) |
| | Answer: halogens and noble gases |
| 38 | Nonmetals have properties almost opposite those of metals. Nonmetals are usually very brittle and do not conduct electricity or heat well. Most nonmetals are gases at ordinary temperatures, although some are liquids or solids. An unknown element exists as a gas at room temperature. How would you classify the unknown element, as a metal or as a nonmetal? |
| | Answer: nonmetal (With the exception of mercury, which is liquid at room temperature, all metals are solid at ordinary room temperature.) |
| 39 | An unknown element is a solid but does not conduct electricity. The element is probably a (metal, nonmetal) |
| | Answer: nonmetal (Some nonmetals are solids, although most are gases at room temperature. Nonmetals do not conduct electricity well, but metals usually do.) |
| 40 | A third category of elements is classified as metalloids because they don't clearly fall into either the metal or nonmetal categories. Metalloids border the steplike line on the periodic table and include elements such as silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), boron (B), tellurium (Te), polonium (Po), and astatine (At). Metalloids could be expected to have some of the properties of metals and some of the properties of |
| | Answer: nonmetals |
| 41 | Which of the following elements is (are) classified as metalloid: silicon (Si), phosphorus (P), and sulfur (S)? |
| | Answer: silicon |

MASS AND MASS NUMBER

The following box represents the element sulfur (S) on the periodic table.

16 **S** 32.06

The number 16 represents the atomic number of the element sulfur and also represents the number of protons in an atom of sulfur.

Locate the element nitrogen (N) on the periodic table. The number of protons in an atom of nitrogen is ______.

Answer: seven (same as the atomic number)

By convention, the atomic number is often written as a subscript preceding an element's symbol. The symbol and number ₇N indicates nitrogen with atomic number of 7. Thus, ₂₉Cu indicates the element copper with an atomic number of _____.

Answer: 29

Almost all of the mass of an atom (more than 99.9%) is attributed to the nucleus. The nucleus is made up largely of which two fundamental particles? (protons, electrons, neutrons)

Answer: protons and neutrons

This is the first time we have referred to mass in this book. Mass is a measure of the amount of matter. The mass of an object determines its weight. Weight is the effect of gravity on mass. An astronaut may weigh 180 pounds on earth and 30 pounds on the moon and be weightless in space. That person's mass, however, does not change. In the remaining chapters, we will follow the common practice of most chemistry texts and refer to the masses of objects as their weights to prevent confusion between the two terms. In this chapter and Chapter 2 we will use the term mass.

Adding together the number of protons and neutrons in the nucleus of an atom results in what is known as the mass number of the atom. The mass number is simply the number of protons added to the number of neutrons in an atom. Suppose an atom has a mass number of 15. The atom contains eight protons. How many neutrons does it have?

Answer: seven (The total number of neutrons and protons is 15, the mass number. If eight protons are present, there must be seven neutrons, since 15 - 8 = 7.)

| 46 | The element ₁₈ Ar has a mass number of 40. How many neutrons does its atom contain? |
|----|--|
| | Answer: 22 ($_{18}$ Ar indicates an atomic number of 18 for element Ar. An atomic number of 18 indicates 18 protons. Mass number is equal to protons plus neutrons, 40 = 18 + 22.) |
| 47 | By convention, the mass number is often written as a superscript in front of the element symbol. ⁴⁰ ₁₈ Ar indicates the element argon with a mass number of 40 and atomic number of 18. ²⁰⁰ ₈₀ Hg indicates the element mercury with a mass number of and an atomic number of Answer: 200; 80 |
| 48 | ⁵² ₂₄ Cr indicates chromium with protons and neutrons. Answer: 24; 28 |
| 49 | The element scandium (Sc) contains 21 protons and 24 neutrons in its atom. Write the atomic number and mass number to complete the following symbolic expression. Sc |
| | Answer: 45 Sc |
| 50 | The letter A represents an unknown element. Use the periodic table to identify the element. 23 11 11 |
| | Answer: sodium, Na (The subscript 11 represents the atomic number. Sodium is the element with an atomic number of 11.) |
| 51 | Unknown element X has a mass number of 55 and contains 30 neutrons in its atoms. Identify element X. |
| | Answer: Mn (manganese) (A mass number of 55 indicates 55 protons and neutrons. Subtract 30 neutrons from 55; this leaves 25 protons. The number of protons is equal to the atomic number, 25. Manganese has an atomic number of 25.) |
| 52 | Be (beryllium) contains five neutrons in its atom. Complete the symbolic expression. Be |
| | Answer: ${}_{4}^{9}$ Be (Find the atomic number of Be on the periodic table. The atomic number indicates the number of protons. Add the neutrons, five, to the protons, four, to find the mass number.) |

| 53 | |
|----|--|
| 53 | |
| 53 | |
| 53 | |
| 53 | |
| 25 | |
| 22 | |
| | |
| | |
| | |

| Fill i | n the | required | information | for | the | following | element: | 1 H |
|--------|-------|----------|-------------|-----|-----|-----------|----------|-----|
|--------|-------|----------|-------------|-----|-----|-----------|----------|-----|

- (a) Atomic number is _____.
- (b) Mass number is _____.
- (c) Number of protons:
- (d) Number of neutrons:

Answer: (a) 1; (b) 1; (c) one; (d) zero

You have just learned some properties of metals and nonmetals, the common names of a few families of elements, and how to determine the numbers of protons, neutrons, and electrons in an atom.

Now we are going to look at a model of the atom that helps chemists explain many properties and reactions. Essentially, we try to develop in your mind a picture of the arrangement of the electrons in an atom and how this arrangement relates to the location of the atom in the periodic table. Later, we will use this arrangement in discussing chemical bonding, chemical reactions, and chemical properties.

QUANTUM ATOMIC MODEL

The model we discuss has evolved from the study of quantum mechanics (a theoretical mathematical approach to the study of atomic and molecular structure). We do not attempt an in-depth presentation here. Instead, we present some of the basic concepts so you may use them later in this book or build upon them in other chemistry courses.

Keep in mind that we are studying the basic model of a *very complex* theory. A good way to help you remember the model is to compare it to an apartment building. An apartment building has different floors, different apartments on each floor, and different rooms within each apartment.

We can look upon the electrons of an atom as rather peculiar apartment dwellers. Electrons prefer the floor closest to the ground and the smallest apartments. Electrons also prefer to live one to a room until each room in an apartment has one occupant. The electrons will then pair up until each room has two. Each room in the apartment can hold only two electrons.

Apartment buildings may have several floors. The model we discuss has several floors, but only the first seven floors will be occupied. All the electrons of the elements known today will fit within seven floors of the building. Additional floors are available but will only be occupied in special cases.

| ı | | |
|---|---|---|
| ı | | 1 |
| ı | 2 | 1 |

| The floors in the apartment building are called shells in the electron model and | are |
|--|-----|
| numbered 1 through 7. According to what you have just read, what shell will | be |
| occupied first by electrons? | |

Answer: shell 1 (the first floor)

| (a) A p subshell will hold a maximum of how many electrons? | ich are called. An s subshell d subshell has en will hold a |
|---|---|
| (c) How many will an f subshell hold? | |
| Answer: (a) six (3 rooms × 2 electrons/room); (b) ten (5 rooms × 2 electrons/room); (c) to (7 rooms × 2 electrons/room) Each room in a subshell is called an orbital. From frame 5.5 we know, then, s subshell will consist of one orbital with a capacity (occupancy) of two electrons. (a) A p subshell will consist of three orbitals with a total subshell capalectrons. (b) A d subshell will have orbitals and a total capalectrons. (c) An f subshell will have orbitals and hold electrons. Answer: (a) six (3 orbitals × 2 electrons per orbital); (b) five, ten; (c) seven, fourteen the first shell (floor) has only one subshell (apartment), which is an s secause of its location on the first shell, it is called a 1s subshell. (a) How many orbitals (rooms) are there in this 1s subshell? | |
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| electrons. (b) A d subshell will have orbitals and a total capa electrons. (c) An f subshell will have orbitals and hold electrons. Answer: (a) six (3 orbitals × 2 electrons per orbital); (b) five, ten; (c) seven, fourteen The first shell (floor) has only one subshell (apartment), which is an s s Because of its location on the first shell, it is called a 1s subshell. (a) How many orbitals (rooms) are there in this 1s subshell? (b) How many electrons will the subshell hold? Answer: (a) one (s subshells have only one orbital); (b) two (each orbital holds electrons) The second shell (floor) only has an s subshell (apartment) and a p subshell (a) If the s subshell is called 2s, what do you suppose the p subshell is called 1s are in that p subshell? (c) How many orbitals (rooms) are in that p subshell? (d) How many orbitals are there in the second shell? (e) How many electrons can occupy the second shell? (e) How many electrons can occupy the second shell? (f) the subshells have three orbitals); (c) two (s and p); (d) for the subshells have three orbitals); (c) two (s and p); (d) for the subshells have three orbitals); (c) two (s and p); (d) for the subshells have three orbitals); (c) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshells have three orbitals); (e) two (s and p); (d) for the subshell have three orbitals); (e) two (s and p) | |
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| (c) How many subshells are in the second shell? | ll is called? |
| (d) How many orbitals are there in the second shell? (e) How many electrons can occupy the second shell? Answer: (a) 2p; (b) three (p subshells have three orbitals); (c) two (s and p); (d) fo | |
| (e) How many electrons can occupy the second shell? | |
| Answer: (a) $2p$; (b) three (p subshells have three orbitals); (c) two (s and p); (d) fo | |
| | |
| |); (d) four (one |

| 59 | The third shell has three subshells: s , p , and d . |
|----|---|
| | (a) What are they called? |
| | (b) How many subshells are in the third shell? |
| | (c) How many orbitals are in the third shell? |
| | (d) How many electrons can be in the third shell? |
| | Answer: (a) 3s, 3p, 3d; (b) three; (c) nine (one s orbital, three p orbitals, and five d orbitals; (d) 18 (9 orbitals \times 2 electrons/orbital) |
| 60 | Shells 4 through 7 each have four subshells: s, p, d , and f . |
| | (a) What would you call the subshells on the fourth shell?(b) Sixth shell? |
| | Answer: (a) 4s, 4p, 4d, 4f, (b) 6s, 6p, 6d, 6f |
| 61 | How many subshells are there in the fifth shell? Seventh shell? |
| | Answer: four; four |
| 62 | How many orbitals are there in the fourth shell? How many electrons will that shell hold? |
| | Answer: 16 (one s orbital, three p orbitals, five d orbitals, and seven f orbitals); 32 (16 orbitals \times 2 electrons/orbital) |
| 63 | Let's review what we have just learned. Assume that we have only seven floors in our "building." |
| | (a) A shell may have as many as subshells or as few as subshell(s). |
| | (b) A subshell may have as many as orbitals or as few as orbital(s). |
| | (c) A subshell may hold as many as electrons or as few as electron(s), assuming full occupancy. |
| | (d) A shell may hold as many as electrons or as few as electrons, assuming full occupancy. |
| | Answer: (a) four, one; (b) seven, one; (c) 14, two; (d) 32, two |

As we have mentioned previously, electrons prefer the lower shells (floors) and the smaller subshells (apartments). Electrons prefer the smaller subshells to such a degree that they will sometimes occupy a smaller subshell on the next higher shell rather than the larger subshell on the lower shell.

By experimentation, it has been determined that electrons will fill the 1s subshell (apartment) first. They will then fill the 2s subshell, and then the 2p subshell. Next, they will fill the 3s subshell and then the 3p subshell. However, before going into the large five orbital 3d subshell, electrons will first fill the 4s subshell. After filling the 4s subshell, electrons will then proceed to fill the 3d subshell. The 4p subshell is filled next. The electrons prefer to fill the small 5s subshell before filling the larger 4d subshell. The 4d is filled after 5s. Next, the electrons fill the 5p subshell. Then the small 6s subshell is filled. The very large 4f subshell is occupied only after 6s is filled. After 4f comes 5d. Next is 6p, then 7s, and then 5f.

A diagram to help you remember the order of filling the subshells appears on page 16.

Note that as we fill consecutive subshells, the energy of the electrons increases. Electrons in the 2s subshell have a higher energy than electrons in the 1s subshell; 2p electrons have a higher energy than 2s electrons, and so on.

| 64 | Using the diagram, which subshell is filled first? |
|----|--|
| | Answer: 1s |
| 65 | Is the 4s subshell filled before or after the 3d subshell? |
| | Answer, before |

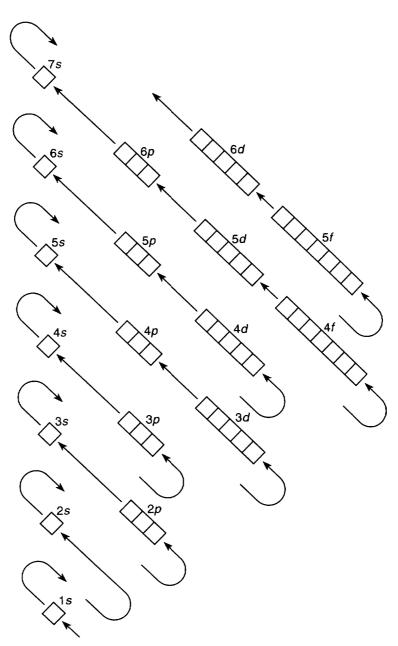
Neon has ten electrons. The order of filling its subshells is first 1s, then 2s, and finally 2p. What is the order of filling the subshells in an atom of magnesium (Mg)? (Use the periodic table to determine the number of electrons in an atom of magnesium.)

Answer: Since there are 12 electrons in an atom of magnesium, the order of filling of the subshells is 1s 2s 2p 3s.

The following notation is used to indicate the number of electrons in each subshell of an atom. For example, neon has ten electrons, therefore its subshells are written as $1s^2 2s^2 2p^6$. The numbers to the upper right of each subshell indicate the number of electrons in each subshell. If we add these numbers (2 + 2 + 6 = 10) we get the number of electrons in a neon atom.

How would you use this notation for the magnesium (Mg) atom?

Answer: $1s^2 2s^2 2p^6 3s^2 (2 + 2 + 6 + 2 = 12)$



Order of Filling of Subshells and Approximate Energy Ranking

ELECTRON CONFIGURATION

You have just learned the notation a chemist uses to indicate the arrangement of electrons in an atom. This arrangement is called its electron configuration. Use the diagram on page 16 to determine the electron configuration of argon, 18Ar.

Answer: 1s2 2s2 2p6 3s2 3p6

Chlorine (17Cl) is an example of an atom in which the last subshell is not completely filled. Its electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$. Note that the 3p subshell has only five electrons and all other subshells are filled.

Oxygen is another example of an atom in which the last subshell is unfilled. What is its electron configuration?

Answer: $1s^2 2s^2 2p^4 (2 + 2 + 4 = 8 \text{ electrons})$

What are the electron configurations of the following elements?

- (a) Potassium (K)
- (b) Arsenic (As)

Answer: (a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

We can also identify an atom if we are given its electron configuration. For example, this configuration $1s^2 2s^2 2p^6 3s^2 3p^1$ has 13 electrons. Only the aluminum atom has 13 electrons; therefore, the configuration above must be that of an aluminum atom.

What atom has this electron configuration? $1s^2 2s^2 2p^6 3s^2 3p^4$

Answer: sulfur, 5(2+2+6+2+4=16)

Another way to represent the arrangement of electrons around an atom is to use arrows as electrons and boxes to represent orbitals (see frame 72). The boxes become occupied by electrons as we "build up" the atoms of each element in the periodic table. Remember, only one electron will occupy an orbital in a given subshell until all the orbitals in that subshell have one electron in them. Then and only then will a second electron occupy each orbital.

Using this method, the electron arrangement for 12 Mg follows.

$$1s \bigcirc 2s \bigcirc 2p \bigcirc 3s \bigcirc 3s \bigcirc$$

The arrow notation for 7N is

Note the unpaired or single electrons in the partially filled 2p subshell. The electrons occupy as many orbitals as possible in the same subshell before pairing with another electron. This is known as the Principle of Maximum Multiplicity.

Using the Principle of Maximum Multiplicity and the arrow notation, indicate the arrangement of electrons for the following.

- (a) ₁₄Si _____
- (b) ₁₆S _____
- (c) ₂₃V _____
- (d) ₂₆Fe _____

Answer:

The electron configurations of the noble gases are given below.

$$_{2}$$
He $_{1}s^{2}$
 $_{10}$ Ne $_{1}s^{2}$ $_{2}s^{2}$ $_{2}p^{6}$
 $_{18}$ Ar $_{1}s^{2}$ $_{2}s^{2}$ $_{2}p^{6}$ $_{3}s^{2}$ $_{3}p^{6}$
 $_{36}$ Kr $_{1}s^{2}$ $_{2}s^{2}$ $_{2}p^{6}$ $_{3}s^{2}$ $_{3}p^{6}$ $_{4}s^{2}$ $_{3}d^{10}$ $_{4}p^{6}$
 $_{54}$ Xe $_{1}s^{2}$ $_{2}s^{2}$ $_{2}p^{6}$ $_{3}s^{2}$ $_{3}p^{6}$ $_{4}s^{2}$ $_{3}d^{10}$ $_{4}p^{6}$ $_{5}s^{2}$ $_{4}d^{10}$ $_{5}p^{6}$
 $_{86}$ Rn $_{1}s^{2}$ $_{2}s^{2}$ $_{2}p^{6}$ $_{3}s^{2}$ $_{3}p^{6}$ $_{4}s^{2}$ $_{3}d^{10}$ $_{4}p^{6}$ $_{5}s^{2}$ $_{4}d^{10}$ $_{5}p^{6}$ $_{6}s^{2}$ $_{4}f^{14}$ $_{5}d^{10}$ $_{6}p^{6}$

With the exception of ${}_{2}$ He, the subshell of greatest energy (last subshell) in each noble gas consists of six electrons occupying a(n) (s, p, d, f) subshell.

Answer: p

With the exception of ₂He, the similar properties of the noble gases are due to their similar electron configuration.

| Noble gas | Subshells of the outermost shell |
|------------------|----------------------------------|
| ₁₀ Ne | $2s^2 2p^6$ |
| ₁₈ Ar | $3s^2 3p^6$ |
| ₃₆ Kr | $4s^2 4p^6$ |
| ₅₄ Xe | 5s ² 5p ⁶ |
| ₈₆ Rn | 6s ² 6p ⁶ |

The subshell of greatest energy of each noble gas is (mark the correct answer):

- ____ (a) completely filled with electrons.
- ____ (b) half-filled with electrons.
- ____ (c) can take one more electron each.

Answer: (a) (Only six electrons can occupy the orbitals in a p subshell.)

75 The electron configurations of the halogens are as follows.

$$_{9}$$
F $_{17}$ Cl $_{1s^2}$ $_{2s^2}$ $_{2p^6}$ $_{3s^2}$ $_{3p^5}$ $_{35}$ Br $_{1s^2}$ $_{2s^2}$ $_{2p^6}$ $_{3s^2}$ $_{3p^6}$ 4s² $_{3d^{10}}$ 4p⁵ $_{53}$ I $_{1s^2}$ $_{2s^2}$ $_{2p^6}$ $_{3s^2}$ $_{3p^6}$ 4s² $_{3d^{10}}$ 4p⁶ $_{5s^2}$ 4d $_{10}$ 5p⁵ $_{85}$ At $_{1s^2}$ $_{2s^2}$ $_{2p^6}$ $_{3s^2}$ $_{3p^6}$ 4s² $_{3d^{10}}$ 4p⁶ $_{5s^2}$ 4d $_{10}$ 5p⁶ $_{6s^2}$ 4f $_{14}$ 5d $_{10}$ 6p⁵

The incomplete subshell in each halogen is made up of how many electrons?

______ In what subshell? ______

Answer: five; p

The electron configurations of the alkaline earth metals are as follows.

The subshell of the outermost shell in each alkaline earth is made up of _____ electrons in a(n) _____ subshell.

Answer: two; s

Each group of elements in the periodic table has similar subshells with similar numbers of electrons in the outermost shell. The outermost shell consists of the subshells that are filled last. This situation serves to explain the (similar, greatly different) _____ chemical properties of elements within the same groups.

Answer: similar

The knowledge of what constitutes an atom is important to the discussion of atomic weights and molecular weights. The arrangement of the electrons around the atom is important to the discussion of chemical bonding, chemical formulas,

and chemical properties — all topics of later chapters. What you have learned so far will be the springboard to a greater understanding of chemistry as you continue your study.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test.

| 1. | | | m on the right that <i>best</i> describes each item on the lic table if you wish. |
|----|--|---------------------------------------|--|
| | (a) proton (b) Ba (c) Na (d) Cl (e) electron | proton | (1) an alkaline earth |
| | | · | (2) a halogen |
| | | | (3) a noble gas |
| | | | (4) an alkali metal |
| | | | (5) responsible for nuclear charge |
| | (c) | Cicci oii | (6) occupies subshells |
| | does the new | utral atom have electrons | : ²³ Na. How many electrons, protons, and neutrons? protons; neutrons; uration of the element in question 2? |
| 4. | | outermost sub | shell electron configuration common to all of the |
| 5. | | that shines and | conducts heat and electricity is a (metal, nonmetal, |
| 6. | | | ron configuration 1s ² 2s ² 2p ⁶ 3s ² 3p ¹ ? ound in the periodic table? |
| 7. | How would | you write the b | ox and arrow notation for ₂₅ Mn? |
| | | · · · · · · · · · · · · · · · · · · · | |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses after the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. (a) 5 (frames 12, 13)
 - (b) 1 (frames 28, 76)
 - (c) 4 (frames 27, 30)
 - (d) 2 (frames 31, 75)
 - (e) 6 (frames 54-63)
- 2. 11; 12; 11 (frames 42-53)
- 3. 1s² 2s² 2p⁶ 3s¹ (frames 64–76)
- 4. p⁵ (frame 75)
- 5. metal (frame 41)
- 6. aluminum, Group IIIA (frames 71-77)
- 7. 1s 1 2s 1 2p 1 1 3s 1 3p 1 1 4s 1 3d 1 1 (frames 72–76)

2 Atomic Weights

Now that you have some idea of what is in an atom, let's look at the weight of atoms. Each atom has a definite and characteristic weight. This weight provides a very convenient way to state the amount of substance required for a chemical reaction.

In this chapter we discuss how the weights of atoms were determined experimentally. You will encounter for the first time a very formidable number — 602,300,000,000,000,000,000,000,000 (6.023×10^{23}) — called Avogadro's number. The number becomes very important in later chapters, so be sure you understand its significance!

OBJECTIVES

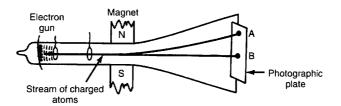
After completing this chapter, you will be able to

- recognize and apply or illustrate: isotope, atomic weight, atomic mass unit (amu), mass spectrograph, gram atomic weight, and Avogadro's number;
- explain the fractional atomic weights listed in the periodic table;
- calculate the number of atoms in a given weight of an element and vice versa;
- calculate the approximate atomic weight of an element when given the abundance and approximate mass of its isotopes;
- distinguish between atomic weight expressed in amu and gram atomic weight.

| 1 | Let's review a bit. The notation $^{35}_{17}$ Cl indicates a neutral atom of chlorine. |
|---|--|
| | (a) What is its atomic number? |
| | (b) What is its mass number? |
| | (c) How many protons does it have? |
| | (d) How many electrons? |
| | (e) How many neutrons? |

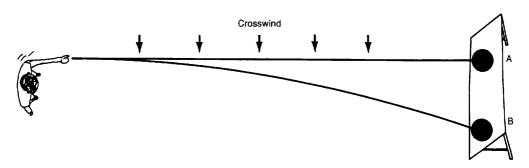
Answer: (a) 17; (b) 35; (c) 17; (d) 17; (e) 18

| 2 | Different atoms of the same element can have different numbers of neutrons and, therefore, different mass numbers. Here is another neutral chlorine atom: ³⁷ ₁₇ Cl. |
|---|--|
| | (a) What is its mass number? |
| | (b) How many protons does it have? |
| | (c) How many neutrons? |
| | Answer: (a) 37; (b) 17; (c) 20 |
| 3 | Since neutrons and protons combine to make up the mass number, two atoms of the same element can have different mass numbers. Chlorine can exist as $^{37}_{17}$ Cl and as $^{35}_{17}$ Cl. The only difference between these atoms of chlorine is that $^{37}_{17}$ Cl contains two more neutrons than $^{35}_{17}$ Cl. Antimony can exist as $^{121}_{51}$ Sb and $^{123}_{51}$ Sb. The only difference between these atoms of antimony is that $^{123}_{51}$ Sb contains two more than $^{121}_{51}$ Sb. |
| | Answer: neutrons |
| 4 | ³⁷ Cl has a greater mass than ³⁵ Cl because of the two extra neutrons. Which of the following atoms of antimony has the greater mass, ¹²¹ Sb or ¹²³ Sb? |
| | Answer: 123 Sb (because it has two more neutrons) |
| 5 | Atoms of the same element having different masses are called isotopes. Elements as found in nature are usually mixtures of two or more isotopes. The atom $^{123}_{51}$ Sb is one isotope of the element antimony and $^{121}_{51}$ Sb is another isotope of antimony. The main difference between two isotopes of the same element is the number of (protons, neutrons, electrons) |
| | Answer: neutrons |
| 6 | Isotopes exist for every known element. The isotopes of the element neon were first discovered by two English scientists, J. J. Thomson and F. W. Aston. Thomson and Aston continued in their work to discover other isotopes through inventing the mass spectrograph (also called the mass spectrometer). In the mass spectrograph, atoms of different masses of the same element (mixtures of isotopes) are charged (no longer neutral) and accelerated by an electron |
| | beam toward a target such as a photographic plate. A strong magnetic field bends the paths of the charged atoms. Atoms of greater mass have their paths bent to a lesser degree than atoms of lighter mass. |
| | In the diagram of the mass spectrograph at the top of page 24, where do the lighter atoms strike, point A or point B? |



Answer: point A (because the path of the lighter atoms is bent to a greater degree)

An analogy to the mass spectrograph would be to roll a bowling ball and a basketball at the same speed at a target while a stiff crosswind is blowing. The bowling ball is considerably heavier than a basketball. Look at the diagram below. Which ball would strike the target at point B?



Answer: the basketball (The basketball is lighter, therefore, its path is more readily changed by the crosswind.)

In the rolling balls analogy to the spectrograph, the bowling ball and basketball are analogous to isotopes of different mass. The strong crosswind is analogous to the

(Refer to the diagram of the spectrograph, if necessary.)

Answer: magnetic field (or magnet)

Thomson and Aston invented an instrument that detects the presence and characteristics of isotopes. What is this instrument called?

Answer: mass spectrograph (or mass spectrometer)

The atomic weights of the elements are listed in the periodic table. The atomic weight of sodium, for example, is listed as 22.98977. The atomic weight listed for sodium is actually the atomic weight of a mixture of isotopes, ²²₁₁Na and ²³₁₁Na. The proportion of these isotopes is generally constant wherever sodium is found.

| | The atomic weight of an element is the average weight of a mixture of two or more |
|-----|--|
| | 11 ← Atomic number Na 22,98977 ← Atomic weight |
| | Answer: isotopes |
| 111 | The periodic table lists the atomic weight of Al as |
| | Answer: 26.98154 |
| 12 | Atomic weights are based on the "Carbon 12" scale. That is, Carbon 12 or ${}_{6}^{12}$ C, the most abundant isotope of carbon, is used as the standard unit in measuring atomic weights. By international standard, one atom of the ${}_{6}^{12}$ C isotope has an atomic weight of exactly 12 atomic mass units, abbreviated amu. The atomic weight of the ${}_{6}^{12}$ C isotope is exactly amu. |
| | Answer: 12 |
| 13 | All atomic weights can be expressed in atomic mass units. By international agreement, 12 amu would equal the mass of a single ${}^{12}_{6}$ C atom. One amu is equal to what fraction of a single ${}^{12}_{6}$ C atom? |
| | Answer: $\frac{1}{12}$ the mass of a single ${}^{12}_{6}$ C atom |
| 14 | Although the ${}^{12}_{6}\text{C}$ isotope weighs exactly 12.000 amu by definition, the atomic weight of C as listed on the periodic table is 12.011 amu. The atomic weight of carbon as listed on the periodic table is greater than that of the ${}^{12}_{6}\text{C}$ isotope. Why? |
| | Answer: The atomic weight of an element is the average weight of a mixture of two or more isotopes. |
| 15 | While the element carbon as found in nature is made up largely of the ${}^{12}_{6}\text{C}$ isotope (98.9%), a small quantity of ${}^{13}_{6}\text{C}$ isotope (1.1%) is mixed uniformly as part of the element. The ${}^{12}_{6}\text{C}$ isotope has an atomic weight of 12.000 amu. The ${}^{13}_{6}\text{C}$ isotope has an atomic weight of 13.003 amu. The resultant average atomic weight would be slightly (heavier, lighter) than 12.000 amu. |
| | Answer: heavier (In fact, the periodic table lists the atomic weight of carbon as 12.011 amu.) |

The atomic weights on the periodic table are the average atomic weights of the isotopic mixtures in the element. We can determine the average atomic weight of an element if we know the approximate mass of each isotope and the proportion of each isotope within the element.

Here are the steps for calculating the average atomic weight of the element carbon. Look at the table as you read through the steps.

Multiply the mass of the $^{12}_{6}$ C isotope times its decimal proportion (12.000 × 0.989).

Multiply the mass of the ${}^{13}_{6}\text{C}$ isotope times its decimal proportion (13.003 × 0.011).

Add the results to find the average atomic weight of the element C.

| Element | Isotope | Mass of isotope | | Proportion in element | | Mass × proportion | | | Sum |
|---------|------------------------------|-----------------|---|-----------------------|---|-------------------|---|---|-----|
| C | ¹² ₆ C | 12.000 | × | 0.989 | = | 11.868 | | _ | |
| C | 13 6 | 13.003 | × | 0.011 | = | 0.143 | + | = | |

Now you do the final calculation step, adding the two results. Fill in the blank in the "Sum" column. Round off this answer and all others to the nearest hundredth (two places to the right of the decimal) unless otherwise indicated.

Answer: The calculated atomic weight of C is 12.011, rounded off to 12.01 amu.

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Now calculate the atomic weight for fluorine.

| Element | Isotope | Mass of isotope | | Proportion in element | | Mass × proportion | | | Sum |
|---------|-----------------|-----------------|---|-----------------------|---|-------------------|---|---|-----|
| r | ¹⁹ F | 19.000 | × | 99.7% or 0.997 | = | | | | |
| r | ¹⁸ F | 18.000 | × | 0.3% or 0.003 | = | | + | Ξ | |

The calculated atomic weight of F is rounded off to 19.00 amu.

18

Sodium has two isotopes, ²³₁₁Na and ²²₁₁Na. The isotope ²³₁₁Na has an atomic mass of approximately 23.000 amu, and its proportion in the element is 99.2%. The

isotope $^{22}_{11}$ Na has a mass of approximately 22.000 amu and a proportion within the element of 0.8%. Determine the atomic weight of sodium. (Remember, 0.8% = 0.008 and 99.2% = 0.992.) Use a separate sheet of paper to set up a table as we have done in the past few frames. Here again are the column headings you will need.

| | | Mass of | Proportion | Mass × | |
|---------|---------|---------|------------|------------|-----|
| Element | Isotope | isotope | in element | proportion | Sum |

Answer:

| Element | Isotope | Mass of isotope | _ | Proportion in element | _ | Mass × proportion | | | Sum |
|---------|------------------|-----------------|---|-----------------------|---|-------------------|---|----|--------|
| | ²³ Na | 23.000 | × | 0.992 | = | 22.816 | | | |
| Na | ²² Na | 22.000 | × | 0.008 | = | 0.176 | + | == | 22.992 |

The calculated atomic weight of Na is 22.99 amu.

The element cobalt has an isotope ${}_{27}^{60}$ Co that has an approximate mass of 60.00 and constitutes 48.0% of the element. Another isotope, ${}_{27}^{58}$ Co, has an approximate mass of 58.00 and constitutes 52.0% of the element. Calculate the atomic weight of Co using the given data. Use a separate sheet of paper to set up a table of calculations.

Answer:

| Element | Isotope | Mass of isotope | | Proportion in element | | Mass × proportion | | | Sum |
|---------|------------------|-----------------|---|-----------------------|---|-------------------|---|---|-------|
| | ⁶⁰ Co | 60.00 | × | 0.480 | = | 28.80 | | | |
| Co | 58 27 Co | 58.00 | × | 0.520 | = | 30.16 | + | = | 58.96 |

The calculated atomic weight of Co is 58.96 amu.

The percentage proportions of all the isotopes within an element must add up to a total of ______ %. The decimal proportions of all the isotopes within an element must add up to _____ . (Hint: See above example, 0.480 + 0.520.)

Answer: 100; 1

We've been calculating atomic weight given the mass and proportion of isotopes. We can also determine the proportion of each individual isotope within an element if we know the atomic weight of the element. Set up a table like the ones you have

been using and fill in the information given below. Use letters such as A and B to represent unknown proportions.

The element Cr, which has an overall atomic weight of 51.996 amu, has two isotopes: ${}_{24}^{52}$ Cr with atomic mass of 52.000 amu and ${}_{24}^{51}$ Cr with an atomic mass of 51.000 amu. Just fill in the "givens" and "unknowns" for now; don't try to solve the problem yet.

| Α | n. | sv | ve | r: |
|---|----|----|----|----|

| Element | Isotope | Mass of isotope | | Proportion in element | | Mass × proportion | | | Sum |
|---------|------------------|-----------------|---|-----------------------|---|-------------------|---|---|--------|
| | ⁵² Cr | 52.000 | × | Α | = | 52.000 × A | | | |
| Cr | 51 24 Cr | 51.000 | × | В | = | 51.000 × B | + | = | 51.996 |

To solve this equation with two unknowns, you must form a second equation showing the relationship between A and B. You have already learned the answer to the following question in frame 20. Add the decimal proportions. A + B =

Answer: 1

Modify the equation in frame 22 so that just B remains on the left side of the equation. B =

Answer: 1 - A

Here is the equation you need for calculating the sum of the isotopes' mass \times proportion: (52.000A) + (51.000B) = 51.996. Substitute the expression (1 - A) for B in the equation.

Answer: [52.000A] + [51.000(1 - A)] = 51.996

Solve the equation derived in frame 24 to determine the value of A (the proportion of ${}_{24}^{52}$ Cr in an average mixture of chromium) to the nearest thousandth. Use a separate sheet of paper for your calculations.

Answer: [52.000A] + [51.000(1 - A)] = 51.996 (52.000A) + (51.000) - (51.000A) = 51.996 1.000A + 51.000 = 51.996 1.000A = 0.996A = 0.996

Since B = 1 - A, what is the value of B (nearest thousandth)? $B = \underline{\hspace{1cm}}$

Answer: B = 1 - A B = 1 - 0.996B = 0.004

Here is a similar problem. In the next few frames, you will determine the proportion of the $^{35}_{17}$ Cl isotope in an average mixture of chlorine, which is made up of both $^{35}_{17}$ Cl and $^{37}_{17}$ Cl. Here is our table of givens and unknowns.

| Element | Isotope | Mass of isotope | | Proportion in element | | Mass × proportion | | | Atomic weight |
|---------|----------|-----------------|---|-----------------------|---|-------------------|---|---|---------------|
| | 35 17 | 34.97 | × | A | = | 34.97 × <i>A</i> | | | |
| Cl | | | | | | | + | = | 35.45 |
| | 37 17 | 36.97 | × | В | = | $36.97 \times B$ | | | |

The values of A and B added together must equal _____.

Answer: 1

Since
$$A + B = 1$$
, then $B =$ _____.

Answer: 1 - A

The proportion
$$1 - A$$
 has been substituted for B in the following table.

| Element | Isotope | Mass of isotope | | Proportion in element | | Mass × proportion | | | Atomic weight |
|---------|----------|-----------------|---|-----------------------|---|-------------------------|---|---|------------------|
| _, | 35 17 | 34.97 | × | Α | = | 34.97 × <i>A</i> | | | |
| Cl | 37 17 | 36.97 | × | (1 – <i>A</i>) | = | 36.97 × (1 – <i>A</i>) | + | = | 35.45 |

Using the table above, determine the proportion of $^{35}_{17}$ Cl within the element chlorine (find the value of A). Use a separate sheet of paper for your set of equations.

Answer:
$$_{17}^{35}$$
Cl mass × $A + _{17}^{37}$ Cl mass × $(1 - A) = 35.45$

$$34.97A + 36.97(1 - A) = 35.45$$

$$34.97A + 36.97 - 36.97A = 35.45$$

$$36.97 - 2.00A = 35.45$$

$$36.97 = 35.45 + 2.00A$$

$$1.52 = 2.00A$$

$$0.76 = A$$

Determine the proportion of
$${}_{17}^{37}$$
Cl in Cl (find *B*).

Answer: The proportion of $^{37}_{17}\text{Cl}$ in Cl has been given the value of B in the table.

$$B = 1 - A$$

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$$B = 1 - 0.76$$

$$B = 0.24$$

Neon has two isotopes: $^{22}_{10}$ Ne and $^{20}_{10}$ Ne. The approximate mass of $^{22}_{10}$ Ne is 22.000 amu, and the mass of $^{20}_{10}$ Ne is approximately 20.000 amu. The atomic weight of neon is 20.179 amu. Determine the proportion (to the nearest thousandth) of the $^{22}_{10}$ Ne isotope within the element. (Let the proportion of $^{20}_{10}$ Ne within Ne be equal to B.) Use a separate sheet of paper for your table of calculations and set of equations.

Answer:

| Element | Isotope | Mass of isotope | | Proportion in element | · | Mass × proportion | | | Atomic weight |
|---------|--------------------------------|-----------------|---|-----------------------|---|----------------------|---|---|------------------|
| | ²² ₁₀ Ne | 22.000 | × | A | = | (22.000 × A) | | | |
| Ne | ²⁰ Ne | 20.000 | × | В | = | (20.000 × <i>B</i>) | + | = | 20.179 |

(22.000A) + (20.000B) = 20.179 B = 1 - A 22.000A + 20.000(1 - A) = 20.179 22.000A + 20.000 - 20.000A = 20.179 2.000A + 20.000 = 20.179 2.000A = 0.179A = 0.090 (the proportion of $^{22}_{10}$ Ne)

What is the proportion (to the nearest thousandth) of the other isotope, ²⁰₁₀Ne, within the element Ne?

Answer: The proportion of $^{20}_{10}$ Ne is equal to the value of B in the table.

B = 1 - A B = 1 - 0.090B = 0.910

So far, we have considered all atomic weights in terms of atomic mass units (amu).

- (a) An atomic weight expressed in amu represents the average weight of how many atom(s) of an element?
- (b) Carbon has an atomic weight of 12.011 amu, which represents the average weight of how many atom(s) of carbon?

Answer: (a) one (An atomic weight expressed in amu represents the average weight of one single atom of an element.); (b) one

GRAM ATOMIC WEIGHT

Since it is impossible to measure the weight of one atom with a laboratory balance, another unit for expressing atomic weight must be used. Atomic weight can be expressed in grams as well as amu. An atomic weight expressed in grams (called a

gram atomic weight) contains 6.023×10^{23} atoms. This number, called Avogadro's number, will be encountered often in this book.

- (a) If the atomic weight of carbon is expressed as 12.011 amu, it represents the average weight of how many atom(s)?
- (b) If the atomic weight of carbon is expressed as 12.011 grams, it represents the average weight of how many atom(s)?

Answer: (a) one; (b) 6.023×10^{23}

Using information in frame 34, answer the following question. One gram is how many times heavier than 1 amu?

Answer: 6.023×10^{23} (One gram is equivalent to 6.023×10^{23} amu.)

One ton is equivalent to 2000 pounds. One pound represents $\frac{1}{2000}$ of a ton. 6.023 \times 10²³ amu is equivalent to 1 gram. One amu represents what fraction of a gram?

Answer: $\frac{1}{6.023 \times 10^{23}}$

Avogadro's number (6.023×10^{23}) is written in exponential notation (sometimes called scientific notation). It actually represents a very large number: 602,300,000,000,000,000,000,000. Exponential notation will be used throughout this book, as in most other chemistry texts. You may already be familiar with exponential notation and with multiplying and dividing numbers with exponents. If so, you may skip to frame 38. If you need a quick refresher of exponential notation, we have summarized the basic rules in the examples below.

$$400 = 4 \times 10 \times 10 = 4 \times 10^{2}$$

$$5000 = 5 \times 10 \times 10 \times 10 = 5 \times 10^{3}$$

$$645,000 = 6.45 \times 10 \times 10 \times 10 \times 10 \times 10 = 6.45 \times 10^{5}$$

The exponent indicates the number of places that the decimal must be moved. The number 645,000 has the decimal moved five places to the left (645,000.). The result is 6.45×10^5

We can also use exponential notation as in the examples below.

$$0.00004 = 4 \times 10^{-5}$$
$$0.073 = 7.3 \times 10^{-2}$$

In these two cases, we moved the decimal to the right, with the result that the exponent is negative.

0.00004 (Move the decimal five places to the right to arrive at the notation 4×10^{-5} .)

0.073 (Move the decimal two places to the right to arrive at the notation 7.3×10^{-2} .)

For 0.073, we could have moved the decimal three places to the right, with a result of 73×10^{-3} . We could also move the decimal one place to the right, with a result of 0.73×10^{-1} . Normally, in chemistry calculations we write a single digit of value 1 through 9 to the left of the decimal.

To *multiply* two numbers with exponential notation, multiply the decimal portions of the numbers and *add* the *exponents*.

$$(2 \times 10^5) \times (4 \times 10^3) = (2 \times 4) \times 10^{(5+3)} = 8 \times 10^8$$

 $(3 \times 10^4) \times (2 \times 10^{-3}) = (3 \times 2) \times 10^{(4-3)} = 6 \times 10^1$

To *divide* two numbers with exponential notation, divide the decimal portions of the numbers and *subtract* the *exponent* in the denominator from the exponent in the numerator.

$$(6 \times 10^{4})/(2 \times 10^{2}) = (6/2) \times 10^{(4-2)} = 3 \times 10^{2}$$

$$(8 \times 10^{6})/(2 \times 10^{-4}) = (8/2) \times 10^{(6-(-4))} = 4 \times 10^{10}$$

$$(8 \times 10^{-4})/(4 \times 10^{-2}) = (8/4) \times 10^{(-4-(-2))} = 2 \times 10^{-2}$$

Try these problems.

(c)
$$(7.0 \times 10^{-5}) \times (4.0 \times 10^{8}) =$$

(d)
$$\frac{9.0 \times 10^8}{3.0 \times 10^5} =$$

(e)
$$\frac{6.0 \times 10^{-4}}{3.0 \times 10^{-6}} =$$

Answer:

- (a) 4.2×10^4
- (b) 4.65×10^{-3}

(c)
$$(7.0 \times 4.0) \times 10^{(-5+8)} = 28 \times 10^3 = 2.8 \times 10^4$$

(d)
$$\left(\frac{9.0}{3.0}\right) \times 10^{(8-5)} = 3.0 \times 10^3$$

(e)
$$\left(\frac{6.0}{3.0}\right) \times 10^{(-4-(-6))} = 2.0 \times 10^2$$

Look at the following examples of fractions that are converted to exponential notation. Then fill in the correct answer for the equivalence of amu to grams, by

using the same process of eliminating the fraction and expressing the equivalence in proper exponential notation.

- 1 pound equals $\frac{1}{2000}$ ton
- 1 pound equals $\frac{1}{2 \times 10^3}$ ton
- 1 pound equals $\frac{1}{2} \times 10^{-3}$ ton
- 1 pound equals 0.5×10^{-3} ton
- 1 pound equals 5.0×10^{-4} ton
- 1 amu equals $\frac{1}{6.023 \times 10^{23}}$ gram
- 1 amu equals_____

Answer: $\frac{1}{6.023 \times 10^{23}} = \frac{1}{6.023} \times 10^{-23} = 0.166 \times 10^{-23} = 1.66 \times 10^{-24} \text{ gram}$

- You should memorize Avogadro's number (6.023×10^{23}) and its meaning.
 - (a) How many atoms are in an atomic weight expressed in grams?
 - (b) One gram is equivalent to the weight of how many amu?

Answer: (a) 6.023×10^{23} atoms per gram atomic weight; (b) 6.023×10^{23} amu per gram

- The average atomic weight of neon is 20.179 according to the periodic table (rounded off to the nearest thousandth).
 - (a) The average weight of one neon atom is how many amu?
 - (b) The average weight of 6.023×10^{23} neon atoms is how many grams?

Answer: (a) 20.179; (b) 20.179

There are 6.023×10^{23} atoms in 1 gram atomic weight (atomic weight expressed in grams). The element neon has a gram atomic weight of 20.179 grams. How many atoms are contained in 10.0895 grams of neon? _____ (Hint: 10.0895 grams of neon is half of the gram atomic weight of neon.)

Answer: Since 10.0895 grams is half of a gram atomic weight, the number of atoms is half of 6.023×10^{23} atoms, or 3.012×10^{23} atoms.

UNIT FACTOR ANALYSIS (FACTOR LABEL ANALYSIS/DIMENSIONAL ANALYSIS)

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If the problem in frame 41 had been more difficult, we would have used the unit factor method (also called factor label analysis and dimensional analysis in some texts) for solving problems, a mathematical procedure used in most chemistry text-books for its convenience in calculations. We would have set up the problem in the manner shown below.

10.0895 grams of Ne ×
$$\frac{1 \text{ gram atomic weight}}{20.179 \text{ grams of Ne}} \times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ gram atomic weight}}$$

= 3.012 × 10²³ atoms

All of the unit names except "atoms" cancel out during multiplication.

10.0895 grams of Ne ×
$$\frac{1 \text{ gram atomic weight}}{20.179 \text{ grams of Ne}} \times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ gram atomic weight}}$$

= 3.012 × 10²³ atoms

Just the numbers and the name "atoms" are left after cancellation of unit names.

$$10.0895 \times \frac{1}{20.179} \times \frac{6.023 \times 10^{23} \text{ atoms}}{1} = 3.012 \times 10^{23} \text{ atoms}$$

The unit factor method involves multiplying the given value by one or more conversion factors. In this problem, we multiplied the 10.0895 grams of Ne by the conversion factors of

$$\frac{1 \text{ gram atomic weight}}{20.179 \text{ grams of Ne}} \quad \text{and} \quad \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ gram atomic weight}}$$

The conversion factors come from definitions. For example, 1 gram atomic weight is equal to 6.023×10^{23} atoms, and 20.179 grams of Ne are equal to 1 gram atomic weight of Ne. The conversion factors are arranged so that the unit names will cancel out. They convert the units of the given values to those of the answer being sought and will give us the correct numerical answer.

Here is another example using the unit factor method. The necessary definitions are: 1 meter = 39.37 inches, and 1 yard = 36 inches.

The first conversion factor can be
$$\frac{39.37 \text{ inches}}{1 \text{ meter}}$$
 or $\frac{1 \text{ meter}}{39.37 \text{ inches}}$.

The second conversion factor can be $\frac{1 \text{ yard}}{36 \text{ inches}}$ or $\frac{36 \text{ inches}}{1 \text{ yard}}$.

Suppose we wish to determine the number of meters in 2.12 yards. We arrange the conversion factors so that the answer will be in meters and all other unit names will cancel.

$$2.12 \text{ yards} \times \frac{1 \text{ meter}}{39.37 \text{ inches}} \times \frac{36 \text{ inches}}{1 \text{ yard}}$$

= 1.94 meters (rounded to the nearest hundredth)

Use these conversion factors to determine the number of yards in 3.55 meters (nearest hundredth).

Answer: 3.55 meters
$$\times \frac{39.37 \text{ inches}}{1 \text{ meter}} \times \frac{1 \text{ yard}}{36 \text{ inches}} = 3.88 \text{ yards}$$

The gram atomic weight of silicon is 28.09 grams. Using the unit factor method shown in frame 42, calculate the number of atoms in 2.00 grams of silicon (Si).

Answer: 2.00 grams of Si ×
$$\frac{1 \text{ gram atomic weight}}{28.09 \text{ grams of Si}} \times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ gram atomic weight}}$$

= $4.29 \times 10^{22} \text{ atoms}$

The atomic weight of silicon is 28.09. Determine the average weight (in amu) of one silicon atom. _____ amu

Answer: 28.09 (same as the atomic weight).

There is a big difference between an atomic weight expressed in amu and an atomic weight expressed in grams. You have already determined that one silicon atom weighs 28.09 amu. Now calculate the weight of one silicon atom in grams.

$$\frac{28.09 \text{ grams of Si}}{1 \text{ gram atomic weight}} \times \frac{1 \text{ gram atomic weight}}{6.023 \times 10^{23} \text{ atoms}} = \frac{\text{grams/atom}}{1 \text{ gram atomic weight}}$$

Answer: 4.66 × 10⁻²³

Determine the mass in grams of one boron (B) atom. (The gram atomic weight of boron is 10.81 grams.)

Answer:
$$\frac{10.81 \text{ grams of B}}{1 \text{ gram atomic weight}} \times \frac{1 \text{ gram atomic weight}}{6.023 \times 10^{23} \text{ atoms}}$$
$$= 1.79 \times 10^{-23} \text{ grams/atom}$$

If one boron atom weighs 1.79×10^{-23} grams, what would 1,000,000 atoms of boron weigh? $(1,000,000 = 1 \times 10^6)$

Answer:
$$1 \times 10^6$$
 atoms of B $\times \frac{1.79 \times 10^{-23} \text{ grams}}{1 \text{ atom of B}} = 1.79 \times 10^{-17} \text{ grams}$ (Even a million atoms weigh very little.)

The atomic weight of gold is 196.97. If you were offered an atomic weight of gold for only one dollar, would you buy it? Why or why not?

Answer: We wouldn't. The atomic weight of gold would be expressed as 196.97 amu, so you are buying one atom of gold for a dollar, definitely no bargain. (However, a *gram* atomic weight of gold weighs 196.97 grams, which would definitely be a bargain for one dollar.)

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How much would a billion billion atoms (1×10^{18} atoms) of magnesium weigh? The gram atomic weight of magnesium is 24.305 grams. (Hint: Find the weight of one atom of magnesium and multiply the result by 1×10^{18} .)

Answer: Here are two methods for solving this problem.

The first method is one long step.

$$1 \times 10^{18}$$
 atoms of Mg × $\frac{1 \text{ gram atomic weight}}{6.023 \times 10^{23} \text{ atoms}} \times \frac{24.305 \text{ grams}}{1 \text{ gram atomic weight}}$
= 4.04×10^{-5} grams of Mg

The second method involves two shorter steps.

$$\frac{24.305 \text{ grams}}{1 \text{ gram atomic weight}} \times \frac{1 \text{ gram atomic weight}}{6.023 \times 10^{23} \text{ atoms}} = 4.04 \times 10^{-23} \text{ grams/atom}$$

$$1 \times 10^{18} \text{ atoms of Mg} \times \frac{4.04 \times 10^{-23} \text{ grams}}{1 \text{ atom}} = 4.04 \times 10^{-5} \text{ grams of Mg}$$

What are the most important concepts in this chapter?

- The weights assigned to atoms are relative weights. That is, all atoms are compared to the weight of a single ¹²₆C atom.
- All atoms of the same element do not have the same weight (elements exist as isotopes).
- The isotopes of an element are not present in nature in equal amounts.
- The atomic weight of an element may be determined experimentally.
- Atoms have very small weights. A chemist deals with large numbers of atoms (on the order of 6×10^{23}) in the laboratory.

In Chapter 3 you will see that atomic weight is one of several periodic properties. You will encounter atomic weights throughout the remainder of this book, especially in Chapters 4 and 7, so you should have their meaning and significance clearly in mind before proceeding.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test. Calculate answers to the nearest hundredth unless otherwise indicated.

| 1. | Wh | at is a mass spectrograph used for? |
|----|-----|---|
| 2. | The | atoms ³⁷ ₁₇ Cl and ³⁵ ₁₇ Cl are called of chlorine. |
| | | at are the atomic weights of the following elements? chromium (Cr); potassium (K); aluminum (Al) |
| 4. | | are given 0.100 gram atomic weight of gold (Au). The atomic weight of gold 96.97 grams to the nearest hundredth. |
| | (a) | How many atoms would you have? |
| | (b) | How many grams? |

- 5. The atomic weight of iron is 55.85 amu to the nearest hundredth and it has isotopes with approximate masses of 55.000 amu and 56.000 amu. What is the proportion of the ⁵⁶₂₆Fe isotope? (The other isotope is ⁵⁵₂₆Fe.)
- 6. If you could cash it in, which would you rather have, 1×10^{40} amu of silver or 150 grams? (Hint: The problem is to determine which value has the greater number of atoms.)

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. to detect the presence of isotopes of each element (frame 6)
- 2. isotopes (frames 5, 6)
- 3. Cr = 51.996; K = 39.0983; Al = 26.98154 (frame 10)
- 4. (a) 0.100 gram atomic weight $\times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ gram atomic weight}} = 6.023 \times 10^{22} \text{ atoms Au}$
 - (b) 0.100 gram atomic weight $\times \frac{196.97 \text{ grams}}{1 \text{ gram atomic weight}} = 19.70 \text{ grams Au}$ (frames 34, 39–43)

5. Let A equal proportion $^{56}_{26}$ Fe isotope, and let 1 – A equal proportion $^{55}_{26}$ Fe isotope.

$$56.000A + 55.000(1 - A) = 55.85$$

$$56.000A + 55.000 - 55.000A = 55.85$$

$$1.000A = 0.85$$

$$A = 0.85$$
 (proportion ${}_{26}^{56}$ Fe)

6. Ag = 107.87 amu/atom, so our two equivalences are:

atoms =
$$1 \times 10^{40}$$
 amu $\times \frac{1 \text{ atom}}{107.87 \text{ amu}} = 9.27 \times 10^{37}$ atoms

atoms = 150 g ×
$$\frac{1 \text{ gram atomic weight}}{107.87 \text{ g}}$$
 × $\frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ gram atomic weight}}$ = 8.38 × 10²³ atoms

You would probably rather cash in the 1 \times 10⁴⁰ amu.

(frames 47-49)

Periodic Properties and Chemical Bonding

In Chapter 1 you learned that the elements in a horizontal row of the periodic table show regular variation in properties from left to right. The elements are arranged in the table in order by increasing atomic number (reading the table left to right, line by line, in the way you are reading this paragraph). The reason this arrangement works so well is that all atoms consist of electrons, protons, and neutrons. The neutrons and protons are in the nucleus with electrons arranged in "shells" around the nucleus.

Why did we consider the electronic arrangement of atoms in such detail? Because the chemical properties of an element depend upon the number of electrons in its outermost shell, the energy levels of its outermost electrons, and the size of the atom. These details of atomic structure determine what kinds and how many chemical bonds can be formed by an atom.

In this chapter we discuss several properties not mentioned in Chapter 1 that depend upon the outermost shell electronic structure. We will review electron configuration and introduce new "dot" symbols. We will then discuss whether atoms gain, lose, or share electrons, and how many, when they combine to form new substances. The major portion of the chapter is devoted to the types of chemical bonds (ionic, covalent, polar covalent) formed between atoms in chemical compounds. Finally, we look briefly at the shapes of compounds and ionization energy.

OBJECTIVES

After completing this chapter, you will be able to

- recognize and apply or illustrate: ion, ionic, covalent, coordinate covalent, molecule, compound, electron dot symbol, formula, electronegativity, polar, ionization energy, metallic character, the octet rule, nonmetallic character, and valence shell electrons;
- write electron dot symbols that represent the number of valence shell electrons for the Group A elements and noble gases;
- write the symbol for the ion formed by any of the Group A elements;

- write equations using dot symbols to show the formation of ionic, covalent, and coordinate covalent compounds;
- predict the type of bond (ionic, covalent, polar covalent) formed when any two elements combine when given the electronegativity of the elements;
- use the octet rule to choose a correct dot structure for a compound;
- predict whether a molecule containing three or more atoms would be polar or nonpolar, if given its shape;
- predict whether an element, according to its position in the periodic table: (1) is metallic or nonmetallic, (2) has a high or low electronegativity, (3) has a high or low ionization energy, and (4) will gain or lose electrons and how many.

OUTER SHELL ELECTRONS

The following chart represents the first 20 elements of the periodic table. Only the symbols and atomic numbers have been included.

| IA | _ | | | | | | VIIIA |
|----------------|---------|----------|-----|----------------|----------------|---------------|--------------------|
| H | IIA | IIIA | IVA | VA | VIA | VIIA | ² He |
| 3 Li | ₄ Be | B | ° C | 7 N | 8 O | 9 F | Ne |
| Na | Mg | Al | Si | 15 P | 16 S | Cl | 18 Ar |
| 19 K | Ca | | | | | | |

The atomic number increases by one each time as the elements are viewed from left to right (11 to 12 to 13 to 14 to 15, and so on). Each time the atomic number increases by one, how many electrons are added?

Answer: one (Remember that the atomic number represents the number of protons. The symbols on the periodic table represent atoms of neutral elements. In a neutral atom the number of protons equals the number of electrons.)

Periodic tables can be made to include different kinds of information. The following table includes the electronic structure for the *outermost shell* for each of the first 20 elements.

| IA | | | | | | | VIIIA |
|---------------|-----------------------|--|--|---|--|--------------------------------------|---|
| H 151 | IIA | IIIA | IVA | VA | VIA | VIIA | He 1s² |
| Li 251 | Be 252 | B 25 ² 2p ¹ | $C_{2s^22p^2}$ | N 2s ² 2p ³ | O 25 ² 2p ⁴ | F 2s ² 2p ⁵ | Ne 25 ² 2p ⁶ |
| Na 351 | Mg 35 ² | Al 3523p1 | Si 35 ² 3p ² | P $3s^23p^3$ | S 35 ² 3p ⁴ | Cl 3523p5 | Ar 35 ² 3p ⁶ |
| K 4s1 | Ca | | | | | | |

There are similarities in the structure of elements within groups. Notice the structure of each outermost shell in Group IA. How many electrons are present in the outer shell of each element in Group IA (H, Li, Na, K, and others)?

Answer: one (Each element in Group IA has only one electron in its outermost shell.)

- Use the periodic table in frame 2 for the following statements.
 - (a) Group IIA elements each have two electrons in their outermost shell. Group IIIA elements each have _____ electrons in their outermost shell.
 - (b) Group IVA elements each have _____ electrons in their outermost shell.
 - (c) Group VA elements have five, Group VIA elements have _____, and Group VIIA elements have _____.
 - (d) Group VIIIA elements (the noble gases) each have eight electrons in their outermost shell with the exception of helium, which has only ______ electrons.

Answer: (a) three; (b) four; (c) six, seven; (d) two

Nitrogen (N), a Group VA element, has ______ electrons in its outermost shell. Aluminum (Al), a Group IIIA element, has _____ electrons in its outermost shell.

Answer: five; three

The outer shell electrons are also known as valence electrons. The periodic table on the next page includes all of the symbols for the first 20 elements. The numbers of valence electrons are listed for lithium (Li), carbon (C), and argon (Ar). Fill in the number of valence electrons for each remaining element on this periodic table.

Remember that helium (He) is an exception in Group VIIIA, since it only has a total of two electrons in its entire atom, both of which are valence electrons.

| IA | | | | | | | VIIIA |
|--------|--------|--------|--------|-------------|------|--------|--------|
| () H | IIA | IIIA | IVA | VA | VIA | VIIA | () He |
| (1) Li | () Be | () B | (4) C | () N | ()0 | () F | () Ne |
| () Na | () Mg | () Al | () Si | () P | ()\$ | () Cl | (8) Ar |
| () K | () Ca | | | | | | |

Answer:

| IA | | | | | | | VIIIA |
|--------|--------|--------|--------|-------|-------|--------|----------------|
| (1) H | IIA | IIIA | IVA | VA | VIA | VIIA | (2) He |
| (1) Li | (2) Be | (3) B | (4) C | (5) N | (6) O | (7) F | (8) Ne |
| (1) Na | (2) Mg | (3) Al | (4) Si | (5) P | (6) S | (7) Cl | (8) A r |
| (1) K | (2) Ca | | - | | | | |

The outer shell or valence electrons are especially important because those electrons are involved when atoms unite chemically to form compounds.

When an atom of magnesium unites with another different atom to form a compound, what electrons of the magnesium atom are primarily involved?

Answer: the two valence or outer shell electrons

ELECTRON DOT SYMBOLS (LEWIS SYMBOLS)

The outer shell or valence electrons may also be represented by a series of dots. Magnesium, with two valence electrons, can be represented as Mg: (each dot represents one valence electron).

:Čl· represents a chlorine atom with how many valence electrons?

Answer: seven

The first 20 elements and their electron dot symbols are as follows.

| ٠Η | | | | | | | :Не |
|-----|-----|------------|------|-----|--------------|------|------|
| ·Li | :Ве | : <u>B</u> | :Ç∙ | :Ņ· | :Ö· | :Ë· | :Ņe: |
| ·Na | :Mg | :Ål | :Śi· | :Þ· | : <u>Š</u> · | :Ċl· | :Är: |
| ·K | :Ca | | | | | | |

Note that some books will have boron (B) represented as \dot{B} , Al as $\dot{A}l$, C as \dot{C} , and Si as $\dot{S}i$. Such a representation is used to simplify the explanation of how many bonds a given element may have or form with other elements, but does not agree with the quantum mechanical concept of the atom (Chapter 1).

We do not discuss the *number* of bonds an element has in a compound in this book. Later in this chapter we discuss a type of bonding that requires agreement with what is called the octet rule and involves pairs of electrons, so we have chosen to use the scheme shown in this table.

Which elements in the table have five valence electrons?

Answer: :Ņ· and :Þ·

Notice in the table as we go from left to right that the first two electrons pair up, while all additional electrons remain single until all four sides of a symbol are occupied. The symbol :Mg is the same as Mg or Mg: or Mg. The placement of the dots is not critical as long as the proper number of electron pairs and unpaired

electrons are represented. The symbol Al is the same as $Al \cdot or \cdot Al$ or $\cdot Al$ or any arrangement of one pair and one single electron. Note that $\cdot Al \cdot is$ not correct since one pair and a single electron are called for and not three single electrons.

Nitrogen is pictured in electron dot symbols as $:\dot{N}\cdot$ with one pair and three single electrons. Which of the following are also correct symbols for nitrogen? $:\dot{N}\cdot$, $:\dot{N}\cdot$, $:\dot{N}\cdot$, $:\dot{N}\cdot$

Answer: \dot{N} and \dot{N} : (since they show three single electrons and one pair)

The dot symbols showing the valence electrons for the third period elements of the periodic table are as follows.

$$Na \cdot \quad Mg \colon \quad \ddot{Al} \cdot \quad \cdot \ddot{Si} \cdot \quad \cdot \ddot{P} \cdot \quad : \ddot{S} \cdot \quad : \ddot{Cl} \cdot \quad : \ddot{Ar} :$$

Remember that the first two electrons pair up while all additional electrons remain single until all four sides of a symbol are occupied. The first pair of electrons represent an s subshell while the next six electrons represent a p subshell. By the Principle of Maximum Multiplicity, electrons in a subshell prefer to remain unpaired until each orbital contains one electron. The dot diagrams reflect this principle.

The element arsenic (As) has five valence electrons in its outermost shell. The outermost shell consists of two electrons in an s subshell and three electrons in a p subshell. Draw an electron dot symbol for As.

Answer: : As · (or any arrangement with one pair and three single electrons)

The element selenium (Se) has six valence electrons. Its outermost shell consists of a completed s subshell and four electrons in a p subshell. Draw an electron dot symbol for Se.

Answer: :Se· (or any arrangement with two single electrons and two pairs of electrons)

At this point, you may be wondering how these electron dot symbols can be used. You already know that the dots represent valence electrons, and that the valence electrons are especially important because they are involved when two or more atoms combine chemically to form compounds. The electron dot symbol arrangement changes when atoms combine to form compounds.

Before you can use the dot symbols to show compounds, however, you must learn to distinguish between two major categories of chemical compounds.

These two categories, ionic and covalent, will be introduced next. The valence electron arrangements for these two kinds of compounds are different, but both arrangements can be shown through the use of dot symbols.

IONS

| 12 | An ion is an atom or group of atoms that is no longer neutral. The numbers of electrons and protons in an ion are <i>not equal</i> . You have learned that a proton has a positive (+) charge and an electron has a negative (-) charge. A neutral atom, on the other hand, has an equal number of + and - charges, with the net result that the charges cancel each other. The number of protons (atomic number) remains unchanged when an atom becomes an ion, but one or more electrons may be gained or lost. This results in an ion with either fewer or more electrons than protons. |
|----|--|
| | (a) Oxygen (O), with an atomic number of 8, was found to have ten electrons. Is it an ion or a neutral atom? |
| | (b) Aluminum, with an atomic number of 13, also was found to have ten electrons. Is it an ion or a neutral atom? |
| | (c) Magnesium, with an atomic number of 12, was found to have 12 electrons. Is it an ion or a neutral atom? |
| | Answer: (a) ion; (b) ion; (c) neutral atom |
| 13 | The symbol for an ion is determined as follows, using two of the examples from frame 12. An oxygen ion with ten electrons and an atomic number of 8 has gained two extra electrons. Since each electron has a negative (-) charge the oxygen has a 2- charge. The 2- is written to the upper right of the (O) symbol to indicate two extra electrons, O ²⁻ . The aluminum ion has ten electrons and an atomic number of 13. It has <i>lost</i> three electrons and its symbol is Al ³⁺ . The 3+ to the upper right of Al indicates that the protons outnumber the electrons by three. The calcium ion (Ca ²⁺) has 20 protons (same as atomic number) andelectrons. |
| | Answer: 18 (It has lost two electrons; therefore, the protons outnumber the electrons by two.) |
| 14 | A chlorine ion has gained one electron. It is symbolized by Cl ⁻ . A sodium ion has lost one electron. It is symbolized by Na ⁺ . (Note that the number 1 is implied and |

is not written as part of the symbol for an ion.)

A potassium ion is symbolized as K⁺. It has (lost, gained) ______ elec-

Answer: lost; one

trons. How many?

| 15 | If copper (Cu) has lost two electrons, write the symbol for its ion | _ |
|----|--|---|
| | If fluorine (F) has gained one electron, write the symbol for its ion. | _ |

Answer: Cu2+; S2-; F-

An ion is formed when a neutral atom gains or loses one or more electrons. You may be wondering why an atom would gain or lose electrons to form an ion. As a general rule, atoms tend to form sets of eight electrons in their outermost shells (valence electrons) when they combine to form compounds. Atoms with six or seven valence electrons have a great attraction for one or two extra electrons, and atoms with only one, two, or three valence electrons have only a weak hold on those electrons. An atom with six or seven valence electrons will tend to gain electrons from another atom with one, two, or three valence electrons when those atoms combine chemically.

Calcium (Ca) has two valence electrons. Oxygen (O) has six valence electrons. If an atom of calcium and an atom of oxygen are combined chemically, which atom would gain electrons and which atom would lose electrons?

Answer: Oxygen would gain electrons while calcium would lose electrons.

- By gaining two electrons, the oxygen atom, which had six valence (outer shell) electrons, becomes an ion with a total of eight outer shell electrons. The ion symbol is O²⁻. By losing two valence electrons, the calcium atom becomes a positive ion symbolized by Ca²⁺. The general tendency of atoms to form sets of eight electrons in their outermost shells (valence electrons) when they combine to form compounds is commonly called the octet rule.
 - (a) When a calcium ion and an oxygen ion combine to form a compound, the oxygen ion (O²⁻) has a total of how many electrons in its outermost shell?
 - (b) According to what rule?

Answer: (a) eight; (b) the octet rule

The noble gases (Group VIIIA on the periodic table) already have eight electrons in their outermost shells (with the exception of helium). When atoms combine to form compounds, the atoms generally tend to form electron configurations that are similar to the noble gases.

A neutral chlorine (Cl) atom has 17 electrons in its electron configuration. Its total electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$. Its outermost shell configuration

(the third shell) is represented by $3s^2 3p^5$, which adds up to 2 + 5 = 7 outer shell (valence) electrons. When combining chemically with another atom such as sodium, the chlorine atom will gain one electron to form the chloride ion (Cl⁻). The chlorine atom (Cl) has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^5$. The chloride ion (Cl⁻) has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$.

The chlorine *atom* has seven outer shell electrons and a total of 17 electrons. The chloride *ion*, however, has how many outer shell electrons? ______ How many total electrons? _____

Answer: eight;18

Remember that when atoms combine to form compounds, the atoms generally tend to form electron configurations that are similar to the noble gases. When a chlorine atom becomes an ion, it gains one electron. Instead of having 17 electrons in its total electronic structure, it gains one electron to have a total of 18 electrons. The resulting chloride ion has attained an electron configuration that is similar to that of a noble gas atom.

What neutral noble gas atom has a total of 18 electrons? _____(Hint: Use the periodic table for your answer.)

Answer: Argon (Ar) has an atomic number of 18 and, therefore, has 18 electrons in its neutral atom.

When chlorine (Cl) and sodium (Na) combine to form NaCl, both atoms become ions. Chlorine gains one electron from sodium to become the Cl⁻ ion. The sodium atom loses its one outer shell electron to chlorine and becomes the Na⁺ ion.

The sodium atom originally had 11 electrons in its electron configuration $(1s^2 2s^2 2p^6 3s^1)$. In becoming an ion, sodium loses its only outer shell electron $(3s^1)$ and becomes the Na⁺ ion with a total of ten electrons. What neutral atom has the same number of electrons as the sodium ion (Na^+) ? ______ To what family of elements does that neutral atom belong? ______ (Use the periodic table.)

Answer: Ne (neon) (has ten electrons); noble gas family

All of the elements in Group VIIA of the periodic table (F, Cl, Br, I, and At) have outer shell structures with seven electrons. Each element in Group VIIA has just one less electron than the corresponding noble gas in each period and each, when forming an ion, tends to gain one electron. You are already familiar with the chloride ion, which is symbolized by Cl⁻. The single minus sign to the upper right of the Cl symbol indicates a gain of one electron.

Write the symbol for the ion of each of the following neutral atoms in Group VIIA. Assume that each ion has gained one electron.

Answer:

Answer:

| Atoms | Ions |
|-----------------------|-----------------|
| F, Cl, Br, I, At | Cl ⁻ |
| | |
| wer: | |
| Ions | |
| F-, Cl-, Br-, l-, At- | |

An atom of each element in Group VIA has six electrons in its outermost shell. In 22 order to become ions with eight electrons, these atoms must gain two electrons. You are already familiar with the symbol for an oxygen ion (O^{2-}) . The symbol represents two electrons gained.

Write the symbols for the ions of each of the following neutral atoms from Group VIA. Each has gained two electrons. (The first has been filled in.)

An atom of each element in Group IA has only one electron in its outermost shell. 23 An atom of each element in Group IIA has two electrons in its outermost shell. These atoms readily give up their outer shell electrons to become positive ions. You are already familiar with the sodium ion (Na⁺), which has lost one electron, and the calcium ion (Ca²⁺), which has lost two electrons.

Write the symbols for the ions of each of the following neutral atoms from Group IA and Group IIA. Use the periodic table to determine whether an atom is from Group IA or Group IIA.

Many of the elements in groups other than IA, IIA, VIA, and VIIA can commonly 24 form ions with more than one value. In some cases the octet rule is followed, and in some cases it is not. For example, the element copper (Cu) can form Cu⁺ as well as Cu²⁺. In other words, an atom of copper can lose either one electron or two electrons to form two different kinds of ions. When such ions are encountered in this and later chapters, you will be informed of the number of electrons lost or gained or be given the proper symbol for the ion.

| Use the periodic | table to | write | the proper | ion sym | bol for e | each of the | following |
|-------------------|----------|-------|------------|---------|-----------|-------------|-----------|
| atoms from Groups | IA, IIA, | VIA, | or VIIA. | · | | | |

Answer:

lons

Br-, S2-, Be2+, Rb+, Na+

A copper (Cu) atom loses two electrons to become an ion. An iron (Fe) atom loses three electrons to become an ion. Write the proper symbols for these ions.

Answer: Cu2+, Fe3+

Metals generally form positive ions (ions with a + charge) while nonmetals generally form negative ions (ions with a - charge). Na⁺, Ca²⁺, and Fe³⁺ are some examples of metallic ions, and Cl⁻, O²⁻, and Br⁻ are examples of nonmetallic ions.

Metals, in forming ions, would generally be expected to (lose, gain) electrons. Nonmetals, in forming ions, would generally be ex-

pected to (lose, gain) ______ electrons.

Answer: lose; gain

IONIC BONDS

Compounds can be formed from the combination of a negative ion and a positive ion. Such compounds are called ionic compounds. The negative and positive ions of the compound are held together by an ionic bond (sometimes called an electrovalent bond). You are already familiar with the ionic compound NaCl, which is made up of two ions with opposite charges. One ion is positive and metallic. The other ion is negative and nonmetallic. Write the appropriate symbols for the ions that make up NaCl.

Answer: Na+ and Cl-

An ionic (electrovalent) bond involves oppositely charged ions held together by the attraction from their opposite electrical charges. (Oppositely charged particles attract.) Circle those pairs of ions that could probably form ionic compounds.

K⁺ and F⁻ Mg²⁺ and O²⁻ Ca²⁺ and Ba²⁺ Br⁻ and At⁻

Answer: K⁺ and F⁻; Mg²⁺ and O²⁻ (The other pairs of ions have like charges and will not form ionic bonds, since like charges repel.)

| 29 | In an ionic (electrovalent) bond, the two ions are of opposite charge. When a potassium (K) atom and a fluorine (F) atom combine to form a compound, the F atom with only seven valence electrons gains one electron from the K atom, which has only one valence electron to lose. The result is the K ⁺ ion is united in an ionic bond with the F ⁻ ion. Both ions have achieved an electron configuration similar to the noble gases and are held together by their opposite electrical charges. |
|----|---|
| | (a) The metallic ion is (K ⁺ , F ⁻) |
| | (b) The nonmetallic ion is (K^+, F^-) |
| | (c) The K ⁺ ion has the same number of electrons as which noble gas atom? (Use the periodic table.) |
| | (d) The F ⁻ ion has the same number of electrons as which noble gas atom? (Use the periodic table.) |
| | Answer: (a) K+; (b) F-; (c) Ar (argon) (with 18 electrons); (d) Ne (neon) (with ten electrons) |
| 30 | When the formula (set of symbols representing a compound) for an ionic compound is written, the most metallic element is written first. In the case of NaCl, it should be clear that Na is much more metallic than Cl (since Na is a metal and Cl is a nonmetal). As you may remember, the most metallic elements are located on the left side of the periodic table and the most nonmetallic elements are located on the right. Which of the following ionic compounds are correctly written with the most metallic element first? MgO, BrK, LiCl, SCa |
| | Answer: MgO and LiCl (The other two are incorrect. Since K is more metallic than Br, it should be written as KBr, and since Ca is more metallic than S, the formula is written as CaS.) |
| 31 | Up to this point, you have dealt only with compounds made of ions with opposite but equal charges. Suppose we wish to make an ionic compound with Ca ²⁺ and Cl ⁻ ions. In this case, the calcium (Ca) atom has two electrons to lose to form an ion, but the chlorine (Cl) atom only needs to gain one electron to form an ion. We can form the compound by using two Cl ⁻ ions for each Ca ²⁺ ion. The result is an ionic compound written as CaCl ₂ . The number 2 written at the lower right side (subscript) of Cl in the formula indicates that there are two Cl ⁻ ions for each Ca ²⁺ ion. Write the formula for the compound made up of the ions Mg ²⁺ and Br ⁻ . |
| | Answer: MgBr ₂ (This requires two Br ⁻ ions for each Mg ²⁺ ion.) |
| 32 | The formula Li ₂ O represents an ionic compound. Based upon what you have just learned, how many Li ⁺ ions are necessary for each O ²⁻ ion? |
| | Answer: Two Li ⁺ ions are necessary for each O ²⁻ ion. |

Write the formulas for ionic compounds that are made up of the following sets

| 33 | Write the formulas for ionic compounds that are made up of the following sets of ions. |
|--------|--|
| | (a) Ca ²⁺ , I ⁻ |
| | (b) O ²⁻ , K ⁺ |
| | (c) Na ⁺ , S ²⁻ |
| | (d) Fe ³⁺ , Cl ⁻ |
| | Answer: (a) Cal ₂ ; (b) K ₂ O; (c) Na ₂ S; (d) FeCl ₃ |
| | The next few frames discuss a second type of bonding that occurs when atoms <i>share</i> electrons instead of actually exchanging them. |
| COVALE | NT BONDS |
| 34 | In the formation of an ionic (electrovalent) bond, one or more valence electrons are removed from one atom and taken by another atom and, in the process, both atoms become ions. The resulting atoms are bonded together by the attraction of their opposite charges. A different type of bond is the covalent bond. In a covalent bond, one or more valence electrons from each atom are <i>shared</i> . The resultant compound is made up of molecules, not ions. Carbon monoxide exists as a molecule composed of carbon and oxygen with shared outer shell electrons. Carbon monoxide uses what kind of bonding? (ionic, electrovalent, covalent) |
| | Answer: covalent |
| 35 | Covalent bonds are usually formed between nonmetals. Ionic bonds are usually formed between a metal and a nonmetal. The bond between nitrogen and oxygen in the compound NO would most likely be (ionic, covalent) |
| | Answer: covalent (because both atoms are nonmetals, on the right side of the periodic table) |
| 36 | Carbon tetrachloride is composed of one carbon and four chlorine atoms. Both carbon and chlorine are nonmetals. What type of bonding is probably involved in this compound? |
| | Answer: covalent |
| 37 | Carbon tetrachloride, a compound with covalent bonding, is made up of (ions, molecules) |

Answer: molecules

- Which type of bonding (ionic or covalent) could more likely be expected in a compound whose atoms:
 - (a) are all nonmetals?
 - (b) share valence electrons?
 - (c) have become ions?
 - (d) have transferred valence electrons from one atom to another?

Answer: (a) covalent; (b) covalent; (c) ionic; (d) ionic

Electron dot symbols can be used to represent both ionic and covalent bonding. The dot symbols below represent the ionic bonding of KI (potassium iodide). A potassium (K) atom transfers its single valence electrons to an iodine (I) atom and both become ions. The brackets, [], show that all eight electrons in the outer shell now belong to the negative ion. The comma placed between the negative and positive ions is there only to separate the two ionic symbols.

$$K \cdot + : \ddot{I} \cdot \rightarrow K^{+}, [: \ddot{I} :]^{-}$$

The following dot symbols represent covalent bonding. Two fluorine atoms share a pair of electrons to become one fluorine gas molecule.

$$: \ddot{F}\cdot + \cdot \ddot{F} \colon \rightarrow : \ddot{F} \colon \ddot{F} \colon$$

What type of bonding do the following symbols represent?

Ca:
$$+ \cdot \ddot{O}: \rightarrow Ca^{2+}, [: \ddot{O}:]^{2-}$$

Answer: ionic bonding (The two valence electrons from Ca were transferred to the O atom and both atoms become ions.)

Assume ionic bonding for the following reaction. Complete the dot symbols equation. The strontium atom gives up both valence electrons to the sulfur atom and the atoms become ions.

$$Sr: + \cdot \ddot{S}: \rightarrow \underline{\hspace{1cm}}, \underline{\hspace{1cm}}]$$

Answer: Sr2+, [:\boxed{S}:]2-

Ionic bonding for gallium iodide, GaI₃, is represented as follows.

$$\ddot{G}a \cdot + 3 : \ddot{I} : \rightarrow Ga^{3+}, 3[: \ddot{I} :]^{-}$$

Note that three iodine atoms each take one electron from the three available valence electrons of gallium. The number 3 placed in front of the brackets indicates three iodide ions each having a charge of 1-.

Complete the ionic bonding equation for MgCl₂ in which two chlorine atoms each take one electron from the two available valence electrons of magnesium.

$$Mg + 2:Cl: \rightarrow \underline{\hspace{1cm}}, \underline{\hspace{1cm}}$$

Answer: Mg²⁺, 2[:C|:]-

Look at the following ionic bonding equations.

$$\begin{aligned} \mathsf{Ca:} + \cdot \ddot{\mathsf{O}} &: \to \mathsf{Ca}^{2+}, \, [: \ddot{\mathsf{O}} :]^{2-} \\ \dot{\mathsf{K}} + : \ddot{\mathsf{I}} &: \to \mathsf{K}^{+}, \, [: \ddot{\mathsf{I}} :]^{-} \\ \mathsf{Sr:} + : \ddot{\mathsf{S}} &: \to \mathsf{Sr}^{2+}, \, [: \ddot{\mathsf{S}} :]^{2-} \\ \mathsf{Mg:} + 2 : \ddot{\mathsf{C}} :: \to \mathsf{Mg}^{2+}, \, 2 [: \ddot{\mathsf{C}} :]^{-} \end{aligned}$$

Answer: eight; the octet rule

All noble gas atoms, with the exception of helium, have eight outer shell electrons. In following the octet rule, bonding atoms tend to form an outer shell electron configuration similar to that of the noble gases. Fluorine (F₂) is composed of two fluorine atoms and is covalently bonded, as indicated in the following bonding equation.

$$: \ddot{F}\cdot + \cdot \ddot{F}: \rightarrow : \ddot{F}: \ddot{F}:$$

Including the shared electron pair, how many electrons are in the outer shell of each atom?

Answer: eight (Note that one pair is shared by both atoms.)



Each circle contains eight electrons.

The correct bonding equation for N₂ must be written so that each N atom has eight electrons, following the octet rule. More than one pair of electrons can be shared.

$$\cdot \ddot{N} \cdot + \cdot \ddot{N} \cdot \rightarrow N \quad N$$

Knowing that each N atom within the N_2 molecule must have eight electrons, which of the following is the correct outer shell electron structure for N_2 ? (You may wish to draw circles around each atom to decide your answer. Be sure to circle all of the shared electrons around each atom.)

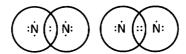
$$:\dot{\mathbb{N}}:\dot{\mathbb{N}}:$$
 or $:\dot{\mathbb{N}}:\dot{\mathbb{N}}:$ or $:\mathbb{N}:::\mathbb{N}:$

Answer: :N:::N: (This structure showing three pairs of shared electrons — a triple bond — is the only structure that allows each atom access to eight electrons.)



Each circle contains eight electrons.

The others are not correct as shown by the number of electrons in each circle.



Select the proper electron dot structure for the outer shell electrons of the O₂ molecule. Follow the octet rule.

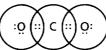
$$: \ddot{\bigcirc} \cdot + : \ddot{\bigcirc} \cdot \rightarrow \underline{\hspace{1cm}} (: \ddot{\bigcirc} :: \ddot{\bigcirc} : \text{ or } \cdot \ddot{\bigcirc} :: \ddot{\bigcirc} : \text{ or } : \dot{\bigcirc} :: \ddot{\bigcirc} : \text{ or } : \ddot{\bigcirc} :: \ddot{\bigcirc} :$$

Answer: ·Ö::Ö· or :Ö::Ö: (These structures give each atom eight electrons. Two pairs of electrons must be shared to give each atom eight electrons.)

Which of the following is the correct representation of the valence electrons of the carbon dioxide molecule? Four covalent bonds are included in the molecules.

$$\cdot\ddot{\mathbf{C}}\cdot + 2:\ddot{\mathbf{O}}\cdot \rightarrow$$
 (: $\ddot{\mathbf{O}}:\mathbf{C}:\ddot{\mathbf{O}}:$ or : $\mathbf{O}::\mathbf{C}::\mathbf{O}:$ or : $\mathbf{O}::\mathbf{C}::\mathbf{O}:$)

Answer: :Q::C::Q: (This is the only structure that allows each atom eight electrons, no more or less.)



The H₂ molecule electron structure shows that each hydrogen atom prefers the helium noble gas structure with two shared electrons.

$$H \cdot + H \cdot \rightarrow H : H$$

Determine the electron outer shell structure of the HCl gas molecule. The hydrogen atom prefers the helium structure and the chlorine atom follows the octet rule.

Answer: H:Çl: (H has two electrons and CI has eight electrons.)

Not all compounds follow the octet rule, but it serves as a useful rule for showing most electronic bonding structures. The general tendency in bonding is for atoms or ions to attain the noble gas outer shell structure.

| | With the exception of helium, the noble gases have how many electrons in their outer shells? Helium has how many electrons in its outermost (and only) shell? |
|----|--|
| | Answer: eight; two |
| 49 | In a regular covalent bond, a shared pair of electrons originates when each of two atoms supplies one electron. A special type of covalent bond is known as the coordinate covalent bond. In a coordinate covalent bond, both electrons in a shared pair of electrons come from the same atom. The bonding between the nitrogen atom in ammonia (NH ₃) and the boron atom in boron trifluoride (BF ₃) is an example of a coordinate covalent bond. |
| | H :F: H:F: H:N: + B:F: → H:N:B:F: H :F: H:F: |
| | In the above equation, which atom supplied <i>both</i> electrons to form the coordinate covalent bond? (H, N, B, or F) |
| | Answer: The N atom supplied both electrons to form a coordinate covalent bond. (Notice that in NH ₃ on the left side of the equation, the N is already shown with eight electrons.) |
| 50 | A coordinate covalent bond is like any other covalent bond except for the origin of the shared electron pair. Does the molecule below conform to the octet rule (with the exception of the hydrogen atoms)? |
| | H:F: H:N:B:F: H:F: |
| | Answer: Yes, all the atoms in the molecule (except the hydrogen atoms) have eight outer shell electrons. |
| 51 | Review your understanding of ionic, covalent, and coordinate covalent bonding. |
| | (a) A bond in which one or more electrons are removed from one atom and taken by another is called a(n) bond. |
| | (b) A bond in which two atoms share a pair of electrons with one electron coming from each atom is called a(n) bond. |
| | (c) A bond in which two atoms share a pair of electrons with both electrons coming from one atom is called a(n) bond. |
| | Answer: (a) ionic; (b) covalent; (c) coordinate covalent |
| | Up to this point we have assumed that the electrons in a covalent bond are shared equally between the bonding atoms, that is, the electrons are midway between the bonding atoms. In the frames that follow we discuss what happens if the |

electrons are not equally shared, that is, if the electron pair is closer to one atom than the other.

POLAR BONDS

When all the atoms in a covalent molecule are identical, the attraction each atom has for shared electrons is equal. When the atoms in a covalent molecule are different, the attraction for the shared electrons is not equal. In a covalent molecule such as Cl₂, the attraction for the shared electron pair by both atoms within the molecule is equal. This is obvious since the two chlorine atoms are exactly the same. A molecule of HCl gas is also covalently bonded, but the attraction for electrons by the H and Cl atom is *not* the same. The Cl atom has a greater attraction for electrons than the H atom.

Which of the following molecules (all have covalent bonds) should have atoms with *equal* attraction for electrons? (H₂, F₂, HF, NH₃)

Answer: H_2 and F_2 are molecules with an identical pair of atoms that equally attract electrons.

The attraction an atom has for the electrons in a covalent bond is called electronegativity. In the HCl molecule, the shared pair of electrons spend more time nearer the chlorine atom. In the HF molecule, the shared electrons spend more time nearer the F atom. Based on this information, which of the two atoms would be more electronegative? (H or F)

Answer: F is more electronegative because it attracts the electron pair more than H.

A molecule that has atoms with differing electronegativities has a slight + charge on one side of the molecule and a slight - charge on the other side because the shared electron pair is located nearer the more electronegative atom. When this happens, the molecule has "poles" (like the earth) or regions of + and - charge and is said to be polar. Later, in Chapter 11, you will see how polarity affects the properties of a compound. HCl is a covalent molecule with a slight - charge on the chlorine side and a slight + charge on the hydrogen side of the molecule. Is HCl a polar molecule?

Answer: yes (It has regions of slight + and - charges in the molecule.)

HCl is a polar molecule. The Cl atom has a greater electronegativity than the H atom. As a result, the bonding electron pair is shared unequally and spends more time near the Cl than the H. The HCl molecule therefore has a slight negative charge on the Cl side and a slight positive charge on the H side. The slight negative charge is equal but opposite the slight positive charge. Based upon what you have

| | learned so far, which of the following covalent molecules <i>cannot</i> be polar molecules. (HF, H ₂ , F ₂ , NH ₃) |
|----|---|
| | Answer: H_2 and F_2 are definitely <i>not</i> polar molecules because the atoms are identical. HF is polar (frame 53), but you have insufficient information to judge NH_3 now. |
| 56 | HBr is a polar covalent molecule. The shared bonding electrons are nearer the Br than the H. Since electrons are negative charges, which of the following correctly describes this polar molecule? |
| | (a) Slightly negative H and slightly positive Br |
| | (b) Slightly positive H and slightly negative Br |
| | Answer: (b) |
| 57 | Iodine is more electronegative than hydrogen, so HI is a polar molecule. Which atom is slightly negative? Which is slightly positive? |
| | Answer: I; H |
| 58 | The small Greek letter δ (delta) is sometimes used to show a partial positive or negative charge on a polar covalent molecule. For example, the HCl molecule could be symbolized as: |
| | ^{δ+} H:Ċ̈[: ^{δ-} |
| | The partial positive and negative charges are indicated near the proper atoms. Fluorine is more electronegative than hydrogen. Which of the following symbols is correct? |
| | (a) δ+H:F;δ- |
| | (a) ^{δ+} H:;;; ^{δ-} (b) ^{δ-} H:;; ^{δ+} |
| | Answer: (a) |
| 59 | Carbon monoxide (CO) is also a polar covalent molecule. The structure for CO is: |
| | :C:::O: |
| | Oxygen is more electronegative than carbon. Which of the following is correct? |
| | (a) δ^+ :C:::O: δ^- |
| | (b) ^{δ-} :C:::O: ^{δ+} |
| | Answer: (a) |
| 60 | Note that the partial + and - charges in a polar covalent molecule are much smaller than the unit + or - charges of a proton or electron. The polar charge is always much less than the charges that hold ions together in an ionic compound. Which |

type of bonding has the greater charge difference holding the atoms together? (ionic, polar covalent, covalent)

Answer: ionic

61

For compounds consisting of only two atoms it is possible to classify the bond(s) as covalent, polar covalent, or ionic based upon the electronegativity difference between the atoms. Electronegativity is abbreviated "en" and the electronegativity difference is shown as Δen . We will use this scheme of classification. The compound is:

> covalent if Δ en is less than 0.5 en units; polar covalent if Δ en is between 0.5 and 1.5 en units; ionic if Δ en is greater than 1.5 en units.

The purpose of such a classification is to provide a rough rule of thumb for predicting the type of bond that might form when two atoms combine. To be sure, any difference in electronegativities will result in a polar bond. However, it is the degree or extent of the difference that will permit you to tell whether one compound is more or less polar than other compounds, or a particular bond is more or less polar than another, or more ionic than covalent. The only time we have a 100% covalent bond is when $\Delta en = 0$, which usually happens only when identical atoms combine. Using the table shown below and the scheme above, CO would be classified as a polar covalent compound.

The electronegativity value is the number below the symbol in the table, C = 2.5and O = 3.5 units. The difference (Δ en) is: 3.5 – 2.5 = 1.0 unit, therefore CO is polar covalent.

| 1 H 2,1 | | | | | | | He - |
|-----------------------|---------|-----------------------|------------------------|-----------------------|-----------------------|------------------------|----------------------|
| 3 Li 1.0 | 4 Be | 5 B 2.0 | 6 C 2.5 | 7 N 3.1 | 8 O 3.5 | 9 F 4.1 | Ne – |
| 11 Na 1.0 | Mg 1,3 | 13 A 1,5 | 14 Si 1.8 | 15 P 2.1 | 16 S 2.4 | 17 Cl 2.9 | 18 Ar – |
| 19 K 0.9 | Ca | | | | | | |

Electronegativities of the First Twenty Elements

How should KF be classified? (ionic, polar covalent, covalent)

Answer: $\Delta en = 4.1$ (fluorine) – 0.9 (potassium) = 3.2, thus it is an ionic bond

62

Using the table again, how should each of the following be classified?

- (a) HCl _____
- (b) LiCl _____
- (c) F₂

Answer: (a) polar covalent (Δ en = 0.8 unit); (b) ionic (Δ en = 1.9 units); (c) covalent (Δ en = 0.0; they are identical atoms)

SHAPES OF MOLECULES

The classification scheme discussed in frames 61 and 62 only works with compounds composed of two atoms. If we have compounds of three or more atoms, the *shape* of the molecule becomes important in determining its polarity.

A discussion of the shapes of molecules requires an exhaustive look at atomic and molecular orbitals and their shapes and spatial orientation, along with a discussion of the valence bond electron repulsion theory. Such a presentation is beyond the scope of this book. We will limit our discussion to a few simple molecules that are known to be linear (all the atoms in the compound can be joined by a single straight line through their nuclei) or bent (nuclei cannot be joined by a straight line). Bent molecules may be planar (all atoms fall within the same flat surface, such as this page) or nonplanar (one or more atoms fall outside the flat surface — say, above or below the plane of this page).

63

Carbon dioxide (CO₂) is a linear molecule with the structure shown below.

$$\ddot{O}$$
: \ddot{O} : \ddot{O} : \ddot{O} = \ddot{O} = \ddot{O} = \ddot{O}

Structure B is introduced to simplify our efforts and yours when dealing with bonds from now on. A single line represents a pair of electrons. Since there are four electrons between the carbon atom and each oxygen atom we draw two lines between them. The other single lines on the oxygen atoms each represent a pair of electrons not involved in the bonding in CO₂. Such a drawing is called a line structure for a molecule. Look at the dot structure for CO in frame 59. What would be the line structure for CO?

Answer: IC≡OI

| 64 | What would be the line structure for HCl in frame 58? |
|----|---|
| | Answer: H-\(\overline{\overline{G}}\) |
| 65 | When a carbon atom and an oxygen atom form a bond or bonds between them, will the electrons be closer to the carbon atom or the oxygen atom? |
| | Answer: oxygen (because it is more electronegative) |
| 66 | Carbon dioxide is a linear molecule. Oxygen (1 below) is pulling on the electrons between it and the carbon to the same extent as oxygen (2) is pulling on its electrons. |
| | $ \overline{O}=C=\overline{O} $ |
| | $(1) \qquad (2)$ |
| | An analogy could be two tug-of-war teams pulling on a rope with neither team moving. Even though each bond <i>within</i> the molecule may be polar, the net result, because the molecule is linear, is that the molecule as a whole is nonpolar. Carbon disulfide (CS ₂) has a line structure of: |
| | $ \overline{S} = C = \overline{S} $ |
| | Would you expect the molecule to be polar or nonpolar? |
| | Answer: nonpolar |
| 67 | Water (H ₂ O) is an example of a bent planar molecule. Its line structure is: |
| | ХОХ Н Н |
| | The "tugs" in this case are not along the same straight line so they do not offset each other. Would you expect H ₂ O to be a polar or nonpolar molecule? |
| | Answer: polar |
| 68 | H ₂ S has a structure similar to water. |
| | (a) What would be its line structure? |

(b) Would you expect it to be polar or nonpolar? _____ (Note: Sulfur and oxygen are both in Group VIA in the periodic table, so they

have the same number of outer shell electrons.)

Answer:

(Or something similar. The molecule is bent and planar but not linear.)

- (b) polar
- Recall that in frame 55 we could not judge whether ammonia, NH₃, would be 69 polar or nonpolar. Ammonia is a bent molecule and is not planar. It looks like a pyramid with a triangular base. The nitrogen atom serves as the "peak" with the hydrogen atoms located at the corners of the base.

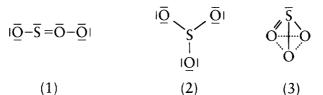


HHH (The dotted lines are not bonds, but outlines of the pyramid base.)

- (a) Would you expect the "tug" on the electrons to be equal and offset?
- (b) Would NH₃ be a polar or nonpolar molecule?

Answer: (a) no; (b) polar

- Planar molecules are nonpolar. A planar molecule consists of a molecule with all of 70 its atoms lying in the same plane. SO3 is both planar and nonlinear.
 - (a) Which of these structures could represent SO₃?



(b) Is SO₃ polar or nonpolar?

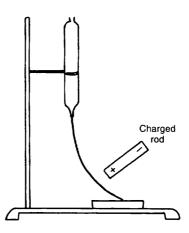
Answer:

- (a) Structure 2 is the only one that is planar and nonlinear.
- (b) nonpolar
- It is also possible to determine experimentally if compounds are polar covalent, nonpolar covalent, or ionic. A liquefied ionic compound, or an ionic compound in water solution, will conduct electricity and a covalent compound will not. A polar covalent compound will be attracted toward a charged rod. A nonpolar compound is not attracted.

A compound that will not conduct electricity and will not be attracted by a charged rod should be which kind of compound?

Answer: nonpolar covalent

A stream of pure water is attracted by a charged rod but the water does not conduct electricity.



Water must be what kind of compound?

Answer: polar covalent

A water solution of KCl is a good conductor of electricity. KCl must be what kind of compound?

Answer: ionic

PERIODIC PROPERTIES

- Use the periodic table for the following review questions.
 - (a) Where are metals located on the periodic table? (right side, left side, both sides of the steplike line) _____
 - (b) Where are nonmetals located?

Answer: (a) left side; (b) right side

The alkali metals (in Group IA) are the most metallic family on the periodic table. Metallic characteristics increase with increased atomic number. Given these statements, which element could be expected to be the most metallic?

Answer: Fr (francium) would be the most metallic, since it is the element of largest atomic

| | number in the most metallic group (IA). |
|----|---|
| 76 | Of the alkaline earth family (IIA), which element could be expected to be the most metallic? |
| | Answer: Ra (radium) is the most metallic element in Group IIA, since it has the largest atomic number in the group. |
| 77 | In the same group, nonmetallic properties <i>decrease</i> as atomic number is increased. Of the halogens (Group VIIA), which is the most <i>nonmetallic?</i> |
| | Answer: F (fluorine) (Since nonmetallic properties decrease with increasing atomic number, the most nonmetallic halogen must be the one of smallest atomic number.) |
| 78 | Which of the noble gases (Group VIIIA) could be expected to have the most non-metallic characteristics? |
| | Answer: He (helium) (the noble gas with the smallest atomic number, therefore the most nonmetallic of the noble gases) |
| 79 | A number of other properties also increase or decrease in relation to position on the periodic table. One such property is electronegativity, which we've just learned is a measure of the tendency of a covalently bonded atom to attract the bonding electron pair. Electronegativity generally increases from left to right across the periodic table and from the bottom to the top. The elements of least electronegativity would be found on the bottom left side of the periodic table. Where would the elements of greatest electronegativity be located? |
| | Answer: top right side of the periodic table (The most electronegative element is fluorine. Note that the electronegativities of the noble gases are unknown.) |
| 80 | Ionization energy (the energy required to remove electrons from a neutral atom) increases and decreases in the same general way as electronegativity. Elements requiring the <i>most</i> ionization energy are found on the top right side of the periodic table. Helium, the element of smallest atomic number in the noble gases, requires the most ionization energy of any element. Which element within the halogen family (Group VIIA) could be expected to require the <i>most</i> ionization energy? |
| | Answer: fluorine (Within a group or family, the element of smallest atomic number would require the most ionization energy. The halogen of lowest atomic number is fluorine.) |
| 81 | In Group IIA (the alkaline earth metals), which element could be expected to require the greatest ionization energy? Which element in Group IIA has the greatest electronegativity? |
| | |

83

Answer: Be (beryllium) is the correct answer to both questions. It has the smallest atomic number within the group. Thus, it has the greatest electronegativity and requires the greatest ionization energy within Group IIA.

Within the third period (the elements from Na on the left to Ar on the right), which element would be expected to require the greatest ionization energy?

Answer: argon (Ionization energy generally increases from left to right.)

Within the fourth period (potassium to krypton), which element would be expected to require the *least* ionization energy?

Answer: potassium

You have just learned that the valence shell electron structure of an atom is the controlling factor of several properties of the atom. It determines whether an atom gains or loses electrons and how many. It also determines the type of chemical bond formed when atoms combine and whether atoms have metallic or nonmetallic properties.

In any vertical column of elements in the A groups of the periodic table, as you go from top to bottom:

- the elements become more metallic;
- the number of electron shells increases;
- the number of valence shell electrons remains the same:
- the ionization energy decreases;
- the electronegativity decreases.

In any horizontal row of the elements in the A groups of the periodic table, as you go from left to right:

- the elements become more nonmetallic;
- the number of electron shells remains the same;
- the number of valence shell electrons increases;
- the ionization energy increases;
- the electronegativity increases.

You have been introduced to ions and how they combine to form compounds. You will learn more about molecules, molecular weights, naming of compounds, and writing formulas of compounds in the chapters that follow.

A key point to remember is that even though we focused primarily on the first 20 elements in the periodic table, you can apply what you have learned to any of the elements in the A groups.

SELF-TEST

| This self-test is designed to show how well you have mastered this chapter's objec- |
|---|
| tives. Correct answers and review instructions follow the test. Use any of the tables |
| presented in the chapter to answer the questions. |

| - | | | | • | | |
|----|-------------|-----------------------------|--------------------|-------------------|------------------|--|
| 1. | | ovalent bon o or more el | | when two atom | s (share or exch | nange) |
| 2. | Hov | w many ele | ctrons are p | resent in the o | utermost shell | of a neutral S atom? |
| 3. | Circ | le the corre | - ect responses | in the following | g questions. | |
| | (a) | Which has | the lower io | nization energy | ?Li or K | |
| | (b) | Which wo | uld be more ¡ | polar? HF or H | 3r | |
| | (c) | Which is m | nore nonmeta | allic? F or I | | |
| | (d) | Which is m | nore electron | egative? K or F | ₹b | |
| | (e) | Which has | more outer | shell electrons? | Ca or C | |
| | (f) | Which wo | uld you expe | ct to be more ic | nic? LiF or HC | I |
| 4. | and | | | | | e formation of MgCl _z type of bond is formed |
| 5. | Her | e are the d | ot symbols of | f four fictitious | elements Q· I | R: :Ÿ: :Ÿ: |
| | (a) | In what g | roups would | elements Q an | d Y be found | in the periodic table |
| | (b) | Would a co | ompound for | med between Q | and Y more like | ly be ionic or covalent |
| | (c) | What ion | would you ex | kpect element X | to form? | |
| | (d) | | | | | ovalent. Which of the ompound? |
| | | :Ÿ::X:Ÿ: | :X:X: :X: | ÿ:X::ÿ: | :Ÿ::Ÿ: | |
| | | (1) | (2) | (3) | (4) | |
| c | ۱۸/۱ | ich nabla a | ine etructura | door Ma hayo y | then it hecomo | s an ion? |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. share (frame 34)
- 2. 6 (S is in Group VIA) (frames 2, 5, 8)
- 3. (a) K (frames 80-83 and summary)
 - (b) HF (frames 54-61)
 - (c) F (frames 75-78)
 - (d) K (frames 53, 61)
 - (e) C (frames 2-6)
 - (f) LiF (frames 54-61)
- 4. Mg: + 2 : Ci→ Mg²+, 2 [: Ci-]-, ionic 2H· + : O· → : O·H, polar covalent H (frames 39–48)
- 5. (a) Q in Group IA, Y in Group VIIA (frames 2, 8)
 - (b) ionic (frames 27-61)
 - (c) 2- (frames 12-26)
 - (d) structure 2 (It is the only one that obeys the octet rule for each atom.) (frames 17, 43–48)
- 6. neon (frames 18-20)

4 Molecular and Formula Weights

Since every molecule is made up of a definite and invariable number of component atoms, it follows that each kind of molecule has a definite and characteristic weight. You may ask, "How did anyone ever determine how many atoms of each kind are in a molecule of any pure substance?" We try to answer that question in this chapter. We may determine the molecular weight of a substance in a number of ways using instrumental techniques that are available today. Specific instrumental methods are not discussed here. Instead, we will rely upon the data that we get by analyzing substances and what you have learned so far in Chapters 1 through 3. We will depend upon the periodic table and the information it provides.

This chapter will teach you how to determine the molecular weight and percentage composition of a compound when given its molecular formula. You will also be able to reverse the process, to determine the molecular formula of a compound given the percentage composition of the compound (or the weight of each element per molecule) and its molecular weight. The important thing to remember is that every molecule consists of a definite number of atoms in a fixed ratio expressed as small whole numbers.

OBJECTIVES

After completing this chapter, you will be able to

- explain the difference between a molecule of a compound and a molecule of an element;
- calculate the molecular weight of a compound when given its actual formula;
- explain the difference between an empirical formula and an actual formula;
- calculate the percent by weight of each element in a compound when given its actual formula or empirical formula;
- determine the actual formula of a compound when given its empirical formula and molecular weight;
- calculate the actual formula of a compound when given its percentage composition and its molecular weight.

In Chapter 2 you learned that each atom has an average atomic weight expressed in atomic mass units (amu) and that atomic weights are included on the periodic table. You also learned that an atomic weight expressed in grams represents the weight of 6.023×10^{23} atoms.

In Chapter 3, you learned that atoms combine to form compounds of two major categories, depending upon the kind of chemical bond involved. In this chapter you will learn how to determine the weights of compounds.

Just to review a bit, the atomic weight of a Cl atom is _____ amu. What is the weight in grams of 6.023×10^{23} atoms of Cl? _____

Answer: 35.453; 35.453

The chlorine gas molecule (Cl₂) is made up of two chlorine atoms. If one atom of chlorine weighs 35.45 amu (to the nearest hundredth), one molecule of Cl₂ should weigh ________. (Note: Calculate your answer to the nearest hundredth for this and further questions unless otherwise stated.)

Answer: $70.90 \text{ amu } (35.45 \times 2 = 70.90)$

MOLECULAR WEIGHT

Carbon monoxide (CO) is a molecule made up of one atom of carbon and one atom of oxygen. If an atom of carbon weighs 12.01 amu and an atom of oxygen weighs 16.00 amu, a molecule of CO should weigh (to the nearest hundredth).

Answer: 28.01 amu (12.01 + 16.00 = 28.01)

The molecular weight of a molecule is the sum of the combined atomic weights of the atoms within the molecule. If the atomic weight of H is 1.01 amu and the atomic weight of Cl is 35.45 amu, a molecular weight of HCl is _____ amu (to the nearest hundredth).

Answer: 36.46 (1.01 + 35.45 = 36.46)

From Chapter 3, you learned that a molecule of a compound consists of two or more different types of atoms that are chemically combined by one or more chemical bonds. The molecule carbon dioxide (CO₂) is made up of one atom of carbon and two atoms of oxygen. If the atomic weight of C is 12.01 amu and the atomic weight of O is 16.00 amu, the molecular weight of CO₂ is _____ amu.

Answer: 44.01 (1 C + 2 O = 12.01 + 32.00 = 44.01)

Molecule can mean either a *molecule of an element* or a *molecule of a compound*. A molecule of an element consists of one or more atoms of the *same* kind. Examples

are H₂ (which exists as a diatomic molecule), Ar (which exists as a single argon atom), and S₈ (which exists as a molecule of eight sulfur atoms).

Since argon normally exists as a single atom, the single atom (Ar) can be called either the argon atom or the argon molecule. The atomic weight of Ar is 39.95 amu. The molecular weight of Ar is _____ amu.

Answer: 39.95 (The weight of one atom of Ar is the same as the weight of the Ar molecule because the Ar molecule is the Ar atom.)

A single atom molecule is an exception to the rule. Most molecules of either an element or a compound will usually involve two or more atoms combined with covalent bonds.

The molecular weight of O_2 is _____ amu. The molecule O_2 is a molecule of a(n) (compound, element) _____.

Answer: 32.00 (twice the weight of a single O atom); element (since only one element, oxygen, is included in the molecule)

The atomic weight of S is 32.06 amu. The molecular weight of S_8 is _____ amu. S_8 is a molecule of an element because _____.

Answer: 256.48 (8 x 32.06 = 256.48); only one element (sulfur) is included in the molecule

The following example shows a simple procedure for finding the molecular weight of sucrose sugar $(C_{12}H_{22}O_{11})$.

| Element | Number of atoms | Atomic weight | Atoms × weight |
|---------|-----------------|---------------|----------------------------|
| С | 12 C | 12.01 | 12 × 12.01 = 144.12 |
| Н | 22 H | 1.01 | 22 × 1.01 = 22.22 |
| 0 | 11 0 | 16.00 | $11 \times 16.00 = 176.00$ |

- (a) The molecular weight of $C_{12}H_{22}O_{11}$ is _____ amu. (Hint: Add the results of Atoms × weight.)
- (b) Sucrose $(C_{12}H_{22}O_{11})$ is a molecule of a(n) (compound, element) ______.

Answer: 342.34; compound (because more than one element is included in the molecule: carbon, oxygen, and hydrogen)

Determine the molecular weight of ethyl alcohol (C_2H_5OH). From now on you should use the periodic table to determine the appropriate atomic weights (to the nearest hundredth). Below are the column headings we used for our table in frame 9. Use a separate sheet of paper and make a similar table to calculate the molecular weight of C_2H_5OH .

| Element | Number of atoms | Atomic weight | Atoms × weight | |
|---------|-----------------|---------------|----------------|--|
| | | | · <u> </u> | |

The molecular weight of C_2H_5OH is _____ amu.

Answer:

| Element | Number of atoms | Atomic weight | Atoms × weight |
|---------|-----------------|---------------|-----------------------------|
| С | 2 C | 12.01 | 2 × 12.01 = 24.02 |
| Н | 6 H | 1.01 | $6 \times 1.01 = 6.06$ |
| 0 | 10 | 16.00 | $1 \times 16.00 = 16.00$ |
| | | М | olecular weight is 46.08 am |

FORMULA WEIGHT

11

From Chapter 3, you learned that there were two general categories of compounds, depending upon whether the type of chemical bonding involved was covalent or ionic. Covalent bonding generally results in molecular compounds while ionic bonding results in ionic compounds. The term molecular weight, therefore, should properly refer only to molecular compounds and not to ionic compounds. Chemists have coined the term formula weight to refer to either molecular compounds or ionic compounds. The formula weight of a molecule is the same as the molecular weight. The formula weight can also refer to the weight of an ionic compound.

The weight of CO₂ (a covalent compound) is 44.01 amu. Is 44.01 amu the molecular weight, the formula weight, or either molecular or formula weight?

The weight of NaCl (an ionic compound) is 57.44 amu. Is 57.44 amu the molecular weight, the formula weight, or either molecular or formula weight?

Answer: either molecular or formula weight; formula weight

Determine the formula weight of copper sulfate, CuSO₄. Use a separate sheet of paper to set up a table similar to those in frames 9 and 10.

Answer:

| Element | Number of atoms | Atomic weight | Atoms × weight |
|---------|-----------------|---------------|----------------------------|
| Cu | 1 Cu | 63.55 | 1 × 63.55 = 63.55 |
| S 1 S | | 32.06 | $1 \times 32.06 = 32.06$ |
| 0 | 4 O | 16.00 | $4 \times 16.00 = 64.00$ |
| | | F | ormula weight is 159.61 an |

- Answer the following questions for Vitamin C ($C_6H_8O_6$).
 - (a) Calculate the formula weight of Vitamin C. (Set up a table to calculate the amu.)
 - (b) Vitamin C is a covalent compound. What is its molecular weight?

Answer:

(a)

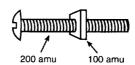
| Elements | Number of atoms | Atomic weight | Atoms × weights | |
|----------|-----------------|---------------|-----------------------------|--|
| C | 6 C | 12.01 | 6 × 12.01 = 72.06 | |
| Н | 8 H | 1.01 | 8 × 1.01 = 8.08 | |
| 0 | 6 O | 16.00 | $6 \times 16.00 = 96.00$ | |
| | | Fo | ormula weight is 176.14 amu | |

- (b) 176.14 (Molecular weight is the same as the formula weight for a covalent compound.)
- Carbon monoxide (CO) is a molecule with one atom of carbon and one atom of oxygen. The molecular weight of CO is 28.01 amu. The atomic weight of C is 12.01 amu. The atomic weight of O is 16.00 amu. Which atom (carbon or oxygen) accounts for more than half of the molecular weight of the CO molecule?

Answer: oxygen

PERCENTAGE COMPOSITION

To find the actual proportion by weight (percentage) of an element in a compound, the weight of the part must be divided by the weight of the whole. For example, a bolt and nut can be compared to a molecule with two atoms. If the nut weighed 100 amu and the bolt weighed 200 amu, the whole thing would weigh 100 + 200 = 300 amu.



The nut is a part of the whole. To find the percentage by weight that the nut occupies within the whole, divide the weight of the nut by the weight of the whole and multiply by 100. Here's how this percentage is calculated.

$$\frac{100 \text{ amu}}{300 \text{ amu}} \times 100\% = 33.3\%$$

The percentage of the weight contributed by the nut is equal to 33.3% of the weight of the whole.

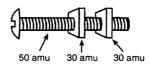
Assume that a bolt weighs 50 amu and a nut weighs 30 amu. What percentage by weight does the nut contribute in relation to the whole? The nut weighs _______ % of the whole.

Answer:

nut = 30 amu bolt = 50 amu the whole = 50 + 30 = 80 amu

percentage by weight of the nut = $\frac{\text{nut}}{\text{whole}} \times 100\% = \frac{30 \text{ amu}}{80 \text{ amu}} \times 100\% = 37.5\%$

A bolt has two nuts.



Each nut weighs 30 amu and the bolt weighs 50 amu. What percentage by weight do the nuts contribute in relation to the whole? The nuts weigh ______ % of the whole.

Answer:

nuts = $2 \times 30 = 60$ amu bolt = 50 amu the total whole = 60 + 50 = 110 amu

percentage by weight of nuts = $\frac{\text{nuts}}{\text{whole}} \times 100\% = \frac{60 \text{ amu}}{110 \text{ amu}} \times 100\% = 54.5\%$

The carbon monoxide molecule can be considered analogous to the bolt and nut combination. The molecule consists of one carbon atom weighing 12.01 amu (the atomic weight of carbon) and one oxygen atom weighing 16.00 amu (the atomic weight of oxygen). The whole molecule weighs 12.01 + 16.00 = 28.01 amu (formula weight). The oxygen atom weighs ______ % of the whole molecule.

Answer:

oxygen atom = 16.00 amu carbon atom = 12.01 amu whole molecule = 16.00 + 12.01 = 28.01 amu

percentage by weight of oxygen in carbon monoxide
$$= \frac{\text{oxygen atom}}{\text{formula weight}} \times 100\% = \frac{16.00 \text{ amu}}{28.01 \text{ amu}} \times 100\% = 57.1\%$$

To find the percentage by weight of any element within a compound, divide the total atomic weight of that element by the formula weight of the compound and multiply the result by 100%.

The molecule carbon dioxide (CO_2) has a total formula weight of 44.01 amu and consists of one carbon atom with atomic weight of 12.01 and two oxygen atoms with combined atomic weights of _____ amu.

Answer: $32.00 (16.00 \times 2 = 32.00 \text{ amu})$

Using the information in frame 18, find the percentage by weight of oxygen within the compound carbon dioxide (CO₂).

Answer: $\frac{32.00 \text{ amu}}{44.01 \text{ amu}} \times 100\% = 72.7\%$ oxygen by weight

Now calculate the percentage by weight of carbon within carbon dioxide.

Answer: You could do this in two ways. Since you just found that carbon dioxide consists of 72.7% oxygen by weight, the rest must be carbon:

$$100\% - 72.7\% = 27.3\%$$
 carbon by weight

Or, if you did not already know the percentage of oxygen, then:

$$\frac{12.01 \text{ amu}}{44.01 \text{ amu}} \times 100\% = 27.3\%$$
 carbon by weight

Calculate the percentage by weight of hydrogen (H) in water (H₂O). (Find the formula weight of H₂O first.)

Answer:

To find the formula weight of H₂O:

| Element | Number of atoms | Atomic weight | Atoms | × weight |
|---------|-----------------|---------------|-------------------|----------------|
| Н | 2 H | 1.01 | 2 × 1.01 = | = 2.02 |
| 0 | 10 | 16.00 | 1 × 16.00 = | = <u>16.00</u> |
| | | | Formula weight is | 18.02 amu |

To find the percentage composition by weight:

percentage hydrogen in
$$H_2O = \frac{\text{weight of hydrogen}}{\text{formula weight}} \times 100\%$$

$$= \frac{2.02 \text{ amu}}{18.02 \text{ amu}} \times 100\% = 11.2\%$$

Determine the percentage of carbon by weight in glucose $(C_6H_{12}O_6)$. % carbon = _____

Answer:

The formula weight of glucose ($C_6H_{12}O_6$):

| Element | Number of atoms | Atomic weight | Atoms × weight |
|---------|-----------------|---------------|------------------------------|
| С | 6 C | 12.01 | 6 × 12.01 = 72.06 |
| Н | 12 H | 1.01 | $12 \times 1.01 = 12.12$ |
| 0 | 6 O | 16.00 | $6 \times 16.00 = 96.00$ |
| | | | Formula weight is 180.18 amu |

percentage carbon in glucose =
$$\frac{\text{weight of carbon}}{\text{formula weight of glucose}}$$

= $\frac{72.06 \text{ amu}}{180.18 \text{ amu}} \times 100\% = 39.99\%$

In the preceding example (glucose, C₆H₁₂O₆), the percentage composition by weight of *all* elements (carbon, hydrogen, and oxygen) *totaled together* should equal _______%.

Answer: 100 (Since all the partial weights of all elements add up to the weight of the whole compound, all percentages also add up to their whole, which is 100%.)

EMPIRICAL FORMULA

A chemist often must determine the formula of a compound when only the percentage composition by weight is known. Assume a compound is composed of only two elements, carbon and hydrogen. By analysis, the compound is found to contain 92.2% carbon by weight. What is the percentage composition by weight of hydrogen in this compound?

Answer: 7.8% (All partial composition percentages must add up to 100%. Since there are only two elements in the compound, their percentages must add up to 100%. If carbon accounts for 92.2%, then hydrogen must account for the other 7.8%.)

A compound of undetermined formula contains 92.2% carbon by weight and 7.8% hydrogen by weight. This means that for every 100 amu of that compound, 92.2 amu

would be contributed by carbon. How many amu would be contributed by hydrogen?

Answer: 7.8 amu

Knowing that 100 amu of a compound contains 92.2 amu of carbon and 7.8 amu of hydrogen gives us the relative weights of the elements in a compound. In order to determine a chemical formula, we need to know the relative number of atoms of each element in the compound. We need to know the ratio of carbon atoms to hydrogen atoms. A 100 amu sample of a compound contains 92.2 amu of carbon and 7.8 amu of hydrogen. We know that the atomic weight of carbon is 12.01 amu and represents the weight of one carbon atom. A weight of 92.2 amu represents the weight of how many carbon atoms (to the nearest tenth)?

Answer: 92.2 amu × $\frac{1 \text{ carbon atom}}{12.01 \text{ amu}}$ = 7.7 carbon atoms

A 100 amu sample of a compound contains 92.2 amu of carbon (representing 7.7 atoms of carbon) and 7.8 amu of hydrogen. How many atoms of hydrogen are contained in the sample (to the nearest tenth)?

Answer: 7.8 amu × $\frac{1 \text{ hydrogen atom}}{1.01 \text{ amu}}$ = 7.7 hydrogen atoms

To arrive at a tentative formula for this unknown compound, we need to know the ratio of carbon atoms to hydrogen atoms within a single molecule. Since there are 7.7 atoms of hydrogen for 7.7 atoms of carbon, there must be how many atom(s) of hydrogen for each atom of carbon?

Answer: one

 $\frac{7.7 \text{ atoms of hydrogen}}{7.7 \text{ atoms of carbon}} = \frac{1 \text{ atom of hydrogen}}{1 \text{ atom of carbon}}$

Since carbon and hydrogen are in a ratio of 1:1 in this unknown compound, the simplest formula is CH (or HC). The simplest possible chemical formula that represents the ratios of the atoms within an unknown molecule is called an empirical formula. The simple formula (CH) is called a(n) _______.

Answer: empirical formula

An unknown compound with an empirical formula of CH could be any of several compounds. For example, both acetylene (C_2H_2) and benzene (C_6H_6) have an empirical formula of CH. The formulas for acetylene and benzene (C_2H_2) and

| | C ₆ H ₆) are called molecular formulas because they describe the actual number of atoms contained in each molecule. |
|----|---|
| | (a) A formula describing the simplest ratio between atoms in an unknown molecule is called a(n) |
| | (b) A formula describing the actual number of atoms contained in each molecule is called the |
| | Answer: (a) empirical formula; (b) molecular formula |
| 31 | An empirical formula is sometimes the same as an actual molecular formula. A formula determined by percentage weight analysis is considered to be an empirical formula since it only represents the ratio of one atom to another. By weight analysis, a compound is found to consist of carbon and oxygen in a 1:1 ratio. A formula of CO is assigned to the compound and you suspect that the compound could be carbon monoxide but have no proof. The formula CO is in this case a(n) (empirical, molecular) formula. |
| | Answer: empirical (If by simple weight analysis, the compound has a carbon and oxygen ratio of 1:1, then the assigned formula CO is empirical. If it is determined by additional testing that the compound is indeed carbon monoxide, then the formula CO would be a molecular formula.) |
| 32 | To determine an empirical formula if given percentage composition, follow these three steps. |
| | 1. Drop the percent signs and replace them with amu. The result is the weight composition of a 100 amu sample. |
| | 2. Multiply each of the results of step 1 by the appropriate atoms per atomic weight conversion factor (as shown in frames 26 and 27). The result is the relative "number" of atoms in a 100 amu sample. |
| | 3. Divide each of the relative "number" of atoms obtained in step 2 by the smallest number to obtain the simplest ratio of atoms in whole numbers. |
| | A compound is found to be 20% Ca and 80% Br by weight. Following step 1, a 100 amu sample of this compound would be composed of amu of Ca and amu of Br. |
| | Answer: 20; 80 |
| 33 | Using step 2 from frame 32, determine how many atoms (rounded to the nearest tenth) of the component elements are present in the 100 amu sample. |
| | (a) atoms of Ca = |
| | (b) atoms of Br = |
| | |

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(a) 20 amu
$$\times \frac{1 \text{ Ca atom}}{40.08 \text{ amu}} = 0.5 \text{ atom of Ca}$$

(b) 80 amu ×
$$\frac{1 \text{ Br atom}}{79.90 \text{ amu}} = 1.0 \text{ atom of Br}$$

In this 100 amu sample of an unknown compound, composed of 20 amu of Ca and 80 amu of Br, are 0.5 atoms of Ca and 1.0 atoms of Br. However, 0.5 atoms is not a whole number. Using step 3 from frame 32 to obtain the simplest ratio of atoms in whole numbers, divide both 0.5 atoms of Ca and the 1.0 atoms of Br by the smallest number, which is 0.5. (Note: If the answers obtained in step 2 are whole numbers, step 3 is unnecessary.)

$$\frac{0.5}{0.5} =$$
 atom(s) of Ca; $\frac{1.0}{0.5} =$ atom(s) of Br

Answer: one; two

The simplest empirical formula derived from a ratio of one atom of Ca to two atoms of Br would be ______.

Answer: CaBr₂

A compound is made up of 79.9% carbon and 20.1% hydrogen by weight. What is its empirical formula? (Apply the three steps from frame 32. Round to the nearest whole number.)

Answer:

- 1. A sample of the unknown compound weighing 100 amu is made up of 79.9 amu of carbon and 20.1 amu of hydrogen (replacing percent with amu to express weight composition).
- 2. The relative number of atoms in the 100 amu sample are as follows. A 79.9 amu weight of carbon contains 6.7 atoms of carbon.

79.9 amu ×
$$\frac{1 \text{ C atom}}{12.01 \text{ amu}}$$
 = 6.7 C atoms

A 20.1 amu weight of hydrogen contains 19.9 atoms of hydrogen.

$$20.1 \text{ amu} \times \frac{1 \text{ H atom}}{1.01 \text{ amu}} = 19.9 \text{ atoms}$$

3. We must divide the 6.7 atoms and the 19.9 atoms obtained in step 2 by the smallest number (6.7) to find the simplest whole number ratio of atoms.

$$\frac{6.7}{6.7}$$
 = 1 atom of carbon $\frac{19.9}{6.7}$ = 3 atoms of hydrogen

4. The ratio of one atom of carbon to three atoms of hydrogen provides an empirical formula of CH₃ (or H₃C).

The same procedure can be used to determine the empirical formula of a compound with three or more elements. A sample of a compound is composed of 40% calcium (Ca), 12% carbon (C), and 48% oxygen (O) by weight. A 100 amu sample of this compound would be composed of _____ amu of Ca, ____ amu of C, and ____ amu of O.

Answer: 40; 12; 48

What is the empirical formula of the compound from the previous frame? (Write the formula in the order of the elements given — Ca, C, O. Use the three-step procedure.)

Answer:

- 1. In a 100 amu sample, Ca = 40 amu, C = 12 amu, and O = 48 amu.
- 2. In that 100 amu sample there are:

40 amu ×
$$\frac{1 \text{ atom of Ca}}{40.08 \text{ amu}}$$
 = 1.0 atom of Ca
12 amu × $\frac{1 \text{ atom of C}}{12.01 \text{ amu}}$ = 1.0 atom of C
48 amu × $\frac{1 \text{ atom of O}}{16.00 \text{ amu}}$ = 3.0 atoms of O

3. Dividing by the smallest number given in step 2 in order to obtain a simple whole number ratio is not necessary in this case. We already have simple whole numbers.

The empirical formula must be CaCO₃ (elements listed from most metallic to least metallic).

Determine the empirical formula of a compound made up of 28.7% K, 1.5% H, 22.8% P, and 47.0% O. Write the formula in the order of the elements given (K, H, P, O). (In step 2, calculate to the nearest thousandth.)

Answer:

- 1. In a 100 amu sample, K = 28.7 amu, H = 1.5 amu, P = 22.8 amu, and O = 47.0 amu
- 2. In that 100 amu sample there are:

28.7 amu ×
$$\frac{1 \text{ atom of K}}{39.10 \text{ amu}} = 0.734 \text{ atom of K}$$

1.5 amu × $\frac{1 \text{ atom of H}}{1.01 \text{ amu}} = 1.485 \text{ atoms of H}$
22.8 amu × $\frac{1 \text{ atom of P}}{30.97 \text{ amu}} = 0.736 \text{ atom of P}$
47.0 amu × $\frac{1 \text{ atom of O}}{16.00 \text{ amu}} = 2.938 \text{ atoms of O}$

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$$\frac{0.734}{0.734}$$
 = 1.0 atom of K

$$\frac{1.485}{0.734}$$
 = 2.0 atoms of H

$$\frac{0.736}{0.734}$$
 = 1.0 atom of P

$$\frac{2.938}{0.734}$$
 = 4.0 atoms of O

KH₂PO₄ is the empirical formula.

Determine the empirical formula of a compound composed of 15.15% K, 10.45% Al, 24.80% S, and 49.60% O. Write the formula in the order of the elements given (K, Al, S, O). (In step 2, calculate to the nearest thousandth.)

Answer:

- 1. In a 100 amu sample, K = 15.15 amu, Al = 10.45 amu, S = 24.80 amu, and O = 49.60 amu.
- 2. In the 100 amu sample, there are:

15.15 amu ×
$$\frac{1 \text{ atom of K}}{39.10 \text{ amu}} = 0.387 \text{ atom of K}$$

10.45 amu × $\frac{1 \text{ atom of Al}}{26.98 \text{ amu}} = 0.387 \text{ atom of Al}$
24.80 amu × $\frac{1 \text{ atom of S}}{32.06 \text{ amu}} = 0.774 \text{ atom of S}$

$$49.60 \text{ amu} \times \frac{1 \text{ atom of O}}{16.00 \text{ amu}} = 3.100 \text{ atoms of O}$$

3. Divide each of the above answers by the smallest answer to find the simplest whole number ratio.

$$\frac{0.387}{0.387}$$
 = 1.0 atom of K

$$\frac{0.387}{0.387}$$
 = 1.0 atom of Al

$$\frac{0.774}{0.387}$$
 = 2.0 atoms of S

$$\frac{3.100}{0.387}$$
 = 8.0 atoms of O

KAIS₂O₈ is an acceptable empirical formula.

To review, one atom of chlorine (Cl) weighs _____ amu and 6.023×10^{23} atoms of chlorine (Cl) weigh _____ grams.

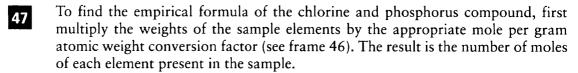
Answer: 35.453; 35.453

| 42 | The number 6.023×10^{23} appears often in chemical calculations. The term mole means 6.023×10^{23} chemical units and is much easier to write and remember than the number it represents. |
|----|---|
| | One mole of atoms means 6.023×10^{23} atoms. One mole of electrons means 6.023×10^{23} electrons. One mole of ions means 6.023×10^{23} ions. |
| | The current abbreviation for mole is mol . We will use the abbreviation in all calculations involving mole. A gram atomic weight of chlorine (Cl) represents the weight of 1 of chlorine atoms. |
| | Answer: mole (mol) (6.023 \times 10 ²³ atoms) |
| 43 | A mole of molecules represents how many molecules? |
| 44 | The atomic weight in grams of calcium (Ca) is 40.08 grams. A mole of Ca atoms weighs how many grams? |
| | Answer: 40.08 |
| 45 | The element calcium (Ca) weighs grams per gram atomic weight. The element calcium (Ca) weighs grams per mole of atoms. |
| | Answer: 40.08; 40.08 (A gram atomic weight is the weight of 1 mol of atoms.) |
| 46 | The mole is a very useful quantity in chemistry and is often encountered. You will begin using the mole in the next part of this chapter. |
| | You have already used the conversion factor of $\frac{1 \text{ atom}}{\text{atomic weight in amu}}$. |
| | You will now begin to use the conversion factor of $\frac{1 \text{ mol of atoms}}{\text{atomic weight in grams}}$. |
| | For example, since 1 mol of chlorine (Cl) atoms weigh 35.45 grams, the conversion factor would be $\frac{1 \text{ mol Cl atoms}}{35.45 \text{ grams}}$. |
| | Instead of percentages, the composition of a compound may be given directly in weights. For example, a 5.00 gram sample of a compound (to the nearest hun- |

dredth gram) consists of only chlorine and phosphorus. If the 5.00 gram sample was known to contain 1.13 grams of phosphorus (P), how many grams of chlorine

(Cl) would be present?

Answer: 3.87 (The 5.00 gram sample was of a compound with only two elements. Since one element made up 1.13 grams, the other element must account for the remainder: 5.00 - 1.13 = 3.87 grams.)



1.13 grams of P ×
$$\frac{1 \text{ mol of P atoms}}{30.97 \text{ grams}}$$
 = 0.0365 mol of P atoms

Use the same method to determine the number of moles of Cl atoms in the sample (rounded to the nearest thousandth).

3.87 grams of Cl
$$\times \frac{1 \text{ mol of Cl atoms}}{35.45 \text{ grams}} = \underline{\hspace{1cm}}$$
 mol of Cl atoms

Answer: 0.109

To determine an empirical formula for this sample, we must determine a whole number ratio of atoms. This can be done by simply dividing each mole quantity by the smallest number.

$$\frac{0.0365 \text{ mol of P atoms}}{0.0365 \text{ mol}} = 1.0 \text{ atom of P}$$

$$\frac{0.109 \text{ mol of Cl atoms}}{0.0365 \text{ mol}} = \frac{\text{atom(s) of Cl}}{\text{atom(s) of Cl}}$$

The resulting empirical formula is ______.

Answer: 3.0; PCl₃ or Cl₃P (One atom of P and three atoms of Cl. PCl₃ is best because the more metallic element is named first.)

- The steps in determining an empirical formula when given a sample are similar to steps 2 and 3 encountered earlier (refer back to frame 32) when using percentage composition to determine empirical formula.
 - **A.** Determine the number of moles of atoms of each element by multiplying the sample portion of each element by its appropriate mole per gram atomic weight conversion factor.
 - **B.** Divide each answer from step A by the smallest answer to find the simplest whole number ratio of one atom to another.

A 10 gram sample of a compound is made up of 2.73 grams of carbon and 7.27 grams of oxygen. Complete step A below. (Round to the nearest thousandth.)

2.73 grams of C ×
$$\frac{1 \text{ mol of C atoms}}{12.01 \text{ grams}}$$
 = 0.227 mol of C atoms
7.27 grams of O = _____ mol of O atoms

Answer: 0.454

Applying step B to the same sample:

$$\frac{0.227 \text{ mol of C atoms}}{0.227 \text{ mol}} = 1 \text{ carbon (C) atom}$$

- (a) Complete step B for oxygen (O) atoms.
- (b) What is the resulting empirical formula of the sample?

Answer:

- (a) $\frac{0.454 \text{ mol of O atoms}}{0.227 \text{ mol}} = 2 \text{ atoms of O}$
- (b) CO₂
- A 5.00 gram sample of a compound made up of calcium (Ca) and chlorine (Cl) is analyzed and contains 1.80 grams of Ca. The 5.00 gram sample contains how many grams of Cl?

Answer: 3.20 (5.00 - 1.80 = 3.20)

- How many moles of atoms are represented by 1.80 grams of Ca and by 3.20 grams of Cl? (Calculate moles to the nearest thousandth.)
 - (a) moles of Ca atoms = _____
 - (b) moles of Cl atoms = _____

Answer:

- (a) 1.80 grams Ca $\times \frac{1 \text{ mol of Ca}}{40.08 \text{ grams}} = 0.045 \text{ mol of Ca}$
- (b) 3.20 grams Cl × $\frac{1 \text{ mol of Cl}}{35.45 \text{ grams}} = 0.090 \text{ mol of Cl}$
- Determine the simplest whole number ratio of Ca atoms to Cl atoms, and give the resulting empirical formula.

Answer:

$$\frac{0.045 \text{ mol of Ca atoms}}{0.045 \text{ mol}} = 1 \text{ atom of Ca}$$

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$$\frac{0.090 \text{ mol of Cl atoms}}{0.045 \text{ mol}} = 2 \text{ atoms of Cl}$$

There is one atom of Ca for every two atoms of Cl, resulting in an empirical formula of CaCl₂.

A 10.00 gram sample of a compound is composed of 1.59 grams of boron (B) and 8.41 grams of fluorine (F). Determine the empirical formula of the compound. (Calculate step A to the nearest thousandth.)

Answer:

A. Determine the number of moles of each element within the sample.

1.59 grams B ×
$$\frac{1 \text{ mol of B}}{10.81 \text{ grams}} = 0.147 \text{ mol of B}$$

8.41 grams F × $\frac{1 \text{ mol of F}}{19.00 \text{ grams}} = 0.443 \text{ mol of F}$

19.00 grams

B. Determine the simplest whole number ratio of B atoms to F atoms.

$$\frac{0.147 \text{ mol of B atoms}}{0.147 \text{ mol}} = 1 \text{ atom of B}$$

$$\frac{0.443 \text{ mol of F atoms}}{0.147 \text{ mol}} = 3 \text{ atoms of F}$$

The empirical formula is BF₃.

A 5.00 gram sample of a compound contains 3.74 grams of carbon (C) and is made up of only carbon (C) and hydrogen (H). Determine the empirical formula for this compound. (Hint: First find the weight of hydrogen in the sample. Calculate step B to the nearest thousandth.)

Answer: Since the sample is 5.00 grams total and carbon (C) contributes 3.74 grams, the hydrogen (H) must weigh 1.26 grams (5.00 - 3.74 = 1.26).

A. Determine the number of moles of atoms of each element within the sample.

3.74 grams C ×
$$\frac{1 \text{ mol of C}}{12.01 \text{ grams}} = 0.311 \text{ mol of C}$$

1.26 grams H × $\frac{1 \text{ mol of H}}{1.01 \text{ grams}} = 1.248 \text{ mol of H}$

B. Determine the simplest whole number ratio of C atoms to H atoms.

$$\frac{0.311 \text{ mol of C atoms}}{0.311 \text{ mol}} = 1 \text{ C atom}$$

$$\frac{1.248 \text{ mol of H atoms}}{0.311 \text{ mol}} = 4 \text{ H atoms}$$

The empirical formula is CH_{4} (or $H_{4}C$).



An empirical formula weight can be expressed in either amu or grams. It is simply the combined atomic weights of the elements in the empirical formula. A sample of a compound has been found to have an empirical formula of CH (one carbon atom for every hydrogen atom). The empirical formula weight for CH is ______ amu.

Answer: 13.02 (C = 12.01 amu and H = 1.01 amu; thus, CH = 12.01 + 1.01 = 13.02 amu)

ACTUAL MOLECULAR FORMULA

For example, instead of CH, the actual formula could be C_2H_2 or C_6H_6 . The empirical formula only tells us the *ratio* of one atom to another. In the case of the empirical formula CH, we know that the actual formula has one C atom for every H atom. After determining the empirical formula, a chemist must devise some other experimental means to determine the actual formula. This is often done by finding the formula weight of the actual compound. Suppose that by experiment, it was determined that the actual formula weight of an unknown compound was double that of the empirical formula weight. The empirical formula is CH. The actual formula would be double that of CH. Which of the following formulas would you expect to be the actual formula? C_2H_2 , C_6H_6

Answer: C2H2

To determine the relationship between the empirical formula and the actual formula, divide the actual formula weight by the empirical formula weight. Suppose the actual formula weight has been found to be 78.11 amu. The empirical formula weight for CH is 13.02 amu.

| (0) | _actual formula weight | _ <u>78.11 amu</u> _ | |
|-----|--------------------------|----------------------|--|
| (a) | empirical formula weight | - 13.02 amu - | |

- (b) The actual formula is how many times larger than the empirical formula?
- (c) If the empirical formula is CH, the actual formula would be ______.

Answer:

- (a) 6.0
- (b) 6 times larger (note that the actual weight is a whole number multiple of the empirical formula)
- (c) C_6H_6
- A compound has been found to have an empirical formula of HO (one atom of hydrogen for every atom of oxygen). The actual formula weight has been found to be 34.02 amu. Determine the empirical formula weight of HO. (Remember, the

| empirical fo | ormula | weight | is the | combined | atomic | weights | of the | elements | in | the |
|--------------|---------|--------|--------|----------|--------|---------|--------|----------|----|-----|
| empirical fo | ormula. |) | | | | | | | | |

- (a) The empirical formula weight of HO is _____ amu.
- (b) What is the actual formula?

Answer:

- (a) 17.01 (16.00 + 1.01 = 17.01 amu)
- (b) Divide the actual formula weight by the empirical formula weight to determine the relationship between the actual formula and the empirical formula.

$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{34.02 \text{ amu}}{17.01 \text{ amu}} = 2$$

The actual formula is 2 times as large as the empirical formula. Since the empirical formula is HO, the actual formula is H_2O_2 .

A compound is found to have an empirical formula of CH₃. The empirical formula weight for CH₃ is _____ amu. (Use a separate sheet of paper to set up a table of calculation for this and the following frames.)

Answer:

| Element | Number of atoms | Atomic weight | Atoms × weight | |
|---------|-----------------|---------------|-------------------------|--|
| С | 1 C | 12.01 | 1 × 12.01 = 12.01 | |
| Н | 3 H | 1.01 | $3 \times 1.01 = 3.03$ | |
| | | Empirical for | mula weight is 15.04 am | |

The empirical formula is CH₃ and the empirical formula weight is 15.04 amu. The actual formula weight has been found to be 30.08 amu. What is the actual formula?

Answer: Divide the actual formula weight by the empirical formula weight.

$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{30.08}{15.04} = 2$$

The actual formula is 2 times as large as the empirical formula. Thus, the actual formula is C_2H_6 .

- A compound has an empirical formula of CH₂O. The actual formula weight has been found to be 180.18 amu.
 - (a) Determine the empirical formula weight.
 - (b) What is the actual formula?

Answer:

(a)

| Element | Number of atoms | Atomic weight | Atoms × weight |
|---------|-----------------|---------------|--------------------------|
| С | 1 C | 12.01 | 1 × 12.01 = 12.01 |
| н | 2 H | 1.01 | $2 \times 1.01 = 2.02$ |
| 0 | 10 | 16.00 | $1 \times 16.00 = 16.00$ |
| | | Empirical for | mula weight is 30.03 am |

(b) Divide the actual formula weight by the empirical formula weight.

$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{180.18}{30.03} = 6$$

The actual formula is 6 times as large as the empirical formula. Thus, the actual formula is $C_6H_{12}O_6$.

- A compound has an empirical formula of CO. The actual formula weight has been found to be 28.01 amu.
 - (a) The empirical formula weight of CO is ______.
 - (b) What is the actual formula? _____

Answer:

- (a) 28.01 amu (16.00 + 12.01 = 28.01)
- (b) Since the actual formula weight and the empirical formula weight are the same, the empirical formula and the actual formula must also be the same.

$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{28.01}{28.01} = 1$$

The actual formula is CO.

- Formula weights can also be expressed in grams. A compound has an empirical formula of NH₂. The actual formula weight has been found to be 32.06 grams.
 - (a) Determine the empirical formula weight in grams.
 - (b) What is the actual formula?

Answer:

(a)

| Element | Number of atoms | Gram atomic weight | Atoms × weight |
|---------|-----------------|--------------------|---------------------------|
| N | 1 N | 14.01 | 1 × 14.01 = 14.01 |
| Н | 2 H | 1.01 | $2 \times 1.01 = 2.02$ |
| | | Empirical form | ula weight is 16.03 grams |

(b) Divide the actual formula weight by the empirical formula weight.

$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{32.06}{16.03} = 2$$

The actual formula is twice as large as the empirical formula. Thus, the actual formula is N_2H_4 .

65

A 10.00 gram sample of a compound is made up of 3.04 grams of nitrogen (N) and the remainder is oxygen (O). The actual formula weight of this compound is 92.02 grams. Determine the actual formula of this compound. (When determining the number of moles of each element, calculate to the nearest thousandth.)

Answer:

First, calculate the amount of oxygen in the sample.

$$10.00 \text{ grams} - 3.04 \text{ grams} = 6.96 \text{ grams of oxygen}$$

Second, determine the number of moles of each element within the sample.

3.04 grams of N ×
$$\frac{1 \text{ mol of N}}{14.01 \text{ grams}}$$
 = 0.217 mol of N

6.96 grams of O ×
$$\frac{1 \text{ mol of O}}{16.00 \text{ grams}} = 0.435 \text{ mol of O}$$

Third, determine the simplest whole number ratio of N atoms to O atoms to find the empirical formula.

$$\frac{0.217 \text{ mol of N atoms}}{0.217 \text{ mol}} = 1 \text{ N atom}$$

$$\frac{0.435 \text{ mol of O atoms}}{0.217 \text{ mol}} = 2 \text{ O atoms}$$

The empirical formula is NO2.

Fourth, determine the actual formula.

| Element | Number of atoms | Atomic weight | Atoms × weight |
|---------|-----------------|---------------|----------------------------|
| N | 1 N | 14.01 | 1 × 14.01 = 14.01 |
| 0 | 2 O | 16.00 | $2 \times 16.00 = 32.00$ |
| | | Empirical for | mula weight is 46.01 grams |

Divide the actual formula weight by the empirical formula weight.

$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{92.02 \text{ grams}}{46.01 \text{ grams}} = 2$$

The actual formula is twice as large as the empirical formula. Thus, the actual formula is N₂O₄.

What you have just learned is very important to a research chemist who is trying to determine the formula of a compound that has just been produced. The

chemist can determine the percentage composition of the compound by a variety of instrumental and chemical processes. In later chapters, you will learn that a chemist can also experimentally determine the formula weight of a compound in several different ways. The combination of these methods permits the researcher to calculate the actual formula of the compound.

You will need to be able to determine formula weights in several of the remaining chapters of this book and in any chemistry course you take. It is important that you have a good understanding of Chapters 1 through 4 before continuing your study.

In Chapter 5 you will learn how chemists name the compounds they produce based upon an internationally accepted scheme.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test. Round answers to the nearest hundredth.

| 1. | What is the formula weight of aspirin (acetylsalicylic acid), $C_9H_8O_4$? |
|----|--|
| 2. | What is the percentage by weight of oxygen in aspirin? |
| 3. | What is the actual formula of a compound that is 39.99% carbon, 6.67% hydrogen, and 53.34% oxygen if its actual formula weight is 150.15 amu? (Use a separate sheet of paper for your calculations.) |
| 4. | Explain the difference between an empirical formula and the actual formula of a compound. |
| 5. | How is a molecule of a compound different from a molecule of an element? |
| | |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. 180.17 amu (frames 4, 9, 13)
- 2. % oxygen = $\frac{64.00 \text{ amu of oxygen}}{180.17 \text{ amu of aspirin}} \times 100\% = 35.52\%$ (frames 18–22)

3. Step 1: atoms of C =
$$\frac{39.99 \text{ amu of C}}{12.01 \text{ amu per atom of C}} = 3.33 \text{ atoms of C}$$

atoms of H = $\frac{6.67 \text{ amu of H}}{1.01 \text{ amu per atom of H}} = 6.60 \text{ atoms of H}$

atoms of O = $\frac{53.34 \text{ amu of O}}{16.00 \text{ amu per atom of O}} = 3.33 \text{ atoms of O}$

Step 2: $\frac{3.33 \text{ atoms of C}}{3.33} = 1.00 \text{ atom of C}$
 $\frac{6.60 \text{ atoms of H}}{3.33} = 2.00 \text{ atoms of H}$
 $\frac{3.33 \text{ atoms of O}}{3.33} = 1.00 \text{ atom of O}$

Step 3: The empirical formula is CH₂O.

Step 4:
$$\frac{\text{actual formula weight}}{\text{empirical formula weight}} = \frac{150.15}{30.03} = 5$$

Therefore, the actual formula is C₅H₁₀O₅. (frames 24-39, 56-59)

- 4. An empirical formula merely indicates the combining ratio of the atoms. The actual formula has the same atomic ratio as the empirical formula, but includes the actual number of each atom present according to the measured formula weight. (frames 29–32)
- 5. A molecule of a compound consists of atoms of *different* elements, whereas a molecule of an element consists of atoms of the *same* element. (frame 6)

5 Nomenclature

Just as you have a given name by which you are recognized, every chemical compound has a name that makes it readily identifiable to every chemist.

In Chapter 4 you were introduced to molecular formulas that indicate the ratio of the combining elements. Our task in this chapter is to teach you how to name a compound when given its molecular formula, and vice versa. To be proficient in naming compounds and writing formulas (and later in writing and balancing chemical equations, Chapter 6), you should begin to memorize the oxidation numbers (valence charge) of the more common elements and groups of atoms that form what we call polyatomic ions. A table of common oxidation numbers is found on page 92.

Just as we are given nicknames by friends and become known by names that are not really our own names, the designation of chemical compounds is sometimes complicated by the use of common names that have been carried through the years. The establishment of an international nomenclature scheme, which we will study in this chapter, is an attempt to clear up this difficulty.

OBJECTIVE

After completing this chapter, you will be able to correctly name binary and ternary compounds, including binary and oxyacids and their salts, when given the correct chemical formula, and vice versa.

Chemical formulas are the chemist's international shorthand for describing a substance being studied. A chemical formula specifies what elements and how many atoms of each element are present in any substance.

Before we start naming compounds and writing formulas, we must cover a few ground rules. We present them here collectively and then separately as we work through the chapter. The scheme that we present is used for inorganic compounds composed of metals and nonmetals, as opposed to organic compounds that consist mainly of C, H, and O and a few other elements. The nomenclature of organic compounds is entirely different and is not covered in this book.

The first compounds we will discuss are binary compounds that contain only two elements. One element is usually a metal and the second element is a nonmetal. Remember that metals are found in Groups IA, IIA, IIIA, all the B groups, and

towards the bottom of Groups IVA, VA, and VIA in the periodic table. Metals form positive charges by giving up electrons. The number of metals is much larger than the number of nonmetals. Nonmetals are located in the upper right hand portion of the periodic table and form negative charges by gaining electrons.

The rules for naming binary compounds are:

- The symbol of the metallic or positively charged element is written first in the formula and named first.
- The symbol of the nonmetallic or negatively charged element is written and named second.
- The name of the metal remains unchanged, but the name of the nonmetal carries the suffix *ide*.

CaO — calcium oxide LiF — lithium fluoride

• Common groups of elements (polyatomic ions) are treated as a single element.

NH₄⁺— ammonium ion OH⁻— hydroxide ion CN⁻— cyanide ion

These are specified as in the following.

NH₄Br — ammonium bromide KOH — potassium hydroxide NH₄CN — ammonium cyanide

• If you check the table of charges on page 92 you will note that each formula we have written above is electrically neutral. That is, the sum of all the positive and negative charges is zero. We chose elements and polyatomic ions that carried numerically the same charge. What if we had chosen Li⁺ and O²⁻ to form a compound? The formula would be Li₂O because it must be electrically neutral (2Li⁺ = 2+, 1O²⁻ = 2-, 2+ and 2- add up to zero). Li₂O means two atoms of Li combined with one atom of O. We use small whole numbers as subscripts to make the formula electrically neutral.

Ba²⁺ and I⁻ form BaI₂, barium iodide Al³⁺ and OH⁻ form Al(OH)₃, aluminum hydroxide Rb and S²⁻ form Rb₂S, rubidium sulfide

In the next section we will learn to name and write the formulas for some binary compounds.

TABLE OF COMMON OXIDATION NUMBERS

Names and Charges of Some Positive Ions:

| Name | Formula and charge | Name | Formula and charge |
|--------------------------|--------------------|--------------------------|--------------------|
| aluminum | Al ³⁺ | lead(II), plumbous | Pb ²⁺ |
| ammonium | NH_4^+ | lead(IV), plumbic | Pb⁴+ |
| barium | Ba ²⁺ | lithium | Li ⁺ |
| calcium | Ca ²⁺ | magnesium | Mg ²⁺ |
| chromium(II), chromous | Cr ²⁺ | manganese(II), manganous | Mn ²⁺ |
| chromium(III), chromic | Cr ³⁺ | manganese(III), manganic | Mn³+ |
| chromium(VI), perchromic | Cr ⁶⁺ | mercury(I), mercurous | Hg₂²+ |
| copper(l), cuprous | Cu⁺ | mercury(II), mercuric | Hg²+ |
| copper(II), cupric | Cu ²⁺ | potassium | K ⁺ |
| gold(I), aurous | Au ⁺ | silver | Ag⁺ |
| gold(II), auric | Au ²⁺ | sodium | Na⁺ |
| hydrogen | H ⁺ | tin(II), stannous | Sn ²⁺ |
| iron(II), ferrous | Fe ²⁺ | tin(IV), stannic | Sn ⁴⁺ |
| iron(III), ferric | Fe ³⁺ | zinc | Zn ²⁺ |

Names and Charges of Some Negative Ions:

| | Formula and | | Formula and |
|----------|-----------------|---------|-----------------|
| Name | charge | Name | charge |
| bromide | Br ⁻ | nitride | N ³⁻ |
| chloride | CI ⁻ | oxide | O ²⁻ |
| fluoride | F- | sulfide | S ²⁻ |
| iodide | I ⁻ | | |

Names and Charges of Some Polyatomic Ions (all are negative except ammonium):

| Name | Formula and charge | Name | Formula and charge |
|--------------|---|-------------|--------------------------------|
| acetate | C ₂ H ₃ O ₂ ⁻ | hypoiodite | 10- |
| ammonium | NH ₄ + | iodate | IO ₃ - |
| bromate | BrO ₃ - | nitrate | NO ₃ - |
| bromite | BrO ₂ - | nitrite | NO ₂ - |
| carbonate | CO ₃ 2- | perchlorate | ClO ₄ - |
| chlorate | ClO ₃ - | periodate | 10 ₄ - |
| chlorite | ClO ₂ - | phosphate | PO ₄ ³⁻ |
| cyanide | CN- | selenate | SeO ₄ ²⁻ |
| hydroxide | OH⁻ | selenide | Se ²⁻ |
| hypobromite | BrO ⁻ | sulfate | SO ₄ ²⁻ |
| hypochlorite | CIO- | sulfite | SO ₃ ²⁻ |

BINARY COMPOUNDS

| 1 | Common table salt is called sodium chloride by chemists. Knowing that NaCl is sodium chloride will help you to remember the names of a whole class of chemical compounds. Two-element compounds are classified as binary compounds. Because NaCl contains two elements, it is classified as a compound. |
|---|--|
| | Answer: binary |
| 2 | The names of all binary compounds end in the letters <i>ide</i> . Note that the written name of NaCl is sodium chloride. The compound KCl is called potassium |
| | Answer: chloride |
| 3 | The compound CaS is called |
| | Answer: calcium sulfide |
| 1 | Na ₂ O is called |
| | Answer: sodium oxide |
| 5 | Several common ions, called polyatomic ions, are treated as single elements. The ammonium ion (NH ₄ ⁺) is treated as a single element and is named <i>first</i> in a compound. The hydroxide ion (OH ⁻) and the cyanide ion (CN ⁻) are also treated as single elements in naming. These two are named <i>last</i> . Give the name for each of the following. |
| | (a) NH ₄ Cl |
| | (b) KCN |
| | (c) NH ₄ I |
| | (d) HCl |
| | Answer: (a) ammonium chloride; (b) potassium cyanide; (c) ammonium iodide; (d) hydrogen chloride |
| 6 | Give the formula for each of the following. |
| | (a) lithium hydroxide |
| | (b) ammonium hydroxide |
| | (c) barium hydroxide |
| | (d) hydrogen bromide |
| | Answer: (a) LiOH; (b) NH₄OH; (c) Ba(OH)₂; (d) HBr |
| | |

Now give the formula for each of the following.

| 7 | Now give the formula for each of the following. |
|----|--|
| | (a) potassium sulfide |
| | (b) magnesium sulfide |
| | (c) aluminum sulfide |
| | Answer: (a) K_2S ; (b) MgS; (c) Al_2S_3 ($2Al^{3+} = 6+$, $3S^{2-} = 6-$, $6+$ and $6-=0$) |
| | You may have noticed that some common metallic elements such as iron, copper, gold, chromium, mercury, tin, and lead are capable of more than one oxidation number (other than zero). This means that iron can combine with chlorine to form two different compounds: FeCl ₂ and FeCl ₃ . We can't call them both iron chloride so we must do something else. There are two accepted methods of naming compounds containing these metals. One method is to write the oxidation number of the metal in Roman numerals to the right of the metal name followed by the name of the nonmetal with its suffix <i>ide</i> . For example, FeCl ₂ is named "iron(II) chloride" because iron in this compound has an oxidation number of 2+, and Cl is 1 FeCl ₃ is named "iron(III) chloride" because iron in this compound has an oxidation number of 3+. |
| 8 | In the compound FeI ₂ , iron has an oxidation number of 2+. FeI ₂ is named iron() iodide. |
| | Answer: (II) |
| 9 | In the compound Fe(OH) ₃ , iron has an oxidation number of 3+. Fe(OH) ₃ is named |
| | Answer: iron(III) hydroxide |
| 10 | Iron, copper, gold, chromium, tin, lead, and mercury can form ions with two oxidation numbers. |
| | (a) In the compound CuO, the oxidation number of O is 2 Thus, the oxidation number of copper is |
| | (b) The name of CuO is |
| | Answer: (a) 2+ (charges must add up to zero); (b) copper(II) oxide |
| 11 | Given the compound Cu ₂ O: |
| | (a) The oxidation number of copper in the compound is |
| | (b) The name of the compound is |
| | Answer: (a) 1+; (b) copper(l) oxide |
| | |

As we mentioned, iron, copper, gold, chromium, mercury, lead, and tin are metals that can form ions with two (or more) oxidation numbers.

| Metal | Possible oxidation numbers | |
|----------|----------------------------|--|
| iron | 2+ and 3+ | |
| copper | 1+ and 2+ | |
| gold | 1+ and 3+ | |
| tin | 2+ and 4+ | |
| chromium | 2+, 3+, and 6+ | |
| mercury | 1+ and 2+ | |
| lead | 2+ and 4+ | |

What is the oxidation number of the metal and the name of the compound for the following?

- (a) AuF_3 if F = 1 -______
- (b) SnCl₄ if Cl = 1-
- (c) PbO₂ if O = 2-
- (d) Cr_2O_3 if O = 2-

Answer: (a) 3+, gold(III) fluoride; (b) 4+, tin(IV) chloride; (c) 4+, lead(IV) oxide; (d) 3+, chromium(III) oxide

- What are the formulas for the following compounds?
 - (a) chromium(II) bromide _____
 - (b) lead(II) hydroxide _____
 - (c) gold(I) cyanide _____
 - (d) mercury(II) oxide _____

Answer: (a) CrBr₂; (b) Pb(OH)₂; (c) AuCN; (d) HgO

An older method of naming compounds made from these metals (iron, copper, gold, chromium, tin, mercury, and lead) is to add *ic* or *ous* to the Latin names of these metals.

The suffix *ic* is added to the name of the element when the *higher* oxidation state is used. The suffix *ous* is added to the element name when the *lower* oxidation state is displayed in a compound. For example:

Gold(I) is the same as aurous. Gold(III) is the same as auric.

Therefore, AuCl could be named gold(I) chloride or aurous chloride.

| Here are more applications of | the naming method | to our group of metals |
|-------------------------------|-------------------|------------------------|
|-------------------------------|-------------------|------------------------|

Lead(II) is the same as plumbous. Lead(IV) is the same as plumbic.

Mercury(I) is the same as mercurous. Mercury(II) is the same as mercuric.

Tin(II) is the same as stannous. Tin(IV) is the same as stannic.

Copper(I) is the same as cuprous. Copper(II) is the same as cupric.

Iron(II) is the same as ferrous. Iron(III) is the same as ferric.

Chromium(II) is the same as chromous. Chromium(III) is the same as chromic.

Chromium(VI) is an exception, since chromium can have three different oxidation states.

Chromium(VI) is also called perchromic, a name you will learn more about later.

| (a) | Two names for Fe ₂ O ₃ are | | _ and |
|-----|--|-----|-------|
| (b) | Two names for CuOH are | -· | _ and |
| (c) | Two names for Cr ₂ S ₃ are | _ · | and |
| (d) | Two names for PbCl ₂ are | | and |

Answer: (a) iron(III) oxide, ferric oxide; (b) copper(I) hydroxide, cuprous hydroxide; (c) chromium(III) sulfide; chromic sulfide; (d) lead(II) chloride, plumbous chloride

Write the formulas for these compounds.

(a) stannous fluoride _____

(b) mercuric iodide _____

(c) plumbous oxide _____

(d) stannic sulfide _____

Answer: (a) SnF₂; (b) Hgl₂; (c) PbO; (d) SnS₂

The most common metals capable of two (or more) oxidation states have been indicated in frame 12. In binary compounds, the nonmetals have only one oxidation number. The halogens are all 1-; oxygen and sulfur are each 2-. The Group IA metals are all 1+, and the Group IIA metals are 2+.

Before you go on you should memorize the oxidation states of the metals, nonmetals, and polyatomic ions as listed on the Table of Common Oxidation Numbers on page 92.

| 16 | Certain pairs of nonmetallic elements form more than one binary compound. Good examples are carbon and oxygen. They combine to form CO and CO ₂ . Carbon is more metallic than oxygen, therefore it is written first. Based upon what you have just learned about naming compounds, their names using Roman numerals would be, respectively, and |
|----|---|
| | Answer: carbon(II) oxide; carbon(IV) oxide |
| | Through previous experience you probably know CO is also commonly called carbon monoxide and CO ₂ is carbon dioxide. The prefixes mono (1), di (2), tri (3), tetra (4), penta (5), hexa (6), hepta (7), and octa (8) indicate the number of atoms of each element present in the compound. Many binary compounds of carbon, nitrogen, sulfur, and oxygen are named using prefixes instead of the Roman numeral scheme. The next few frames will illustrate how prefixes are used. |
| 17 | SO ₂ is called sulfur dioxide. You might have called it monosulfur dioxide, but when naming binary compounds that have only one positive atom in the compound, the mono prefix is dropped. For example, CO ₂ is carbon dioxide not monocarbon dioxide. CO is carbon monoxide not monocarbon monoxide. What is the name for SO ₃ ? |
| | Answer: sulfur trioxide (one atom of sulfur, three atoms of oxygen) |
| 18 | Several binary compounds of oxygen and nitrogen are N_2O , NO , NO_2 , N_2O_3 , and N_2O_5 . N_2O_3 is named <i>di</i> nitrogen <i>tri</i> oxide. NO_2 is named nitrogen <i>di</i> oxide. |
| | (a) NO is named |
| | (b) N_2O is named |
| | (c) N_2O_5 is named |
| | Answer: (a) nitrogen monoxide; (b) dinitrogen monoxide; (c) dinitrogen pentoxide |
| 10 | Use the same system to name the following compounds. |
| 19 | (a) CS ₂ |
| | (b) BF ₃ |
| | (c) CCl ₄ |
| | Answer: (a) carbon disulfide; (b) boron trifluoride; (c) carbon tetrachloride |
| 20 | Write the formula for the following compounds. |
| 20 | (a) nitrogen triiodide |
| | (b) nitrogen dioxide |
| | (c) diphosphorus trioxide |
| | |

| | (d) diphosphorus pentoxide | | | | |
|----|--|--|--|--|--|
| | (e) dinitrogen tetroxide | | | | |
| | Answer: (a) NI ₃ ; (b) NO ₂ ; (c) P ₂ O ₃ ; (d) P ₂ O ₅ ; (e) N ₂ O ₄ | | | | |
| 21 | In the past, prefixes have been used instead of the oxidation numbers in parentheses to name binary compounds of metals when the metal has more than one possible oxidation number. For example, MnO ₂ may be called manganese(IV) oxide or manganese dioxide. SeO ₃ may be called selenium(VI) oxide or selenium trioxide. Likewise, N ₂ O ₃ may be called dinitrogen trioxide or nitrogen(III) oxide. What other name could be given for the following? | | | | |
| | (a) NO ₂ : nitrogen dioxide or | | | | |
| | (b) CCl ₄ : carbon tetrachloride or | | | | |
| | (c) P ₂ O ₃ : diphosphorus trioxide or | | | | |
| | (d) PbO ₂ : plumbic oxide, lead(IV) oxide, or | | | | |
| | Answer: (a) nitrogen(IV) oxide; (b) carbon(IV) chloride; (c) phosphorus(III) oxide; (d) lead dioxide | | | | |
| 22 | What would be the formula for the following? | | | | |
| | (a) lead monoxide | | | | |
| | (b) carbon(IV) sulfide | | | | |
| | Answer: (a) PbO; (b) CS ₂ | | | | |
| 23 | The method of placing the Roman numeral of the oxidation number of the first named element in the compound name, such as carbon(IV) oxide, is the method recommended by the International Union of Pure and Applied Chemistry and is less confusing than other methods. However, as long as other methods of naming exist, you should be able to translate back and forth between methods. Remember that placing the Roman numerals of the oxidation number of the first element in a compound is only valid if the first named element is capable of more than one oxidation number. If the first element is capable of only one oxidation number, we do not use the Roman numeral or a prefix on either name. Name these compounds. | | | | |
| | (a) CaO | | | | |
| | (b) CO | | | | |
| | (c) K ₃ N | | | | |
| | (d) MnCl ₃ | | | | |
| | | | | | |

| Answer: (a) calcium oxide (calcium has only one oxidation number); (b) carbon(II) ox | ide or |
|--|---------|
| carbon monoxide; (c) potassium nitride; (d) manganese(III) chloride or manganese trich | ıloride |

| 24 | Write the formulas for these compounds. |
|--------|---|
| - | (a) manganese difluoride |
| | (b) chromium(VI) oxide |
| | (c) silicon dioxide |
| | Answer: (a) MnF ₂ ; (b) CrO ₃ ; (c) SiO ₂ |
| BINARY | ACIDS |
| 25 | One special class of compounds has the H ⁺ ion serving in place of a metal ion in the compound. These compounds have special properties, which we will identify as acidic properties in Chapter 13. For now we will simply call them acids. The names of these acids have first names that are combinations of prefixes and suffixes attached to the name of another nonmetal and the second name is "acid." In these frames we will look at the scheme for naming binary acids. Remember, binary means only <i>two</i> elements are present. The compound HF can be named as a binary compound with the name |
| | Answer: hydrogen fluoride |
| 26 | The compound HF is an example of a binary acid. It can be named as an ordinary binary compound or it can be named hydrofluoric acid. This method of naming substitutes hydro for hydrogen and adds the suffix ic to the stem or full name of the second element. Name the binary acid HCl in two ways or |
| | Answer: hydrogen chloride; hydrochloric acid |
| 27 | You may already be familiar with HCl as hydrochloric acid. If you remember this name for HCl, you can remember the method for naming all binary acids. HBr can be named or |
| | Answer: hydrogen bromide; hydrobromic acid |
| 28 | Sulfur (S) and selenium (Se) both have only one negative oxidation number, 2 |
| النائب | (a) What would be the formula of the binary compounds formed between hydrogen and sulfur? Between hydrogen and selenium? |
| | (b) What are the names of those compounds? |
| | |

Answer: (a) H₂S; H₂Se; (b) hydrogen sulfide or hydrosulfuric acid; hydrogen selenide or hydroselenic acid

29

Name H₂Te as an acid.

Answer: hydrotelluric acid

OXYACIDS

30

Some very common useful acids contain hydrogen, a nonmetal, and oxygen. Acids that contain these three elements are called **oxyacids**. The *oxy* in oxygen may help you to remember the term oxyacid.

The most common oxyacid is H₂SO₄, sulfuric acid. Another oxyacid is HNO₃, nitric acid. You may already be familiar with these acids.

Which of the following compounds are oxyacids? HCl, H₂SO₃, HI, H₂O, H₃PO₄

Answer: H₂SO₃, H₃PO₄

Oxyacids are probably the most difficult compounds to name because the same three elements may combine in different ratios. We know for example that H, S, and O combine to form H₂SO₄ and H₂SO₃; H, N, and O form HNO₃ and HNO₂. Phosphorus and the halogens form several oxyacids. The next few frames will present a scheme by which oxyacids may be named.

The most common forms of oxyacids are named by adding *ic* to the stem or name of the nonmetal in each acid. The "ic" acids *usually* contain either three or four oxygen atoms in their formulas, but there is no systematic way to know whether an "ic" acid contains three or four oxygen atoms. A handy way to remember whether an "ic" acid contains three or four oxygen atoms is to list several "ic" oxyacids alphabetically according to the first letter of the nonmetals symbol, as shown below. Note that as the alphabet reaches the letter O, the number of oxygen atoms in

the "ic" acid increases from three to four.

| Acid | Name | | |
|--------------------------------|-----------------|--|--|
| HBrO ₃ | bromic acid | | |
| H₂CO₃ | carbonic acid | | |
| HClO₃ | chloric acid | | |
| HNO₃ | nitric acid | | |
| H₃PO₄ | phosphoric acid | | |
| H ₂ SO ₄ | sulfuric acid | | |

| | HIO ₃ follows the rule of thumb. What is the name of HIO ₃ ? |
|----|---|
| | Answer: iodic acid |
| 32 | H ₂ SeO ₄ follows the rule of thumb. What is the name of H ₂ SeO ₄ ? |
| 33 | Note that we have not included any reference to hydrogen in the names of oxyacids as we did with binary acids. Nor have we included prefixes (mono, di, or others). There is no need to do so since the name "acid" tells us there is hydrogen present and the number of hydrogens present is a function of the oxidation number (charge) of the polyatomic ion with which it is combined. Look at the table of common polyatomic ions on page 92 (if you need to) and see if you can find the polyatomic ion and its charge for the following "ic" acids. |
| | (a) H_3PO_4 |
| | (b) H ₂ SO ₄ |
| | (c) HNO ₃ |
| | Answer: (a) PO_4^{3-} ; (b) SO_4^{2-} ; (c) NO_3^{-} |
| 34 | Bromic acid follows the rule of thumb. What is the formula of bromic acid? What is the polyatomic ion and its charge? |
| | Answer: HBrO ₃ ; BrO ₃ ⁻ (the charge is 1–) |
| 35 | Chloric acid follows the rule of thumb. What is the polyatomic ion and its charge for chloric acid? |
| | Answer: CIO ₃ ⁻ (the charge is 1–) |
| 36 | Once you have learned the name and formula of the "ic" acid for any nonmetal, all other oxyacids with the same nonmetal are systematically named (e.g., H ₂ SO ₄ , H ₂ SO ₃). If an oxyacid contains one less oxygen than the "ic" acid, it is named by using the same stem but changing the <i>ic</i> to ous. Since H ₂ SO ₄ is sulfuric acid, H ₂ SO ₃ is sulfurous acid. HClO ₃ is chloric acid. What is the formula for chlorous acid? |
| | Answer: HCIO ₂ (one less oxygen than the "ic" acid) |
| 37 | Write the formulas for the following acids. |
| | (a) Nitrous acid |
| | (b) Phosphorous acid |
| | Answer: (a) HNO ₂ ; (b) H ₃ PO ₃ |
| | |

| 38 | Name the following compounds. |
|----|---|
| | (a) HBrO ₂ |
| | (b) HIO ₂ |
| | (c) H ₂ SeO ₃ |
| | Answer: (a) bromous acid; (b) iodous acid; (c) selenous acid |
| 39 | An acid with <i>two less</i> oxygens than the "ic" acid is named by dropping the <i>ic</i> and substituting <i>ous</i> , and placing the prefix <i>hypo</i> before the nonmetal. Hypo means under or beneath (such as in hypodermic, meaning under the skin). A "hypo-ous" acid has one less oxygen than an "ous" acid. |
| | (a) HClO ₃ is acid. |
| | (b) HClO ₂ is acid. |
| | (c) HClO is acid. |
| | Answer: (a) chloric; (b) chlorous; (c) hypochlorous |
| 40 | Write the formulas for these acids. |
| | (a) hypobromous acid |
| | (b) hypoiodous acid |
| | (c) hypophosphorous acid |
| | Answer: (a) HBrO; (b) HIO; (c) H ₃ PO ₂ |
| 41 | In some cases it may be possible for an acid to have <i>one more</i> oxygen atom than the corresponding "ic" acid. Such an acid is named by placing the prefix <i>per</i> before the nonmetal and keeping the <i>ic</i> in the name. |
| | (a) HClO ₃ is acid. |
| | (b) HClO ₄ is acid. |
| | Answer: (a) chloric; (b) perchloric |
| 42 | Use the naming rule for the following acids. |
| | (a) HBrO ₃ is named |
| | (b) HBrO ₂ is named |
| | (c) HBrO ₄ is named |
| | Answer: (a) bromic acid; (c) bromous acid; (c) perbromic acid |
| 43 | Oxyacids really behave as though they have only two parts: the hydrogen ion(s) (H ⁺) and the polyatomic ion. This polyatomic ion that we have discussed is called |

| the acid polyatomic ion. For example, the acid polyatomic ion of HNO ₃ is NO ₃ ⁻ ; in H_2SO_4 it is SO_4^{2-} ; and in H_3PO_4 it is PO_4^{3-} . The acid polyatomic ion carries its own name, as you may have noticed in the table on page 92. The names of acid polyatomic ions for "ic" acids are derived by dropping the <i>ic</i> ending and replacing it with <i>ate</i> . For example, the NO_3^- polyatomic ion is called the nitrate polyatomic ion. The SO_4^{2-} polyatomic ion is called the sulfate polyatomic ion. The PO_4^{3-} polyatomic ion is called the polyatomic ion. | | | | |
|--|--|--|--|--|
| Answer: phosphate | | | | |
| What are the polyatomic ion names for the following acids? | | | | |
| (a) HClO ₃ | | | | |
| (b) HBrO ₃ | | | | |
| Answer: (a) chlorate; (b) bromate | | | | |
| Similarly, "ous" acids have "ite" acid polyatomic ion names. For example, in HNO ₂ , nitrous acid, the NO ₂ ⁻ is called the <i>nitrite</i> polyatomic ion. What is the acid polyatomic ion name for each of the following? | | | | |
| (a) H ₂ SO ₃ | | | | |
| (b) HClO ₂ | | | | |
| (c) H_3PO_3 | | | | |
| Answer: (a) sulfite; (b) chlorite; (c) phosphite | | | | |
| "Hypo-ous" acids have "hypo-ite" polyatomic ions. | | | | |
| (a) ClO ⁻ is the polyatomic ion. | | | | |
| (b) IO ⁻ is the polyatomic ion. | | | | |
| (c) PO ₂ ³⁻ is the polyatomic ion. | | | | |
| Answer: (a) hypochlorite; (b) hypoiodite; (c) hypophosphite | | | | |
| "Per-ic" acids have "per-ate" polyatomic ions. | | | | |
| (a) CIO is the polyatomic ion | | | | |

SALTS

45

46

47

A very large number of compounds are formed by combining acid polyatomic ions and metal ions. For example, Na⁺ and SO₄²⁻ form Na₂SO₄. Remember, the metal

(b) BrO₄ is the _____ polyatomic ion.

Answer: (a) perchlorate; (b) perbromate

or most positive element is written first, the negative part is written second, and subscripts are used to make the positive charges and negative charges equal zero. These compounds formed from metal ions and acid polyatomic ions are called salts. In Chapter 13, you will see one way in which salts may be prepared in the laboratory. Salts are named by using the name of the metal followed by the name of the acid polyatomic ion. Thus, Na₂SO₄ is called sodium sulfate. It is derived from Na⁺ and SO₄²⁻.

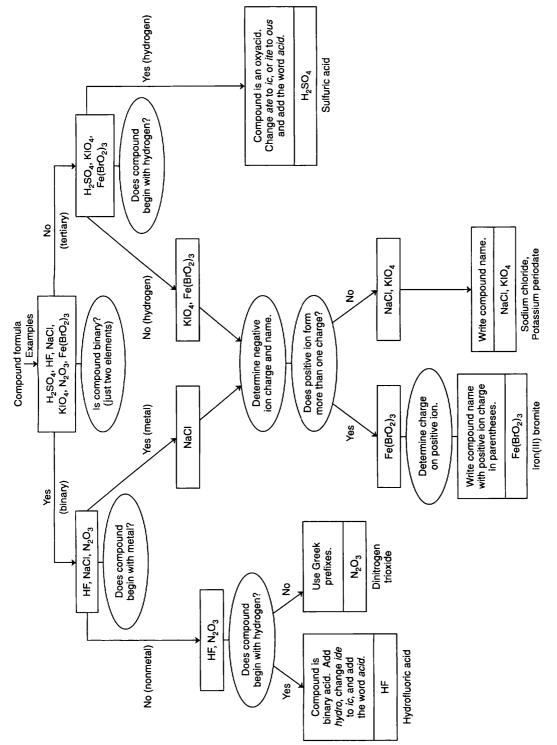
| | from Na ⁺ and SO ₄ ²⁻ . Salts derived from "ic" acids are called "ate" salts. The acid HClO ₃ is named |
|----|---|
| | chloric acid. The salt KClO ₃ is named |
| | Answer: potassium chlorate |
| 49 | H ₂ SO ₄ is acid. CaSO ₄ is |
| | Answer: sulfuric; calcium sulfate |
| 50 | Try your hand on the following. |
| | (a) HNO ₃ is acid. |
| | (b) The formula of the compound formed between Ba^{2+} and NO_3^- is |
| | (c) The compound of Ba ²⁺ and NO ₃ ⁻ is named (Remember, the NO ₃ ⁻ acts as a single unit. It takes two polyatomic ions to balance the 2+ charge of the barium ion.) |
| | Answer: (a) nitric; (b) Ba(NO ₃) ₂ ; (c) barium nitrate |
| 51 | HNO ₃ is nitric acid. Al(NO ₃) ₃ is |
| | Answer: aluminum nitrate |
| 52 | HBrO ₃ is acid. Ca(BrO ₃) ₂ is |
| | Answer: bromic; calcium bromate |
| 53 | What are the formulas of the following compounds? |
| | (a) sodium iodate |
| | (b) magnesium sulfate |
| | (c) lithium phosphate |
| | (d) barium phosphate |
| | Answer: (a) NalO ₃ ; (b) MgSO ₄ ; (c) Li ₃ PO ₄ ; (d) Ba ₃ (PO ₄) ₂ |

| Answer: hypoiodous; lithium hypoiodite | |
|--|--|
| HIO ₄ is acid. KIO ₄ is Answer: periodic; potassium periodate | . • |
| HBrO ₂ is acid. Mg(BrO ₂) ₂ is | . • |
| | HIO_4 is acid. KIO_4 is Answer: periodic; potassium periodate $HBrO_2$ is acid. $Mg(BrO_2)_2$ is |

SUMMARY

You should now be able to write formulas and name compounds with a reasonable degree of proficiency. As with most rules there are exceptions, but you will not encounter them in this book. The decision tree on page 106 is a useful summary for naming compounds.

- I. Binary compounds
 - A. Contain only two different elements.
 - B. Are named by:
 - 1. Writing the name of the metal followed by the name of the nonmetal with an *ide* ending, or
 - 2. Writing the name of the metal followed by the charge of the metal in Roman numerals in parentheses, then the nonmetal name with the *ide* ending, or
 - 3. Using prefixes before the names of the elements with the *ide* ending on the name of the second element.
 - C. Formulas are written by using the symbol of the more metallic element followed by the symbol of the more nonmetallic element, with the necessary subscripts to make the charges equal zero.
- II. Binary acids
 - A. Contain hydrogen and another nonmetal.
 - B. Are named by using a *hydro* prefix and an *ic* suffix with the name of the nonmetal.
 - C. Formulas are written with the hydrogen first and the other nonmetal second, with the appropriate subscripts to make the charges equal zero.
- III. Oxyacids
 - A. Contain hydrogen, a nonmetal, and oxygen.
 - B. Are named according to the most commonly occurring acid, the "ic" acid. The suffix *ic* is added to the name of the nonmetal.



Compound Naming Decision Tree

- 1. Acids with one less oxygen than the "ic" acid are "ous" acids.
- 2. Acids with two less oxygens than the "ic" acid are "hypo-ous" acids.
- 3. Acids with one more oxygen than the "ic" acid are "per-ic" acids.
- C. Formulas are written with the hydrogen followed by the polyatomic acid ion, with necessary subscripts included to make the charges equal zero.

IV. Oxyacid salts

- A. Contain a metal, a nonmetal, and oxygen.
- B. Are derived from oxyacids.
- C. Are named by writing the name of the metal followed by the name of the polyatomic acid ion.
 - 1. "ic" acids form "ate" salts.
 - 2. "ous" acids form "ite" salts.
 - 3. "hypo-ous" acids form "hypo-ite" salts.
 - 4. "per-ic" acids form "per-ate" salts.
- D. Formulas are written with the metal symbol first followed by the polyatomic acid ion, with necessary subscripts to make the charges equal zero.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test.

| 1. | Name the following compounds. | | | |
|----|--|---|-----|---------------------------------|
| | (a) | KI | (h) | HCI |
| | (b) | NaCN | | HNO ₂ |
| | (c) | (NH ₄) ₂ SO ₄ | | HIO ₄ |
| | (d) | Cl ₄ | | Na ₂ SO ₃ |
| | (e) | SeO ₃ | | KCIO |
| | (f) | Fe ₂ O ₃ | | Ba(OH) ₂ |
| | (g) | N ₂ O ₅ | | |
| 2. | 2. Write the formulas for the following compounds. | | | |
| | (a) | lithium bromide | (d) | carbon(IV) sulfide |
| | (b) | carbon monoxide | (e) | cupric hydroxide |
| | (c) | copper(l) oxide | (f) | ammonium carbonate |

| (g) | hypobromous acid | (k) | aluminum nitrate |
|-----|--------------------|-----|---------------------|
| (h) | hydrosulfuric acid | (I) | ferrous iodide |
| ` - | sodium perchlorate | (m) | dinitrogen trioxide |
| • • | ammonium phosphite | ` . | . |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. (a) potassium iodide (frames 1-24)
 - (b) sodium cyanide (frames 1-24)
 - (c) ammonium sulfate (frames 48-56)
 - (d) carbon(IV) iodide or carbon tetraiodide (frames 1-24)
 - (e) selenium(VI) oxide or selenium trioxide (frames 1-24)
 - (f) iron(III) oxide or ferric oxide (frames 1-24)
 - (g) nitrogen(V) oxide or dinitrogen pentoxide (frames 1-24)
 - (h) hydrogen chloride or hydrochloric acid (frames 25-29)
 - (i) nitrous acid (frames 30-47)
 - (j) periodic acid (frames 30-47)
 - (k) sodium sulfite (frames 48-56)
 - (I) potassium hypochlorite (frames 48-56)
 - (m) barium hydroxide (frames 1-24)
- 2. (a) LiBr (frames 1-24)
 - (b) CO (frames 1-24)
 - (c) Cu₂O (frames 1-24)
 - (d) CS₂ (frames 1-24)
 - (e) Cu(OH)₂ (frames 1-24)
 - (f) $(NH_4)_2CO_3$ (frames 48-56)
 - (g) HBrO (frames 30-47)
 - (h) H₂S (frames 25-29)

 - (i) NaClO₄ (frames 43-56)
 - (j) (NH₄)₃PO₃ (frames 48-56)
 (k) Al(NO₃)₃ (frames 48-56)
 - (I) Fel₂ (frames 1-24)
 - (m) N₂O₃ (frames 1-24)

6 Chemical Equations

Now that you are familiar with atoms, symbols, molecules, formulas, and nomenclature, let's look at what happens when we mix substances together. The most important result of your efforts with this chapter will be your ability to write a balanced chemical equation that represents the reaction between two or more different substances that produces at least one new substance.

Chemical equations are the chemist's shorthand. They tell at a glance what substances have been mixed together and what new substance(s) have been produced. A chemist is able to predict the products of a mixture of substances even though he may never have actually mixed the substances in the laboratory. This is very important to a research chemist trying to prepare new products that are useful and beneficial to mankind.

You will learn how to complete and balance several kinds of chemical equations and how chemists recognize whether or not a reaction does indeed occur when substances are mixed.

You will discover that some things remain unchanged during a chemical reaction. A chemist is more concerned with the things that change, so you will learn a scheme that shows what does change during certain chemical reactions.

OBJECTIVES

After completing this chapter, you will be able to

- recognize and apply or illustrate: reactant, product, electrolyte (weak or strong), precipitate, soluble, insoluble, solid, liquid, gas, and aqueous;
- balance a molecular equation when given the formulas of the reactants and products;
- convert word equations to balanced molecular equations;
- convert balanced molecular equations to complete ionic equations and then to net ionic equations;
- identify a chemical equation as an example of combination, decomposition, single displacement, or double displacement type of reaction;
- explain why or how we recognize whether or not a chemical reaction occurs;
- use a solubility table to determine if a compound is soluble or insoluble.

Chemical equations are useful to the chemist because they represent chemical reactions. You have already learned that certain chemical symbols represent molecules, elements, ions, or compounds. These symbols are also used in chemical equations. The substance or substances that are the starting materials in a chemical reaction are called reactants and are located on left side of a chemical equation. The substance or substances produced as the result of a reaction are called products and are located on the right side of a chemical equation.

Hydrogen gas and oxygen gas react to produce water. The chemical equation for this reaction is $2H_2 + O_2 \rightarrow 2H_2O$

- (a) Identify the symbol(s) representing the reactant(s).
- (b) Identify the symbol(s) representing the product(s).

Answer: (a) H₂ and O₂; (b) H₂O

Some reactions require continuing energy in order to occur. Some reactions occur spontaneously when the reactants are mixed together. Other reactions just need energy to get started and will then continue until one or more reactant is used up.

Later in this chapter we will deal with predicting whether or not chemical reactions will actually occur as written.

The following are examples of two types of chemical reactions. The equation $2H_2 + O_2 \rightarrow 2H_2O$ represents a combination reaction because two or more different reactants combine to form a single product. The equation $2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$ represents a decomposition reaction because a single reactant is decomposed to form two or more different products.

- (a) The equation $2H_2O_2 \rightarrow 2H_2O + O_2$ represents what type of reaction?
- (b) Identify the reactant(s) and product(s) in the equation.

Answer: (a) decomposition reaction; (b) H_2O_2 is the reactant. It is on the left side of the equation. H_2O and O_2 are the products, on the right side of the equation.

Identify each of the following equations as either decomposition or combination.

- (a) $2C + O_2 \rightarrow 2CO$
- (b) $2HgO \rightarrow 2Hg + O_2$
- (c) $H_2 + Cl_2 \rightarrow 2HCl$

Answer: (a) combination; (b) decomposition; (c) combination

The following equation represents a single displacement reaction.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

In the reaction, the metal magnesium (Mg) has displaced the hydrogen atom (H) in HCl and formed magnesium chloride and hydrogen gas (H₂) as products. In a single displacement reaction an element and a compound react to form another element and compound.

In contrast with the single displacement reaction, the following equation is called a double displacement reaction; two compounds react to form two different compounds.

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$$

In this reaction, the Ba displaces the Na in Na₂SO₄ to form BaSO₄. The Na displaces Ba in BaCl₂ to form NaCl. In the following examples, two substances react to form two different substances.

(1)
$$2KCl + 2HgNO_3 \rightarrow 2KNO_3 + Hg_2Cl_2$$

(2)
$$2Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2$$

- (a) What type of reaction does equation 1 represent?
- (b) What type of reaction does equation 2 represent?

Answer: (a) double displacement (involves two compounds reacting to form two different compounds); (b) single displacement (involves a compound and an element reacting to form a different compound and an element)

- Identify the following reaction equations as combination, decomposition, single displacement, or double displacement.
 - (a) $2KClO_3 \rightarrow 2KCl + 3O_2$
 - (b) $H_2 + Cl_2 \rightarrow 2HCl$
 - (c) $\operatorname{Zn} + \operatorname{Cu(NO_3)_2} \to \operatorname{Cu} + \operatorname{Zn(NO_3)_2}$
 - (d) $AgNO_3 + KCl \rightarrow AgCl + KNO_3$
 - (e) $FeCl_3 + 3KOH \rightarrow Fe(OH)_3 + 3KCl$

Answer: (a) decomposition; (b) combination; (c) single displacement; (d) double displacement

Double displacement reactions are especially important because a large number of reactions are of this type. Think of double displacement reactions as compounds exchanging partners. Later in this chapter, you will need to predict the products of double displacement reactions when given the reactants. In a double displacement reaction the metal, or NH₄⁺, or H⁺ ion of one reactant replaces the metal, or NH₄⁺, or H⁺ ion in the other reactant, and vice versa.

In the following generalized reaction equation, A and B are positive ions (metals, NH_4^+ , or H^+) and X and Y are negative ions (one or more nonmetal atoms of an ionic compound which remain after the positive ion is removed).

$$AX + BY \rightarrow BX + AY$$

In this equation, A has displaced B and B has displaced A.

In the following double displacement reaction, the products can be predicted.

$$AgNO_3 + NaCl \rightarrow ?$$

The positive metal ions are Ag⁺ and Na⁺. The negative ions are NO₃⁻ and Cl⁻. Predict the products of this reaction.

Answer: AgCl and NaNO3

Predict the products of the following double displacement reactions.

- (a) $CuSO_4 + Ca(OH)_2 \rightarrow$
- (b) $NaC_2H_3O_2 + HCl \rightarrow$

Answer: (a) CaSO₄ and Cu(OH)₂; (b) NaCl and HC₂H₃O₂

BALANCING CHEMICAL EQUATIONS

In an actual reaction, all atoms must be accounted for. Atoms are neither gained 8 nor lost. All of the equations thus far have been balanced, that is, the number of each type of atom on the reactant side of the equation is equal to the number of each type of atom on the product side. The balancing of chemical equations is very important to the chemist, since only a balanced equation can adequately describe the ratios of reactants and products in a reaction. An equation that is not balanced does not truly represent a reaction. Look at the following chemical equation.

$$H_2 + Cl_2 \rightarrow HCl$$

- (a) How many atoms are on the reactant side? H 2 Cl 2 Cl b How many atoms are on the product side? H Cl L
- (c) Is the equation balanced? ______//o__

Answer: (a) two, two; (b) one, one; (c) no (The atoms on the reactant side do not equal those on the product side.)

Balancing equations is often a matter of trial and error. Coefficients (usually of 9 small whole numbers) can be placed in front of reactants or products, when necessary, to obtain equal numbers of atoms on both sides of the equation. Do not change the subscripts within the formulas of the reactants or products.

The molecular formula for water is H₂O. To double the formula for water, which of the following is the correct expression? H_4O_4 , H_4O_2 , $2H_2O_2$.

Answer: 2H₂O (The other two expressions have changed the actual molecular formula.)

The expression 2H₂O indicates two molecules of H₂O. This results in twice as 10 many hydrogen atoms (and doubles the oxygen atoms also). H₂SO₄ is the formula for sulfuric acid and contains two atoms of H, one atom of S, and four atoms of O.

The expression 3H₂SO₄ indicates three molecules of H₂SO₄, containing $\frac{1}{6}$ atoms of H, $\frac{3}{2}$ atoms of S, and $\frac{12}{2}$ atoms of O.

Answer: six; three; 12

Let's consider what is meant by the word "equation." The following mathematical 11 expression is an equation because both sides are equal. It is "balanced" because each side is equal to 12.

$$3 \times 4 = 6 \times 2$$

In the purest sense of the word, a chemical "equation" that is not balanced is not a true equation because the two sides are not equal. Only a balanced equation is a true mathematical equation or true chemical equation. To balance a chemical equation, you may place coefficients (smallest possible whole numbers) in front of any substance in the equation on a trial and error basis until the equation is balanced with equal numbers of atoms on each side.

Balance the following equation by placing coefficients in front of appropriate substances. The coefficients should be the smallest possible whole numbers.

$$H_2 + Cl_2 \rightarrow HCl$$

Answer: $H_2 + Cl_2 \rightarrow 2HCl$

Since the reactant side has two H atoms and two Cl atoms and the product side has only one H atom and one Cl atom, placing a coefficient of 2 before HCl makes the atoms equal on both sides. It is now a true equation. The following answers are also true equations, but the coefficients are not the smallest possible whole numbers. Therefore, they are not correct answers.

$$2H_2 + 2Cl_2 \rightarrow 4HCl$$
, or $3H_2 + 3Cl_2 \rightarrow 6HCl$, or $5H_2 + 5Cl_2 \rightarrow 10HCl$

The following unbalanced equation represents a decomposition reaction some-12 times used in the laboratory to obtain oxygen gas.

$$HgO \rightarrow Hg + O_{2}$$
(a) The reactant side has _____ atom(s) of Hg and _____ atom(s) of O.
(b) The product side has _____ atom(s) of Hg and _____ atom(s) of O.

Answer: (a) one, one; (b) one, two

The first step in balancing the equation in frame 12 is to make the oxygen atoms on the reactant side equal to the oxygen atoms on the product side. This can be accomplished by placing a coefficient of 2 in front of HgO.

$$2\text{HgO} \rightarrow \text{Hg} + \text{O}_2$$

The resulting numbers of atoms are:

| Reactants | Products |
|---------------|--------------|
| 2 atoms of Hg | 1 atom of Hg |
| 2 atoms of O | 2 atoms of O |

Place a coefficient in front of another substance in order to complete the balancing of this equation.

Answer: $2HgO \rightarrow 2Hg + O_2$ (The equation now indicates two atoms of Hg on the product side as well as the reactant side.)

The chemical equation $2HgO \rightarrow 2Hg + O_2$ is a true equation and is balanced because

Answer: the number of each kind of atom is equal on both reactant and product sides of the equation

The following unbalanced equation represents a single displacement reaction. Add up the atoms on each side on the equation.

$$Mg + HCl \rightarrow MgCl_2 + H_2$$

| Reactants | Products |
|---------------|---------------|
| atom(s) of Mg | atom(s) of Mg |
| atom(s) of H | atom(s) of H |
| atom(s) of Cl | atom(s) of Cl |

Answer:

| Reactants | Products |
|--------------|---------------|
| 1 atom of Mg | 1 atom of Mg |
| 1 atom of H | 2 atoms of H |
| 1 atom of Cl | 2 atoms of Cl |

Use a coefficient to make the chlorine atoms on the reactant side equal to chlorine atoms on the product side.

Answer: $Mg + 2HCl \rightarrow MgCl_2 + H_2$ (place the coefficient of 2 before the HCl)

Is the equation in frame 16 balanced? (Add the atoms on each side to determine if it is balanced.)

Answer: yes (Doubling the HCl resulted in doubling both H and Cl atoms on the reactant side; therefore, the equation is balanced.)

The following unbalanced equation represents a combination reaction. Add up the atoms on each side of the equation. Al + $O_2 \rightarrow Al_2O_3$

| Reactants | Products |
|---------------|---------------|
| atom(s) of Al | atom(s) of Al |
| atom(s) of O | atom(s) of O |

Answer:

| Reactants | Products |
|--------------|---------------|
| 1 atom of Al | 2 atoms of Al |
| 2 atoms of O | 3 atoms of O |

At this point, we can use a coefficient to equalize either the Al atoms or the O atoms. A good rule of thumb to follow is to leave any oxygen or hydrogen atoms until last, placing coefficients elsewhere first. Use a coefficient to equalize the number of atoms of Al on both the reactant and product side.

$$Al + O_2 \rightarrow Al_2O_3$$

Answer: $2AI + O_2 \rightarrow AI_2O_3$ (The numbers of AI atoms are now equal on both sides of the equation, but the equation is not yet balanced.)

Our equation from frame 19 now represents the following number of atoms.

$$2\mathsf{Al} + \mathsf{O_2} \to \mathsf{Al_2}\mathsf{O_3}$$

| Products |
|---------------|
| 2 atoms of Al |
| 3 atoms of O |
| |

- (a) By what number must the oxygen atoms on the reactant side of the equation be multiplied to equal the oxygen atoms on the product side?
- (b) Is that number a small whole number?

Answer: (a) $1\frac{1}{2}$ (which would result in an equation of $2AI + 1\frac{1}{2}O_2 \rightarrow AI_2O_3$); (b) no $(1\frac{1}{2}$ is not a small whole number.)

The equation in the answer to frame 20 is now balanced. However, the coefficients 21 in chemical equations should normally be whole numbers. We should multiply by the smallest possible whole number to eliminate the fraction. Here, we can multiply every item in the equation by what single whole number?

Answer: 2 (Multiplying every item by a factor of 2 gives a balanced equation with no fraction.)

Rewrite the equation, multiplying every item by 2. 22

Answer: $4AI + 3O_2 \rightarrow 2AI_2O_3$

The following unbalanced equation represents a single displacement reaction. De-23 termine the number of each kind of atom in the unbalanced equation.

$$Al + HCl \rightarrow AlCl_3 + H_2$$

| Reactants | Products |
|---------------|---------------|
| atom(s) of Al | atom(s) of Al |
| atom(s) of H | atom(s) of H |
| atom(s) of CI | atom(s) of Cl |

Answer:

| Reactants | Products |
|--------------|---------------|
| 1 atom of Al | 1 atom of A |
| 1 atom of H | 2 atoms of H |
| 1 atom of Cl | 3 atoms of Cl |

Remember, in balancing equations, it often is useful to leave the H atoms and O 24 atoms (if any) until last. Rewrite the equation below to equalize the Cl atoms on both sides.

$$\mathsf{Al} + \mathsf{HCl} \to \mathsf{AlCl}_3 + \mathsf{H}_2$$

Answer: AI + 3HCI \rightarrow AICI₃ + H₂

- Now that the Cl atoms are equal, is the above equation balanced? 25 Answer: no (The reactant side has three atoms of H and the product has two atoms of H.)
- Look at the following equation. 26

$$Al + 3HCl \rightarrow AlCl_3 + H_2$$

What compound or element should be multiplied to make equal numbers of H atoms on both sides of the equation? ______ By what number? _____

Answer: H_2 ; $1\frac{1}{2}$ or $\frac{3}{2}$

It is usually not acceptable to write a fraction in a chemical equation.

Al + 3HCl
$$\rightarrow$$
 AlCl₃ + $\frac{3}{2}$ H₂

The fraction can be eliminated with simple math. Multiply every item in the equation by a factor of 2.

Answer: 2AI + 6HCl → 2AlCl₃ + 3H₂

The above equation is balanced because _____

Answer: it has equal numbers of Al, H, and Cl atoms on each side

The following unbalanced equation represents a combination reaction.

$$P_4O_6 + H_2O \rightarrow H_3PO_3$$

(a) Determine the number of atoms of each element for each side.

| Reactants | Products |
|--------------|--------------|
| atom(s) of P | atom(s) of P |
| atom(s) of O | atom(s) of O |
| atom(s) of H | atom(s) of H |

(b) Use a coefficient to make the number of P atoms equal on both sides.

Answer:

(a)

| Products |
|--------------|
| 1 atom of P |
| 3 atoms of O |
| 3 atoms of H |
| |

(b) $P_4O_6 + H_2O \rightarrow 4H_3PO_3$ (representing four molecules of H_3PO_3)

Now that the P atoms are equal, count the number of atoms on each side of the equation.

$$P_4O_6 + H_2O \rightarrow 4H_3PO_3$$

| Reactants | Products |
|--------------|--------------|
| atom(s) of P | atom(s) of P |
| atom(s) of O | atom(s) of O |
| atom(s) of H | atom(s) of H |

Answer:

| Reactants | Products |
|--------------|---------------|
| 4 atoms of P | 4 atoms of P |
| 7 atoms of O | 12 atoms of O |
| 2 atoms of H | 12 atoms of H |
| | |

Completely balance the equation. (Hint: Equalize the H atoms or the O atoms next.)

$$P_4O_6 + H_2O \rightarrow 4H_3PO_3$$

Answer: $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

Balance the following equation representing a combination reaction.

$$Al + Cl_2 \rightarrow AlCl_3$$

Answer:

The first step is to equalize the Cl atoms on both sides.

$$Al + \frac{3}{2}Cl_2 \rightarrow AlCl_3$$

Then eliminate the fraction.

$$2Al + 3Cl_2 \rightarrow 2A|Cl_3$$

Balance the following equation representing a combination reaction. Leave the H and O atoms until last.

$$P_4O_{10} + H_2O \rightarrow H_3PO_4$$

Answer: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

The following unbalanced equation represents a double displacement reaction.

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + NaCl$$

Balance this equation.

Answer: $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$ (The only change necessary to balance the equation is placing a coefficient of 2 before NaCl.)

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The unbalanced equation below also represents a double displacement reaction.

$$FeCl_3 + KOH \rightarrow Fe(OH)_3 + KCl$$

Balance the equation.

Answer: FeCl₃ + 3KOH → Fe(OH)₃ + 3KCl

WORD EQUATIONS

36

Each chemical equation represents a chemical reaction. You have already learned how to name chemical compounds in Chapter 5. Let's apply what you have already learned about naming compounds to reading chemical equations.

The reaction equation below can read as "sodium hydroxide plus hydrogen chloride (or hydrochloric acid) yields sodium chloride and hydrogen oxide (or water)."

$$NaOH + HCl \rightarrow NaCl + H_2O$$

The reaction equation below reads as: ______ plus _____.

$$AgNO_3 + KCl \rightarrow AgCl + KNO_3$$

Answer: silver nitrate; potassium chloride; silver chloride; potassium nitrate

37

Here are several equations of various types.

- (1) $2P + 5O_2 \rightarrow 2P_2O_5$
- $(2) C + O_2 \rightarrow CO_2$
- (3) $FeCl_3 + 3KOH \rightarrow Fe(OH)_3 + 3KCl$
- (a) Equation 1 reads as ______ plus _____ yields
- (b) Equation 2 reads as ______ plus _____ yields
- (c) Equation 3 reads as _____ plus _____ yields _____.

Answer:

- (a) phosphorus; oxygen; phosphorus(V) oxide (or diphosphorus pentoxide)
- (b) carbon; oxygen; carbon dioxide (or carbon(IV) oxide)
- (c) iron(III) chloride (or ferric chloride); potassium hydroxide; iron(III) hydroxide (or ferric hydroxide); potassium chloride

Write the balanced equation for: sodium plus water yields sodium hydroxide plus hydrogen gas. (Hydrogen gas is H₂.)

Answer:

The unbalanced equation is Na + $H_2O \rightarrow NaOH + H_2$.

The balanced equation is $2Na + 2H_2O \rightarrow 2NaOH + H_2$.

Write the balanced equation for: potassium hydroxide plus hydrochloric acid yields potassium chloride plus water.

Answer: KOH + HCl → KCl + H2O

You have had some practice in balancing equations that represent several types of reactions. In the next section, you will learn how to predict whether or not a reaction will actually occur as written in the equation.

REACTIONS — GO OR NO GO

Many of the reaction equations you have balanced thus far involve ionic compounds and take place in water (aqueous) solutions. The ionic compounds in aqueous solution actually dissociate, meaning that the negative and positive ions separate and move about freely in the solution.

The reaction equation from frame 39 can also be written in complete ionic form.

$$\mathrm{K}^+ + \mathrm{OH}^- + \mathrm{H}^+ + \mathrm{Cl}^- \to \mathrm{K}^+ + \mathrm{Cl}^- + \mathrm{H}_2\mathrm{O}$$

Which item in the complete ionic equation is obviously *not* an ion but is a covalently bonded molecule?

Answer: H₂O

In the ionic equation in frame 40, the whole reaction takes place in water (aqueous) solution. All of the ions are completely dissolved in water. We can show that the reaction takes place in water by writing "(aq)," which means aqueous, behind every ion in the equation.

$$K^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow K^+(aq) + Cl^-(aq) + H_2O(l)$$

Not only did the reaction take place in water (aqueous) solution, but water is also a product. Note that an "(l)" is placed after H_2O to indicate that it is a liquid. The formation of water as a product is one way to know whether a reaction actually occurs.

A second way to know is whether a precipitate is a product. A precipitate is a compound that does not dissolve in water. If a precipitate is formed as a product in a reaction that is taking place in water solution, the precipitate will come out of the

TABLE OF SOLUBILITY OF SOME COMMON COMPOUNDS

- All common compounds made up of alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, or Fr⁺) or NH₄⁺ and negative ions are soluble.
- All compounds containing C₂H₃O₂ or NO₃ and a positive ion are soluble.
- All compounds containing SO₄²⁻ are soluble except when combined with ions of Ba²⁺, Sr²⁺, or Pb²⁺.
- All compounds containing Br⁻, Cl⁻, or I⁻ are soluble except when combined with ions of Ag⁺, Hg₂²⁺, or Pb²⁺.
- Compounds of HCO₃⁻ with alkaline earth metal ions (Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, or Ra²⁺) and alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, or Fr⁺) or NH₄⁺ are soluble. Compounds of HCO₃⁻ are insoluble with all other positive ions.
- Compounds with OH⁻ are soluble only with Ba²⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Fr⁺, or NH₄⁺. Compounds with OH⁻ are *insoluble* with all other positive ions.
- All compounds with CO₃²⁻, PO₄³⁻, or S²⁻ are insoluble except with alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, or Fr⁺) or NH₄⁺.

solution and will normally settle to the bottom of the solution container. In an experimental situation, it is easy to see if a precipitate is formed. We can also use a solubility table, such as the table above, to predict whether or not a precipitate will form.

What are two ways to tell whether or not a reaction will take place?

Answer: A reaction will take place if either of the following is true: (1) if water (H_2O) is a product, or (2) if a precipitate is a product.

If H_2O or a precipitate is not formed as a product, or if other products that will be covered later are not formed, we may just simply have an aqueous solution of the various ions with no reaction taking place at all. It is, therefore, important to determine if a reaction is likely to produce a precipitate. The table above is very useful for determining whether or not a compound formed from a pair of ions is soluble or insoluble in water. Insoluble compounds are precipitates. To use the table, first determine which ions make up the compound. As you learned in Chapter 3, an ionic compound is made up of a positive ion, which is usually a metal or H^+ or NH_4^+ , and a negative ion, which is usually the remainder of the compound and is made up of one or more nonmetal atoms.

After determining the ion pair that makes up the compound, locate the ions on the table and determine if the ion pair will form a precipitate or if the compound is

soluble. For example, the compound CaCl₂ is made up of Ca²⁺ and Cl⁻ ions. According to the fourth statement on the table, all compounds made up of Cl⁻ ions are soluble except when combined with Ag⁺, Hg₂²⁺, or Pb²⁺. Since Cl⁻ is combined with Ca²⁺, the compound is soluble.

Using the table, underline those compounds that are insoluble and would therefore precipitate in aqueous solution.

Answer: AgCl, CaCO₃, and Mg(OH)₂

Underline those compounds listed below that are insoluble and will form precipitates in aqueous solution.

Answer: PbSO₄, Hg₂I₂, and MgCO₃

Does the following reaction actually occur? Why or why not? (Hint: Use the table to check to see if one of the products is a precipitate.)

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

Answer: Yes, the reaction occurs because AgI will precipitate.

Does the following reaction occur? Why or why not?

$$Ba(OH)_2 + MgSO_4 \rightarrow BaSO_4 + Mg(OH)_2$$

Answer: Yes, the reaction occurs because both products are precipitates.

You have already learned two means for determining whether or not a reaction occurs. If either water or a precipitate is a product, a reaction occurs. Other means for determining if a reaction actually occurs are the formation of a gas, a weak electrolyte, or a covalent compound. In an experiment, it is easy to detect a gas as a product since it usually bubbles up from an aqueous solution. Typical gases that you have encountered several times in this and previous chapters are H₂ (hydrogen gas), O₂ (oxygen gas), and CO₂ (carbon dioxide gas). We will specify if gases other than these are products.

Weak electrolytes are ionic compounds that only dissociate partially and, therefore, only conduct a weak electric current in aqueous solutions. We will specify if any products are weak electrolytes. (Later chapters will deal more specifically with weak electrolytes.)

Covalent compounds were described in Chapter 3 as compounds that are not ionic and are typically composed of nonmetal atoms. Typical covalent compounds

include both H₂O and the gases listed above. We will specify if covalent compounds other than these are reaction products.

If none of these products is formed, assume that a reaction does *not* occur at all. Does the following reaction occur? Why or why not?

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

Answer: Yes, the reaction occurs because a gas (H2) is formed.

In the following equation, the products listed are both strong electrolytes (therefore not weak electrolytes). There are no gases or covalent compounds produced. Does the reaction occur? Why or why not?

$$2NaNO_3 + MgCl_2 \rightarrow Mg(NO_3)_2 + 2NaCl$$

Answer: No, the reaction does not occur. The question has already eliminated gases and covalent compounds. Since the products are strong electrolytes, they cannot be weak electrolytes. Water is not a product. Neither of the possible products is a precipitate (according to the solubility table). Therefore, the reaction does not occur.

Here is another double displacement chemical equation. No weak electrolytes, gases, or covalent compounds are produced. Does the reaction occur? Why or why not?

$$2NH_4Br + Pb(NO_3)_2 \rightarrow 2NH_4NO_3 + PbBr_2$$

Answer: Yes, the reaction occurs. Although the products are not weak electrolytes, gases, water, or other covalent compounds, one of the products (PbBr₂) is a precipitate.

IONIC EQUATIONS

Although most of the previous equations involving ions in aqueous solution have been written in *molecular* form (showing complete chemical formulas), a more correct method would be to write an equation showing the ions as *dissociated*. The following equation is in molecular form.

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

A more correct method of writing the same equation would show the reactants as ions. In the following equation (reactant side only), note that water is neither a reactant nor a product. Although the reaction takes place in water solution, it does not participate as either a reactant or product, therefore it can be either left out of the equation or the abbreviation (aq) can be placed behind each ion. Complete the reactant side of this equation in ionic form.

$$Ag^+(aq) + NO_3^-(aq) + \underline{\hspace{1cm}} (aq) + \underline{\hspace{1cm}} (aq) \rightarrow$$

Answer: $Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightarrow$

The complete molecular equation is: AgNO₃ + NaCl → AgCl + NaNO₃. Since the AgCl is a precipitate and remains an undissolved solid, we place an "(s)" behind its formula (which stands for solid). Write the complete ionic equation representing the precipitate and all ions in aqueous solution.

$$(aq) + (aq) + (aq) + (aq) + (aq) + AgCl(s) + (aq) + (aq) + AgCl(s) + (aq) + AgCl(s) + NO3-(aq) + NO3-(aq) + NO3-(aq) + NO3-(aq)$$

The equation in frame 50 is called a complete ionic equation. A complete ionic equation usually includes some ions that did not take part in the reaction and can be found on both sides of the equation. Those ions that do not take part in the reaction are called spectator ions.

Look at the complete ionic equation again.

$$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

The spectator ions are _____ and _____.

Answer: Na+(aq); NO₃-(aq)

A complete ionic equation contains all ions including spectator ions. If the spectator ions are eliminated from both sides of a complete ionic equation, the result is called a net ionic equation.

For the same complete ionic equation, write the net ionic equation.

$$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

Answer: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

A net ionic equation contains no spectator ions. A complete ionic equation includes spectator ions. When NaOH is added to FeCl₃ in aqueous solution, a precipitate Fe(OH)₃ forms. What ions would be included in the complete ionic equation for this reaction? (Forget about balancing the equation for the moment.)

$$(aq) + (aq) + (aq) + (aq) + (aq) + (aq)$$

 $\rightarrow Fe(OH)_3(s) + (aq) + (aq)$

Answer: Na⁺(aq) + OH⁻(aq) + Fe³⁺(aq) + Cl⁻(aq) \rightarrow Fe(OH)₃(s) + Na⁺(aq) + Cl⁻(aq)

Now balance the equation in frame 53 so that there are equal numbers of elements (including ions) on each side. (Hint: You may find it easier to balance the molecular version first. The unbalanced molecular version is: NaOH + FeCl₃ \rightarrow Fe(OH)₃ + NaCl.)

$$Na^{+}(aq) + \underline{\hspace{1cm}} OH^{-}(aq) + \underline{\hspace{1cm}} Fe^{3+}(aq) + \underline{\hspace{1cm}} Cl^{-}(aq)$$

 $\rightarrow Fe(OH)_{3}(s) + \underline{\hspace{1cm}} Na^{+}(aq) + \underline{\hspace{1cm}} Cl^{-}(aq)$

Answer:

The balanced molecular version is:

The balanced complete ionic equation is:

$$3Na^{+}(aq) + 3OH^{-}(aq) + Fe^{3+}(aq) + 3CI^{-}(aq)$$

 $\rightarrow Fe(OH)_{3}(s) + 3Na^{+}(aq) + 3CI^{-}(aq)$

Eliminate the spectator ions on both sides of the ionic equation in frame 54. The resulting equation is:

_____→

The resulting equation is called a(n) ______ ionic equation.

Answer: $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_{3}(s)$; net ionic

An aqueous solution of Na₂CO₃ is added to dilute hydrochloric acid. The resulting carbonic acid, H₂CO₃, breaks down to form CO₂ gas and H₂O. Complete and balance the molecular equation for this reaction.

+ \rightarrow + $CO_2 + H_2O$

Answer: Na₂CO₃ + 2HCl → 2NaCl + CO₂ + H₂O

Write the complete ionic equation representing the reaction in frame 56. CO₂ escapes as a gas, therefore we place a "(g)" behind its formula. Both CO₂ and H₂O are considered to be covalent molecules, therefore CO₂ and H₂O remain in molecular form.

<u></u> →

Answer: $2Na^{+}(aq) + CO_{3}^{2-}(aq) + 2H^{+}(aq) + 2CI^{-}(aq) \rightarrow 2Na^{+}(aq) + 2CI^{-}(aq) + H_{2}O(l) + CO_{2}(g)$

Write the net ionic version of the equation in frame 57.

Answer: $2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$

Complete the following double displacement reaction in molecular form and balance.

 $CuSO_4 + 2LiOH \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

Answer: CuSO₄ + 2LiOH → Cu(OH)₂ + Li₂SO₄

| 60 | What ions are represented on the left (reactant) side of the equation in frame 59? |
|----|---|
| | +++++ |
| | Answer: $Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow$ |
| 61 | Do any pair of the four ions in frame 60 form an insoluble precipitate? (Use the table on page 137.) If yes, what pair of ions? |
| | Answer: yes; Cu^{2+} and $2OH^{-}$ form an insoluble precipitate: $Cu(OH)_2$. |
| 62 | Finish the complete ionic equation below. The precipitate should be in molecular form. |
| | $Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq)$ $\rightarrow \underline{\qquad} + \underline{\qquad} + \underline{\qquad} + \underline{\qquad}$ |
| | Answer: $Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2(s) + 2Li^{+}(aq) + SO_4^{2-}(aq)$ |
| 63 | Write the net ionic equation for the equation in frame 62. → |
| | Answer: $Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2(s)$ |
| 64 | Now give the same information for this reaction. |
| | (a) Complete and balance the following molecular equation. $Ag_2SO_4 + NaI \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$ |
| | (b) What ions are represented on the reactant side of the above equation? |
| | (c) No gases, weak electrolytes, or covalent compounds are products. Will the reaction occur? Why or why not? |
| | (d) Write the complete ionic equation. |
| | (e) Write the net ionic equation. |
| | Answer: |
| | (a) $Ag_2SO_4 + 2NaI \rightarrow 2AgI + Na_2SO_4$ |
| | (b) $2Ag^{+}(aq) + SO_4^{2-}(aq) + 2Na^{+}(aq) + 2I^{-}(aq) \rightarrow$ |
| | (c) Yes, Ag ⁺ and I ⁻ form a precipitate (AgI). |
| | (d) $2Ag^{+}(aq) + SO_4^{2-}(aq) + 2Na^{+}(aq) + 2I^{-}(aq) \rightarrow 2AgI(s) + 2Na^{+}(aq) + SO_4^{2-}(aq)$ |
| | (e) $2Ag^{+}(aq) + 2I^{-}(aq) \rightarrow 2AgI(s)$ We can simplify this net ionic equation by dividing by a factor of 2. Thus: $Ag^{+}(aq) + I^{-}(aq) \rightarrow AgI(s)$. Fither answer is acceptable. |

65 F

Follow the same procedure for this reaction.

(a) Complete and balance the following double displacement reaction in molecular form.

$$BaCl_2 + Na_2SO_4 \rightarrow \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$$

- (b) Does the reaction occur even though there are no gases, weak electrolytes, or covalent compounds formed? Why or why not?
- (c) Write the complete ionic equation for the above.
- (d) Write the net ionic equation.

Answer:

- (a) $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$
- (b) Yes, BaSO₄ precipitates.
- (c) $Ba^{2+}(aq) + 2Cl^{-}(aq) + 2Na^{+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + 2Na^{+}(aq) + 2Cl^{-}(aq)$
- (d) $Ba^{2+}(aq) + SO_a^{2-}(aq) \rightarrow BaSO_a(s)$

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Try it again.

(a) Complete and balance the following molecular equation.

$$AgNO_3 + KCl \rightarrow$$

- (b) No product is a gas, a weak electrolyte, or a covalent compound. Does this reaction occur? Why or why not?
- (c) Write the complete ionic equation for the above.
- (d) Write the net ionic equation.

Answer:

- (a) $AgNO_3 + KCI \rightarrow AgCI + KNO_3$
- (b) Yes, AgCl precipitates.
- (c) $Ag^{+}(aq) + NO_{3}^{-}(aq) + K^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s) + K^{+}(aq) + NO_{3}^{-}(aq)$
- (d) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

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One more time.

(a) Complete and balance the following molecular equation. One of the products of this reaction is H₂CO₃, which immediately breaks down to form H₂O and CO₂.

$$K_2CO_3 + H_2SO_4 \rightarrow$$

(b) Write the complete ionic equation for this reaction.

| , , | TT/7 . 1 | . • | |
|-----|------------------------|---------|--|
| (c) | Write the net ionic eq | iation | |
| 10 | write the net forme eq | <i></i> | |

Answer:

- (a) $K_2CO_3 + H_2SO_4 \rightarrow K_2SO_4 + H_2CO_3$ (Since the H_2CO_3 breaks down into CO_2 and H_2O immediately, it should be written as follows: $K_2CO_3 + H_2SO_4 \rightarrow K_2SO_4 + H_2O + CO_2$)
- (b) $2K^{+}(aq) + CO_{3}^{2-}(aq) + 2H^{+}(aq) + SO_{4}^{2-}(aq) \rightarrow CO_{2}(g) + H_{2}O(l) + 2K^{+}(aq) + SO_{4}^{2-}(aq)$
- (c) $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$

Chemical formulas and equations are extremely useful tools for the chemist. They save a lot of time and words when we try to communicate. You will encounter chemical equations throughout the rest of this book, so it is important that you know the material in this chapter.

In the next chapter you will use balanced chemical equations to examine weight relationships between reactants and products. (Ions and ionic equations will appear again in Chapters 9 and 11 through 13, so you can see how important they are to your understanding of chemistry.)

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test.

| 1. | Complete and balance the following reactions as molecular equations, complete ionic equations, and net ionic equations. | | | |
|----|---|--------------------------------------|--|--|
| | (a) | ammonium hydroxide + sulfuric acid → | | |
| | | | | |
| | (b) | lead(II) nitrate + sodium chloride → | | |
| | | | | |

| (c) | $Fe_2(SO_4)_3 + Ba(OH)_2 \rightarrow$ | | |
|-----|---------------------------------------|------|--|
| | | | |
| | | | |

2. Indicate whether each of the following reactions is combination, decomposition, single displacement, or double displacement.

```
(a) 2HBr \rightarrow H_2 + Br_2
```

(b)
$$4Ag + O_2 \rightarrow 2Ag_2O$$

(c)
$$2Mg + CO_2 \rightarrow 2MgO + C$$

3. Using the table on page 137, underline the insoluble compounds in the list below.

4. Do all the equations in question 1 occur? Why?

| (a) | | | | |
|-----|--|--|--|--|
|-----|--|--|--|--|

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. (a) $2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O$ (molecular) $2NH_4^+(aq) + 2OH^-(aq) + 2H^+(aq) + SO_4^{-2}(aq) \rightarrow 2NH_4^+(aq) + SO_4^{-2}(aq) + 2H_2O(l)$ (complete ionic) $2OH^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l)$ (net ionic)
 - (b) $Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2(s) + 2NaNO_3$ (molecular) $Pb^{2+}(aq) + 2NO_3^{-}(aq) + 2Na^{+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s) + 2Na^{+}(aq) + 2NO_3^{-}(aq)$ (complete ionic) $Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$ (net ionic)
 - (c) $Fe_2(SO_4)_3 + 3Ba(OH)_2 \rightarrow 2Fe(OH)_3(s) + 3BaSO_4(s)$ (molecular) $2Fe^{3+}(aq) + 3SO_4^{2-}(aq) + 3Ba^{2+}(aq) + 6OH^-(aq) \rightarrow 2Fe(OH)_3(s) + 3BaSO_4(s)$ (complete and net ionic because *both* products are precipitates) (frames 6–39, 49–67)
- 2. (a) decomposition; (b) combination; (c) single displacement (frames 1-5)
- 3. AgCl, CuS (frames 41-43)
- 4. (a) yes, because H₂O is produced
 - (b) yes, because the precipitate PbCl₂ is formed
 - (c) yes, because both products are precipitates (frames 40–48)

Just as a dozen is 12 and a gross is 144, a mole of any kind of particle is 6.023×10^{23} of the particles. The weight of a dozen eggs is not the same as the weight of a dozen oranges. Likewise, the weight of a mole of atoms of one element is not the same as the weight of a mole of atoms of another element. The weight of a mole of any kind of particle or unit, expressed in grams, is numerically the same as the weight of one of the individual particles or units, expressed in atomic mass units (amu).

The following are three examples of the mole concept.

- 1. From the table of atomic weights, the atomic weight of hydrogen is given as 1.0079. This means that one H atom has a weight equal to 1.0079 amu. It also means that the weight of 1 mole of H atoms is 1.0079 grams. The weight of a single H atom is 1.673×10^{-24} g. That is, 1.0079 g is the total weight of 6.023 \times 10²³ H atoms; therefore, the weight of one H atom is 1.0079 g divided by 6.023×10^{23} , which gives 1.673×10^{-24} g.
- 2. The formula H_2 for elementary hydrogen means that each hydrogen molecule consists of two H atoms. The weight of two H atoms, 2×1.0079 amu = 2.0158 amu. The weight of 1 mole of H_2 molecules is, therefore, 2.0158 g. The weight of a single H_2 molecule is 3.347×10^{-24} g.
- 3. The formula NO_3^- for a nitrate ion means that the ion consists of one nitrogen atom and three oxygen atoms (together with an additional electron that gives the ion its charge but does not contribute significantly to the weight within the range of our precision limits here). The weight of a nitrate ion is, therefore, the weight of one nitrogen atom plus the weight of three oxygen atoms, or 62.01 amu (to the nearest hundredth). The weight of 1 mole of nitrate ions is, therefore, 62.01 grams, and the weight of an individual nitrate ion is 1.03×10^{-22} g.

In the past, problems involving chemical reactions have been called mass-mass, mass-volume, or volume-volume problems and have been solved using algebraic ratios or proportions. We feel the solution of these problems using the mole concept is superior and fosters a better understanding of what goes on in a reaction than ratio/proportion solving.

The problem solving presented here uses solely the mole concept when we are dealing with chemical reactions. A chemist, chemical engineer, or metallurgist uses this technique to answer very important questions, such as how much raw material

will be required to produce a specified quantity of product. Management then uses the cost of those materials and labor, along with other production costs, to determine the price of the product.

OBJECTIVES

After completing this chapter you will be able to calculate the weight or number of moles of any reactant or product that will be used up (if a reactant) or produced (if a product), given a completely balanced chemical equation, a table of atomic weights, and a specified quantity (weight or moles) of any one reactant or product.

| 1 | Remember, a mole is 6.023×10^{23} (Avogadro's number) particles such as atoms, ions, or molecules. The weight of this number of particles is expressed in grams. A mole of hydrogen ions (H ⁺) contains how many hydrogen ions? How much do they weigh? (Calculate answers in this chapter to the nearest hundredth unless otherwise indicated.) |
|---|---|
| | Answer: 6.023×10^{23} ; 1.01 g |
| 2 | Unless otherwise stated, the term $mole$ means the same as the term $gram$ - $mole$. A gram-mole is the weight of 6.023×10^{23} particles expressed in grams. A gram-mole of atoms is equivalent to the atomic weight expressed in grams. One mole of carbon atoms (C) weighs how many grams? The atomic weight of carbon is how many grams? |
| | Answer: 12.01; 12.01 |
| 3 | One mole of the element lead (Pb) contains atoms and weighs |
| | Answer: 6.023 × 10 ²³ ; 207.2 g |
| 4 | How many atoms of carbon and sulfur are needed to make one molecule of carbon disulfide (CS_2) ? |
| | Answer: one atom of C and two atoms of S |
| 5 | In calculations, the abbreviation mol means mole or moles. To make 1 mol of carbon disulfide (CS ₂) molecules requires how many moles of carbon atoms and sulfur atoms? |
| | Answer: 1 mol of C and 2 mol of S |

| | nole of carbon tetrachloride (CCl ₄) requires how many moles of C atoms and nany moles of Cl atoms? |
|--|---|
|--|---|

Answer: 1 mol of C and 4 mol of Cl

Answer: 153.81 g (Remember to express the answer in grams.)

Thirty-six grams of H₂O represent how many moles?

Answer: 2 mol
$$\left(\text{mol H}_2\text{O} = 36 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 2.00 \text{ mol H}_2\text{O}\right)$$

Answer: 0.50 mol
$$\left(\text{mol H}_2\text{O} = 9 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 0.50 \text{ mol}\right)$$

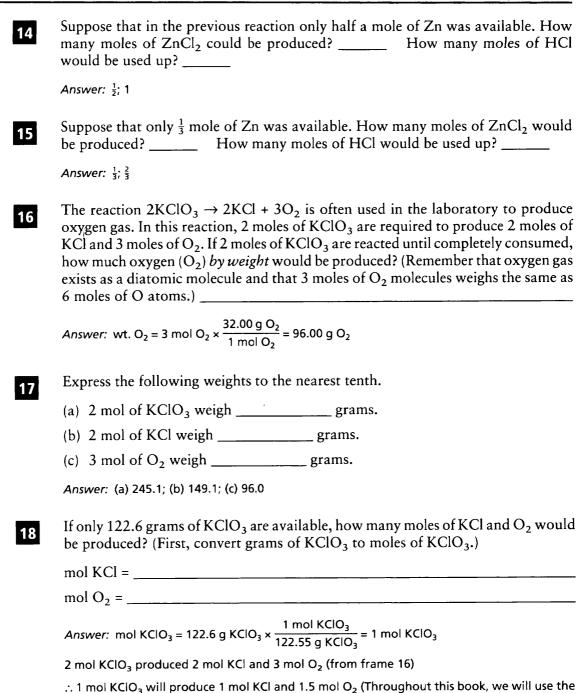
Answer: 0.016 mol
$$\left(0.50 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.05 \text{ g CH}_3\text{OH}} = 0.016 \text{ mol CH}_3\text{OH}\right)$$

Answer: a mole of Cl atoms

Now that you understand what a mole of a substance is, let's apply the concept to some reactions.

In the balanced reaction Zn + 2HCl → H₂ + ZnCl₂, when zinc metal reacts with hydrochloric acid, hydrogen gas and zinc chloride are the products. How many moles of HCl are needed to produce 1 mole of ZnCl₂? _____

Answer: 2



If only 122.6 grams of KClO₃ are available, how many grams of KCl and O₂ would be produced (to the nearest tenth)?

symbol : for the word "therefore.")

| grams of KCl = |
|---|
| grams of O ₂ = |
| Answer: From frame 18, 1 mol KCl and 1.5 mol O ₂ are produced |
| ∴ g KCl = 1 mol KCl × $\frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}}$ = 74.6 g KCl |
| ∴ g $O_2 = 1.5 \text{ mol } O_2 \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 48.0 \text{ g } O_2$ |
| If only 24.5 grams of KClO ₃ are available, how many moles of KClO ₃ are available? |
| Answer: mol KClO ₃ = 24.5 g KClO ₃ × $\frac{1 \text{ mol KClO}_3}{122.55 \text{ g KClO}_3}$ = 0.20 mol KClO ₃ |
| If only 24.5 grams of KClO ₃ are available, how many moles of KCl and O ₂ would be produced? (First convert g KClO ₃ to mol KClO ₃ as you did in frame 18.) |
| mol KCl |
| $\operatorname{mol} \operatorname{O}_2$ |
| How many grams of O ₂ would be produced (to the nearest tenth)? |
| Answer: |
| 2 mol KClO ₃ produces 2 mol KCl and 3 mol O ₂ |
| ∴ 0.20 mol KClO₃ produces 0.20 mol KCl |
| ∴ 0.20 mol KClO ₃ produces 0.30 mol O ₂ |
| ∴ g $O_2 = 0.30 \text{ mol } O_2 \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 9.6 \text{ g } O_2$ |
| $2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$ |
| (a) 2 mol of Fe weigh grams. |
| (b) 3 mol of Cl ₂ weigh grams. |
| (c) 2 mol of FeCl ₃ weigh grams. |
| Answer: (a) 111.70; (b) 212.70; (c) 324.40 |
| How many moles of iron (Fe) and chlorine gas (Cl ₂) are required to produce 32.44 grams of FeCl ₃ ? (First convert g FeCl ₃ to mol FeCl ₃ .) |
| mol Fe |
| mol Cl ₂ |

Answer: mol FeCl₃ = 32.44 g FeCl₃ ×
$$\frac{1 \text{ mol FeCl}_3}{162.20 \text{ g FeCl}_3}$$
 = 0.20 mol FeCl₃

1 mol Fe and 1.5 mol Cl₂ will produce 1 mol FeCl₃

∴ 0.20 mol FeCl₃ will require 0.20 mol Fe and 0.30 mol Cl₂

In the reaction $2H_2 + O_2 \rightarrow 2H_2O$, if 360.4 grams of water are produced, how many moles of H_2 and of O_2 are required? How many grams of O_2 are required?

- (a) mol H₂_____
- (b) mol O₂ _____
- (c) grams O₂

Answer: mol H₂O = 360.4 g H₂O ×
$$\frac{1 \text{ mol H}_2O}{18.02 \text{ g H}_2O}$$
 = 20 mol H₂O

1 mol H₂ plus ½ mol O₂ will produce 1 mol H₂O

(a)20 mol H₂; (b) 10 mol O₂; (c) 320 g O₂
$$\left(10 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1.0 \text{ mol O}_2} = 320 \text{ g O}_2\right)$$

LIMITING REACTANT

For many real-life chemical reactions, one or more of the reactants is limited in quantity. For example, when a car burns 1 gallon of gasoline, the gasoline reacts with oxygen from the air and, while the engine runs, produces chemical reaction products such as CO (carbon monoxide) and H_2O , as well as some others. After the gallon of gasoline is all used up, there is still plenty of oxygen in the air. In fact, after a whole tank full of gasoline is burned, there is still plenty of oxygen in the air. The limiting reactant in this case is the gasoline. It is completely consumed in the reaction.

For the reaction, $C + O_2 \rightarrow CO_2$, only 3 grams of carbon (C) are available but there is plenty of oxygen.

- (a) Which reactant is the limiting reactant, C or O₂?
- (b) How many grams of CO₂ could be produced?

Answer:

- (a) C
- (b) mol C = 3 g C × $\frac{1 \text{ mol C}}{12.01 \text{ g C}}$ = 0.25 mol C 1 mol C will produce 1 mol CO₂ \therefore 0.25 mol C will produce 0.25 mol CO₂ \therefore g CO₂ = 0.25 mol CO₂ × $\frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2}$ = 11.00 g CO₂

- Only 4.01 grams of methane (CH₄) are available for the reaction CH₄ + $2O_2 \rightarrow CO_2 + 2H_2O$. There is plenty of oxygen.
 - (a) Which reactant is the limiting reactant?
 - (b) How many grams of H₂O will be formed?

Answer:

- (a) CH₄
- (b) 9.01 g H_2O The weight of 1 mol of $CH_4 = 12.01 \text{ g} + (4 \times 1.01 \text{ g}) = 16.05 \text{ g}$

$$4.01 \text{ g CH}_4 \times \frac{1 \text{ mol of CH}_4}{16.05 \text{ g}} = 0.25 \text{ mol CH}_4$$

1 mol CH₄ will produce 2 mol H₂O ∴ 0.25 mol CH₄ will produce 0.5 mol H₂O

$$0.5 \text{ mol H}_2\text{O} \times \frac{18.02 \text{ g}}{1 \text{ mol H}_2\text{O}} = 9.01 \text{ g H}_2\text{O}$$

- For the following reaction, 18.02 grams of water are produced and all of the silane (SiH₄) is used up, although oxygen is still available after the reaction: SiH₄ + $2O_2 \rightarrow SiO_2 + 2H_2O$.
 - (a) How many moles of silane (SiH₄) are used up?
 - (b) What is the limiting reactant?

Answer: (a) 0.50 mol SiH₄; (b) silane (SiH₄)

- After the following reaction, all of the oxygen is used up in the reaction vessel and 60.09 grams of SiO_2 are produced. The reaction is: $SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$.
 - (a) What weight of silane (SiH₄) was used up?
 - (b) Which do you think is the limiting reactant?

Answer: (a) 32.13 g SiH₄; (b) Since the oxygen was all used up, it is the limiting reactant. We can assume that some silane still exists in the reaction vessel.

You have just learned how to use the mole concept to solve problems that deal with chemical reactions. You would be able to tell a producer of vinyl chloride how much chlorine would be needed to prepare 1 million pounds of vinyl chloride or a headache remedy producer how much salicylic acid is needed to produce 10 million pounds of acetylsalicylic acid (aspirin), provided you know the formulas of the reactants and the products and their combining ratios as indicated in a balanced chemical equation.

Understanding the mole concept is of utmost importance. You will encounter its use frequently in any chemistry course and in the chapters that follow in this book.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test. Round answers to the nearest hundredth.

1. In the following reaction, 4 moles of oxygen (O₂) molecules are completely consumed to produce water. There is still some hydrogen left in the reaction vessel after the reaction.

$$2H_2 + O_2 \rightarrow 2H_2O$$

- (a) How many moles of water (H₂O) are formed? _____
- (b) What weight of water is formed? _____
- (c) Which reactant is the limiting reactant?
- 2. In the following reaction, 16.02 grams of methyl alcohol (CH₃OH) are burned in open air:

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

- (a) How many moles of oxygen (O₂) are used up? _____
- (b) How many grams of water (H₂O) are formed? _____
- (c) Which reactant is the limiting reactant?

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. 1 mol O₂ produces 2 mol H₂O
 - (a) ∴ 4 mol O₂ produces 8 mol H₂O

(b)
$$g H_2O = 8 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} = 144.16 \text{ g } H_2O$$

- (c) O₂ (frames 13-16, 28)
- 2. mol CH₃OH = 16.02 g CH₃OH × $\frac{1 \text{ mol CH}_3\text{OH}}{32.05 \text{ q CH}_3\text{OH}}$ = 0.50 mol CH₃OH

2 mol CH₃OH uses 3 mol O₂ and produces 4 mol H₂O

(a) ∴ 0.50 mol CH₃OH uses 0.75 mol O₂ and produces 1 mol H₂O

(b)
$$\therefore$$
 g H₂O = 1 mol H₂O × $\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_3\text{O}}$ = 18.02 g H₂O

(c) CH₃OH is the limiting reactant, since there is plenty of oxygen left after the reaction (the reaction takes place in open air). (frames 18–21, 25–27)

8 Gases

Up to this point you have dealt with the states of matter (gases, liquids, and solids) when they appear as reactants or products in chemical reactions. But we have not discussed their properties.

In this chapter we discuss the properties of gases, how they behave, and how they are affected by changes in pressure and temperature. Several new laws will be introduced that deal with the behavior and properties of gases. You will also see how the molecular weights of gases are obtained from experimental measurements of the weights and volumes of samples of gaseous substances. It is possible to determine the molecular weight of any gas using the laws that are presented because all gases respond in much the same manner to changes in temperature and pressure.

As you work through this chapter we suggest that you think about encounters you have had with gases, such as a bicycle pump, a flat tire, a balloon (filled with air or helium), and the odors of ammonia, perfumes, or skunks. When dealing with problems involving gases, remember to use your experience and common sense.

OBJECTIVES

After completing this chapter, you will be able to

- recognize and apply or illustrate: pressure, temperature, partial pressure, kinetic molecular theory, diffusion, effusion, standard conditions (STP), Boyle's Law, Charles's Law, Dalton's Law, Graham's Law, combined gas law equation, ideal gas law, absolute temperature, absolute zero, and compressibility;
- calculate the fourth term in Boyle's or Charles's Laws when given any three of the four terms in the equations;
- calculate the sixth term in the combined gas law equation when given any five of the six terms in the equation;
- calculate the molecular weight of any gas when given:
 - 1. its density (two ways—using the volume per mole of a gas at STP, or Graham's Law);

- 2. the rate of effusion of the gas compared to the rate of another gas (Graham's Law);
- 3. P, V, R, T, and the weight of a sample of the gas (using the ideal gas law);
- calculate the weight of a liter of a gas or the volume occupied by 1 gram of a gas when given its molecular formula;
- state the assumptions of the kinetic molecular theory of gases and how they relate to ideal and real gases;
- calculate, using Dalton's Law:
 - 1. the partial pressure exerted by each gas within a mixture of gases when given the total pressure of the mixture and the mole fraction of each gas in the mixture (or the data necessary to calculate the mole fractions) and vice versa;
 - 2. the volume percent of each gas in a mixture when given the total volume of gases and the mole fraction of each gas (or the data needed to calculate mole fraction) and vice versa.

KINETIC MOLECULAR THEORY

1

The next three chapters will deal with the three states of matter: gases, liquids, and solids. These three states are related. If a solid is heated sufficiently, it will melt and become a liquid. If a liquid is heated sufficiently, it will become a gas or vapor. If a gas is cooled sufficiently, it will liquefy, and if a liquid is cooled sufficiently, it will solidify.

Gases are defined on the basis of the kinetic molecular theory. This theory makes several assumptions about gases. The first assumption is that gases are made up of individual molecules that are in constant rapid motion. The molecules possess kinetic energy (energy of motion) and bounce into each other and the walls of the gas container. Molecules bump into the wall at the top of a container as often as they bump into the bottom. This contrasts with the molecules of a liquid, which can flow and glide over one another but are, as you know, kept toward the bottom of the container. For example, the liquid molecules of a glass of water stay at the bottom of the glass. In a solid, the molecules can vibrate and bend, but they cannot flow or glide over one another or bounce around freely.

The kinetic molecular theory also assumes that the molecules of a gas are much farther apart than molecules of a liquid or solid.

| 1 - 1 | T | | 1 1 | 1 1 | . (1 | | 1 . 5 |
|-------|----------|----------|-----------|----------|-------------|--------|-------------|
| (a) | in which | state do | molecules | nave the | most freedo | m to i | move about? |

| (b) | Which do you expect would contain mor | e molecules, | a liter | of a ga | is such | as |
|-----|---|--------------|---------|---------|---------|----|
| | oxygen or a liter of a liquid such as water | ? | | | | |

Answer:

- (a) gas (Gas molecules can move rapidly in any direction. Molecules of a liquid or solid are more restricted.)
- (b) a liter of liquid (In a gas, the molecules are farther apart than in a liquid. Therefore, there would be fewer molecules in a given volume of a gas such as a liter.)
- The constantly moving gas molecules possess kinetic energy (energy of motion). All gases at the same temperature are assumed to have the same average kinetic energy. In fact, temperature is simply a measure of the average kinetic energy. Heating a gas results in an increase in the temperature of the gas and an increase in the average kinetic energy of gas molecules.

The average kinetic energy of sample A of a gas is greater than sample B of that gas. Which gas sample (A or B) could be expected to have a higher temperature? (All other conditions are equal.)

Answer: sample A (At constant temperature, all gases are assumed to have the same kinetic energy. Therefore the gas with a higher kinetic energy would also be of higher temperature.)

The kinetic molecular theory assumes that the rapidly moving gas molecules collide with each other and the walls of the gas container without any loss of kinetic energy. The collision of the gas molecules with the walls of the gas container results in what we call **pressure**.

A balloon is kept inflated because of pressure caused by _____

Answer: the collision of gas molecules with the inside wall of the balloon

Another assumption of the kinetic molecular theory is that the gas molecules themselves occupy no volume (thus leaving only the space between molecules as the volume occupied by a gas) and have no attraction for each other. Note that a gas that behaves completely according to the kinetic molecular theory assumptions is a theoretically ideal gas. Most actual gases approximate an ideal gas very well at moderate temperatures and pressures because of the large amount of space between the molecules. At low temperatures and high pressures, normal gases deviate from a theoretically ideal gas. We will cover some of these deviations later. Calculations involving pressure, volume, and temperature of gases are much simpler if we assume that gases behave as theoretically ideal. According to the kinetic molecular theory, all of the volume of an ideal gas can be attributed to

Answer: the space between the molecules

| 5 | Gases can be more readily compressed than liquids or solids. Since gas molecules are relatively far apart, an external force or pressure can readily push the molecules closer together. If a certain volume (such as a liter) of gas is compressed to half that volume, what happens to the number of molecules of gas during compression? (increases, decreases, stays the same) | | | | | | | |
|---|---|--|--|--|--|--|--|--|
| | Answer: stays the same (Just the space between the molecules is decreased.) | | | | | | | |
| 6 | Besides greater compressibility than liquids or solids, a characteristic of gases is greater diffusibility than liquids or solids. One gas rapidly diffuses into (mixes completely with) another gas because the space between gas molecules allows ready access to molecules of another gas. Why could you expect gases to diffuse more rapidly than liquids under roughly comparable conditions? | | | | | | | |
| | Answer: The space between molecules of a gas is greater than the space between molecules of a comparable liquid. | | | | | | | |
| 7 | When a gas is compressed, the same number of gas molecules occupies a smaller volume than before compression. That is, the gas container is smaller but contains the same number of molecules. We have defined pressure as the collision of gas molecules with the wall of the gas container. When a gas is compressed would you expect an increase, decrease, or no change in the number of collisions of gas molecules per square unit (such as a square centimeter) of container wall? Why? | | | | | | | |
| | Answer: an increase; There are just as many gas molecules now striking the wall of the smaller container as were striking the wall of the larger container. However, the container is now smaller, therefore the number of collisions per square unit of container wall surface has increased. | | | | | | | |
| 8 | Pressure is often measured as the relative number of collisions on a given area (square unit) of the gas container. Would you expect the pressure of a compressed gas to be greater than, less than, or the same as that of the gas before compression? | | | | | | | |
| | Answer: greater (Under compression, more gas molecules collide on a given area of the gas container.) | | | | | | | |
| 9 | Answer these questions about the effect of pressure on a gas. | | | | | | | |
| | (a) At constant temperature, when the volume of a gas (with a specific and unchanging number of molecules) is decreased by compression, the pressure on a given area of the inside wall of the container is (decreased, increased, unchanged) | | | | | | | |
| | | | | | | | | |

(b) At constant temperature (with a specific number of gas molecules), when the pressure of a gas increases, the volume of the gas is probably being (increased, decreased)

Answer: (a) increased; (b) decreased

BOYLE'S LAW

A scientist named Boyle formalized the relationship between pressure and volume that you have just seen in the previous frame. Boyle's Law states that at constant temperature, the volume of a confined dry gas is inversely proportional to the pressure. (Dry indicates no water present.) Mathematically, Boyle's Law is stated as:

$$PV = a$$
 constant at constant temperature

Pressure and volume are inversely proportional. Mathematically this means that if we multiply pressure by some number, we must divide the volume by that same number, or vice versa. For example, assume the constant is equal to the number 4. Assume that the pressure and the volume each are equal to 2.

$$PV = 2 \times 2 = 4$$

If we divide the pressure by 2, we must multiply the volume by 2 in order for the constant to remain unchanged.

$$PV = 1 \times 4 = 4$$

If we multiply the pressure by 10, we must divide the volume by 10 in order for the constant to remain unchanged.

$$PV = 20 \times 0.2 = 4$$

At constant temperature with a confined specific amount of gas molecules:

- (a) if the volume is decreased, the pressure is ______.
- (b) if the pressure is increased, the volume is ______.

Answer: (a) increased; (b) decreased

The pressure (P) multiplied by the volume (V) is a constant (unchanging) number if the temperature remains constant. Note that Boyle's Law is based upon a theoretically ideal gas. Real gases behave very closely to the ideal gas at moderate temperatures and pressures. Unless otherwise stated, we will assume that all gases behave exactly like an ideal gas. Since all gases are assumed to behave ideally, one gas will behave exactly like any other gas.

- (a) increasing P causes a corresponding _____ in V.
- (b) increasing V causes a corresponding _____ in P.

Answer: (a) decrease; (b) decrease

Boyle's Law can be applied in practical situations involving pressure and volume of a gas at constant temperature. A gas originally occupies a volume, which can be called V_1 , at the pressure of P_1 . By Boyle's Law, we know that multiplying P_1 times V_1 gives a number that is a constant. This same gas undergoes an increase in pressure to P_2 and a corresponding decrease in volume to V_2 . There is no change in temperature. How does the numerical constant obtained by multiplying P_1 times V_1 compare with the numerical constant obtained by multiplying P_2 times V_2 ?

Answer: The numerical constants are exactly the same. (A constant does not change.)

 P_1V_1 is equal to a constant and if P_2V_2 is equal to that same constant, then P_1V_1 must equal P_2V_2 . This is a more practical expression of Boyle's Law. If the new pressure (P_2) of a quantity of gas is greater than the earlier pressure (P_1) of that gas, and the temperature is assumed to be constant, then the new volume (V_2) must be (greater, less) ______ than the earlier volume (V_1) .

Answer: less (Pressure and volume are inversely proportional. As one increases, the other decreases.)

The equation $P_1V_1 = P_2V_2$ has four unknowns. If any three quantities are known, then the fourth can be determined. If P_1 is the unknown, the expression can be written as:

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

by simply dividing both sides of the equation by V_1 . Suppose that V_2 is unknown and P_1 , P_2 , and V_1 are known. Rewrite the equation $P_1V_1 = P_2V_2$ so that only V_2 remains on one side of the equation.

Answer: $\frac{P_1V_1}{P_2}$ (Divide both sides of the equation by P_2 .)

 V_1 is the original volume; P_1 is the original pressure. V_2 is the new volume, and P_2 is the new pressure. Pressure of a gas is measured in the metric system as millimeters of mercury. In honor of Torricelli, who did pioneer work with pressure, a new unit has been accepted. A pressure that will support a column of mercury 1 millimeter

high is called a torr. Millimeters of mercury and torr are equivalent and interchangeable as measures of pressure. Some textbooks use millimeters of mercury. We will be using torr. Volume of a gas is usually designated in liters or milliliters.

Five liters of a gas exist at a pressure of 700 torr. If the pressure is increased to 1400 torr, the volume of the gas is decreased. Let V_2 represent the unknown new volume. Identify V_1 , P_1 , and P_2 in this example.

Answer: 5 liters; 700 torr; 1400 torr

Using the information from frame 15, determine the new volume (V_2) . (Temperature is constant.)

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{700 \text{ torr} \times 5 \text{ liters}}{1400 \text{ torr}} = \frac{5 \text{ liters}}{2} = 2.5 \text{ liters}$$

(Remember to express the volume in liters.)

Five liters of oxygen gas exist at a pressure of 700 torr. If the pressure is decreased to 600 torr and temperature is constant, what will be the new volume? (If rounding is required, round to the nearest hundredth for this answer and others unless otherwise indicated.)

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{700 \text{ torr} \times 5 \text{ liters}}{600 \text{ torr}} = \frac{700 \times 5 \text{ liters}}{600} = \frac{3500 \text{ liters}}{600} = 5.83 \text{ liters}$$

Five liters of oxygen gas exist at a pressure of 700 torr. The pressure of the gas is reduced to $\frac{1}{4}$ of the original pressure. (One-fourth of 700 torr pressure is $\frac{1}{4} \times 700 = 175$ torr.) Temperature is constant. What is the new volume of oxygen?

$$V_2 = \frac{P_1 V_1}{700 \text{ torr} \times 5 \text{ liters}} \quad 700 \times 5 \text{ liters}$$

Answer:
$$\frac{P_1V_1}{P_2} = \frac{700 \text{ torr} \times 5 \text{ liters}}{175 \text{ torr}} = \frac{700 \times 5 \text{ liters}}{175} = 20 \text{ liters}$$

Assume the temperature does not change. Pressure and volume are inversely proportional. If a quantity of gas is compressed to half its volume, the new pressure will be doubled. If a quantity of gas is compressed to $\frac{1}{10}$ of its volume, its new pressure must be how many times as great as that of the original pressure? (If you wish to do so, try this problem on the 5 liters of gas at the pressure of 700 torr. The

new volume would be 0.5 liter.) What is the new pressure in relation to the original pressure?

Answer:
$$\frac{P_1V_1}{V_2} = \frac{700 \text{ torr} \times 5 \text{ liters}}{0.5 \text{ liters}} = \frac{700 \text{ torr} \times 5}{0.5} = 7000 \text{ torr}$$

The new pressure is 10 times the original pressure.

A pressure of 760 torr or millimeters of mercury is equivalent to 1 atmosphere of pressure. One atmosphere is the average pressure produced by the earth's atmosphere at sea level. A pressure of 1 atmosphere supports a column of mercury that is 760 millimeters high. Ten liters of hydrogen gas at a pressure of 1 atmosphere is compressed to a new pressure of 850 torr. What is the new volume of the gas?

Answer:
$$\frac{P_1V_1}{P_2} = \frac{760 \text{ torr} \times 10 \text{ liters}}{850 \text{ torr}} = \frac{760 \times 10 \text{ liters}}{850} = 8.94 \text{ liters}$$

Another unit for pressure is the kilopascal. One atmosphere is equal to 760 torr, which is equal to 101.325 kilopascals (kPa). A quantity of gas with an original pressure of 100 kPa is compressed to 150 kPa. The new volume of gas is 2 liters. What was the original volume of gas?

Answer:
$$\frac{P_2V_2}{P_1} = \frac{150 \text{ kPa} \times 2 \text{ liters}}{100 \text{ kPa}} = 3 \text{ liters of gas}$$

An aerosol spray can has a volume of 0.15 liters. It is designed so that it can deliver 1000 times its original volume to a new pressure assumed equal to one atmosphere. What is the original pressure inside the can? (An answer in terms of either torr or atmosphere is acceptable.)

Answer:

There are several ways to solve this problem. The first two methods use the fact that 1000 times the original 0.15 liter volume is $1000 \times 0.15 = 150$ liters.

Method 1:
$$P_1 = \frac{P_2 V_2}{V_1} = \frac{1 \text{ atmosphere} \times 150 \text{ liters}}{0.15 \text{ liters}} = \frac{150 \text{ atmospheres}}{0.15} = 1000 \text{ atmospheres}$$

Method 2:
$$P_1 = \frac{P_2 V_2}{V_1} = \frac{760 \text{ torr} \times 150 \text{ liters}}{0.15 \text{ liters}} = \frac{760 \text{ torr} \times 150}{0.15} = 760,000 \text{ torr}$$

= 1000 atmospheres

Method 3: Merely knowing that the new volume is 1000 times greater than the original volume is useful. The new volume (V_2) equals $1000 \times V_1$. Substitute $(1000V_1)$ for V_2 .

$$P_1 = \frac{P_2 V_2}{V_1} = \frac{1 \text{ atmosphere} \times 1000 V_1}{V_1} = 1000 \text{ atmospheres}$$

According to Boyle's Law, the pressure times the volume of a gas is a constant at constant temperature. Remember that all gases at a constant temperature are assumed to have the same average kinetic energy. Temperature is simply a measurement of the average kinetic energy of the gas.

Based upon these statements, would you expect the average kinetic energy of a gas to remain the same if the temperature was changed?

Answer: No, a change in temperature indicates a change in the average kinetic energy.

The absolute temperature scale is a measure of the average kinetic energy of gases. Doubling the absolute temperature doubles the average kinetic energy. Doubling the kinetic energy results in doubling the pressure (twice as many collisions of gas molecules with the walls) if the volume is constant, or a doubling of the volume if the pressure is constant. What happens to the average kinetic energy of a gas as the absolute temperature increases?

Answer: The average kinetic energy increases.

CHARLES'S LAW

With the pressure constant, the volume of a gas is directly proportional to the temperature. (That is, if the volume is multiplied by a number, the temperature must be multiplied by that same number. If the volume is divided by some number, the temperature must also be divided by that number.)

A scientist named Charles first stated this relationship formally. Charles's Law can be stated mathematically as:

$$\frac{V}{T}$$
 = a constant at constant pressure

V represents the volume of a gas and T is the absolute temperature of a gas.

- (a) In Boyle's Law, at constant temperature, the pressure and volume are (directly, inversely) _____ proportional.
- (b) In Charles's Law, at constant pressure, the volume and absolute temperature are (directly, inversely) ______ proportional.

Answer: (a) inversely; (b) directly

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$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
 (at constant pressure)

 V_1 is the original volume and V_2 is the new volume. T_1 is the original temperature and T_2 is the new temperature.

A quantity of gas at 200 K (absolute temperature scale) is heated to 400 K. The original volume is 3 liters. What is the new volume (with no change in pressure)?

Answer:

Charles's Law applies here. Modify the equation so that just V_2 is on the left side of the equation by multiplying both sides by T_2 .

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

$$V_2 = V_1 \times \frac{T_1}{T_2} = 3 \text{ liters} \times \frac{400 \text{ K}}{200 \text{ K}} = 6 \text{ liters}$$

Charles's Law is based upon absolute temperature. The absolute (Kelvin) tempera-27 ture scale is comparable to the Celsius scale in size of the degree, but the zero point is different. The zero point for the Kelvin scale is known as absolute zero. The zero point for the Celsius scale is the freezing point of water. The Kelvin scale zero point (0 K) is equivalent to -273°C . The freezing point of water is 0°C , or 273 K. To change from Celsius to Kelvin, just add 273 to the Celsius temperature. To change from Kelvin to Celsius, just subtract 273 from the Kelvin temperature. Fill in the blanks in the following conversions.

Answer: 323; 27°C

At absolute zero, an ideal gas has theoretically no volume at all. A gas loses volume 28 at the rate of $\frac{1}{273}$ for every degree of temperature drop at constant pressure. The temperature at which a theoretically ideal gas has no volume is _____ Celsius.

Answer: -273°

A quantity of gas at 10°C and 2 liters volume is heated to 50°C. Determine the new volume if the pressure remains constant. (Hint: To make calculations simpler when using Charles's Law, change all temperatures to absolute, or Kelvin, scale first.)

Answer: Charles's Law applies here.

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

$$T_2 = 50^{\circ}\text{C} = 323 \text{ K}$$

$$V_1 = 2$$
 liters

$$T_1 = 10^{\circ}\text{C} = 283 \text{ K}$$

$$V_2 = V_1 \times \frac{T_2}{T_1} = 2 \text{ liters } \times \frac{323 \text{ K}}{283 \text{ K}} = 2.28 \text{ liters}$$

A sample of neon gas occupies 100 milliliters (mL) volume at 100°C. The sample is heated to 200°C. What is the new volume (to the nearest tenth) of neon (pressure unchanged)?

Answer:

$$V_1 = 100 \text{ mL}$$

$$T_1 = 100^{\circ}\text{C} = 373 \text{ K}$$

$$T_2 = 200$$
°C = 473 K

$$V_2 = V_1 \times \frac{T_2}{T_1} = 100 \text{ mL} \times \frac{473 \text{ K}}{373 \text{ K}} = 126.8 \text{ mL}$$

- A sample of chlorine gas occupies 100 mL at -11°C. Heating (with no increase in pressure) changes its volume to 150 mL.
 - (a) What is the new temperature as expressed on the absolute temperature scale?
 - (b) Express T_2 in Celsius degrees.

Answer:

(a)
$$V_1 = 100 \text{ mL}$$

 $V_2 = 150 \text{ mL}$
 $T_1 = -11^{\circ}\text{C} = 262 \text{ K}$
 $T_2 = \frac{V_2}{V_1} \times T_1 = \frac{150 \text{ mL}}{100 \text{ mL}} \times 262 \text{ K} = 393 \text{ K}$

(b) 120°C

PARTIAL PRESSURE

32

When two or more different gases are mixed together, each gas in the mixture contributes to the total pressure of the mixture. The pressure contributed by each gas is in direct proportion to the number of molecules of the gas in the mixture. In a particular mixture of nitrogen gas and oxygen gas, there are twice as many nitrogen molecules as oxygen molecules. Each gas molecule contributes equal amounts to the total pressure regardless of what kind of molecule it is. Since there are twice as many nitrogen gas molecules as oxygen molecules in this mixture, we could expect the nitrogen molecules to contribute (half as much, twice as much, an equal amount) _______ to the total pressure as the oxygen molecules.

Answer: twice as much (The pressure contribution of a particular gas to the total pressure of a gas mixture is directly proportional to the relative number of molecules of the gas in the mixture. Twice as many molecules cause twice as much pressure contribution.)

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In a gas mixture of nitrogen and oxygen, there are twice as many nitrogen molecules as oxygen molecules. One-third of the total pressure of the mixture is contributed by the oxygen molecules; two-thirds is contributed by the nitrogen molecules. The total pressure of the gas mixture is 900 torr.

- (a) Nitrogen contributes how much to the total pressure? ______ torr
- (b) Oxygen contributes how much to the total pressure? ______ torr

Answer: (a) 600 (Twice as much, or two-thirds of the total, is contributed by nitrogen: $\frac{2}{3} \times 900 = 600$ torr.); (b) 300 ($\frac{1}{3} \times 900 = 300$ torr)

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The total pressure of a mixture of gas is the sum of all partial pressures. The partial pressures are the pressures contributed by each of the gases. A partial pressure of a particular gas is proportional to the amount (relative number of molecules) of the gas within the mixture. In the previous example, 600 torr is the partial pressure exerted by nitrogen gas, 300 torr is the partial pressure of the oxygen gas, and 900 torr is the total pressure, which is the sum of all partial pressures in the mixture.

Dalton's Law of Partial Pressures (named after its discoverer) states that the total pressure of a mixture of gases is the sum of all of the partial pressures of the individual gases. The molecules of each gas exert the same pressure within the mixture as they would if they were not in the mixture. Dalton's Law can be written mathematically as:

$$P_T = p_1 + p_2 + p_3 + \dots$$

The P_T (in capital letters) represents the total pressure. What do p_1 , p_2 , p_3 , and so on (in lowercase letters) represent?

Answer: partial pressures

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Determining partial pressures of gases is useful when analyzing gas mixtures. In order to determine the partial pressures of the individual gases in a mixture, we must first know the relative number of molecules of each gas in the mixture. Since a molecule is a very small unit, it is easier to use the mole. Partial pressures are proportional to the number of moles of the individual gases in a mixture. Partial pressure can be determined by dividing the moles of each particular gas by the total gas moles in the mixture and multiplying the result by the total pressure. A mixture of argon and xenon gases involves 2 mol of argon and 5 mol of xenon. The total number of moles of the mixture is 2 + 5 = 7 mol. The total pressure exerted by the mixture is 700 torr. The total pressure exerted by argon is $\frac{2}{7}$ mol × 700 torr = 200 torr. What is the partial pressure exerted by xenon? (Remember that according to Dalton's Law the total pressure is equal to the sum of the partial pressures.)

Answer: 700 torr - 200 torr = 500 torr

We could have solved the problem in frame 35 by using the following formula for partial pressure.

$$p_{\rm gas} = \frac{n_{\rm gas}}{n_T} \times P_T$$

The formula symbols represent the following quantities.

 p_{gas} = partial pressure for the gas in question

 $n_{\rm gas}$ = moles of the gas in question

 n_T = total moles of all gases in the mixture

 P_T = total pressure

A mixture of gases exerting a pressure of 840 torr consists of 0.2 mol of O_2 gas, 0.3 mol of H_2 gas, and 0.7 mol of CO_2 gas. The pressure contributed by the H_2 gas is ______ torr.

Answer: H_2 , the gas in question, has 0.3 mol in the mixture. The total moles of gas is 0.2 + 0.3 + 0.7 = 1.2 mol.

$$p_{(H_2 \text{ gas})} = \frac{n_{(H_2 \text{ gas})}}{n_T} \times P_T = \frac{0.3 \text{ mol}}{1.2 \text{ mol}} \times 840 \text{ torr} = 210 \text{ torr}$$

(Because $\rm H_2$ gas accounts for one-fourth of the total moles of gas in the mixture, it accounts for one-fourth of the total pressure.)

In the same gas mixture, the pressure contributed by the CO_2 gas is ______ torr.

Answer:
$$p_{CO_2} = \frac{n_{(CO_2 \text{ gas})}}{n_T} \times P_T = \frac{0.7 \text{ mol}}{1.2 \text{ mol}} \times 840 \text{ torr} = 490 \text{ torr}$$

$$p_{\rm gas} = \frac{n_{\rm gas}}{n_T} \times P_T$$

What part of the above formula represents the mole fraction?

Answer: $\frac{n_{\text{gas}}}{n_{\text{T}}}$

The gas mixture in frame 36 consisted of 0.2 mol of O_2 , 0.3 mol of H_2 , and 0.7 mol of CO_2 . The total gas moles were 0.2 + 0.3 + 0.7 = 1.2 mol. The mole fractions of each of the gas components are as follows.

$$CO_2 = \frac{n_{(CO_2 \text{ gas})}}{n_T} = \frac{0.7}{1.2} = \frac{7}{12} = 0.583$$

$$H_2 = \frac{n_{(H_2 \text{ gas})}}{n_T} = \frac{0.3}{1.2} = \frac{1}{4} = 0.250$$

$$O_2 = \frac{n_{(O_2 \text{ gas})}}{n_T} = \frac{0.2}{1.2} = \frac{1}{6} = 0.167$$

Mole fractions can be expressed in fractional or decimal form. The mole fraction of a gas is the number of moles of a particular gas divided by the total moles of gas in a mixture.

- (a) The mole fraction for CO₂ in the above gas mixture is _____.
- (b) The mole fractions of all gases in the mixture add up to _____

Answer:

- (a) $\frac{7}{12}$ or 0.583
- (b) $1(\frac{7}{12} + \frac{1}{4} + \frac{1}{6} = 1$, or 0.583 + 0.250 + 0.167 = 1.00)
- Mole fractions are very useful for determining percentage volume for each gas in a gas mixture. All mole fractions in a gas mixture add up to 1. If we multiply the individual mole fractions by 100, the results are the percentages by volume of the various gases in the mixture. The previous mixture was made up of $0.250 \times 100 = 25.0\%$ hydrogen, $0.167 \times 100 = 16.7\%$ oxygen, and $0.583 \times 100 = 25.0\%$ carbon dioxide.

Answer: 58.3

A gas mixture is made up of 25.0% H_2 gas, 16.7% O_2 gas, and 58.3% CO_2 gas. If the total volume of the mixture is 100.0 liters, the mixture could be expected to be

made up of how many liters (to the nearest tenth) of H_2 gas? _____ O_2 gas? _____

Answer: 25.0; 16.7; 58.3

A corollary to Dalton's Law of Partial Pressures is the following.

$$V_T = v_1 + v_2 + v_3 + \dots$$

The total volume (V_T) of a mixture of gases is the sum of all partial volumes (v_1, v_2, v_3 , and so on).

A mixture is made up of 25.0 liters of H_2 , 16.7 liters of O_2 , and 58.3 liters of O_2 . What is V_T for the mixture?

Answer: 100 liters (25.0 + 16.7 + 58.3 = 100 liters)

Mole fractions are useful for determining the partial pressure contributed by a particular gas in a mixture or for determining the volume attributable to a gas in a mixture. Mole fractions are particularly useful in chemical analysis of a mixture of gases.

You have already determined mole fractions by dividing the moles of a gas by the total moles in the mixture. A mole fraction can also be determined by dividing the partial pressure of a gas by the total pressure of all gases in the mixture.

$$\frac{p_{\text{gas}}}{P_T}$$
 = mole fraction of a gas

A mole fraction can also be determined by dividing the partial volume of a gas by the total volume of all gases in the mixture.

$$\frac{v_{\text{gas}}}{V_T}$$
 = mole fraction of a gas

A mixture of gases is made up of 10 mL of neon, 20 mL of xenon, and 70 mL of nitrogen. What is the mole fraction of xenon in the mixture?

Answer: $V_T = v_1 + v_2 + v_3 = 10 \text{ mL} + 20 \text{ mL} + 70 \text{ mL} = 100 \text{ mL}$

mole fraction (xenon) =
$$\frac{v_{\text{xenon}}}{V_T} = \frac{20 \text{ mL}}{100 \text{ mL}} = 0.2$$

A mixture of three gases (hydrogen, oxygen, and nitrogen) is chemically treated to absorb one gas at a time, using a process called selective absorption. Pressure is kept constant. The total original volume is 12 liters. After the oxygen is removed, the volume is 10 liters. After the hydrogen is removed, 6 liters of gas remain. The mixture contained:

(b) _____ liters of hydrogen

(c) _____ liters of nitrogen

Answer: $V_T = v_{\text{oxygen}} + v_{\text{hydrogen}} + v_{\text{nitrogen}}$

(a) 2 liters of oxygen (12 - 10 = 2)

(b) 4 liters of hydrogen (10 - 6 = 4)

(c) 6 liters of nitrogen (left after removal of oxygen and hydrogen)

Determine the mole fractions of each gas in the mixture in frame 44 and express them in decimal form. (Where necessary, round to the nearest thousandth.)

(a) mole fraction of O₂ = _____

(b) mole fraction of H₂ = _____

(c) mole fraction of N₂ = ____

Answer:

(a) $\frac{v_{O_2}}{V_T} = \frac{2 \text{ liters}}{12 \text{ liters}} = 0.167$

(b) $\frac{v_{\text{H}_2}}{V_T} = \frac{4 \text{ liters}}{12 \text{ liters}} = 0.333$

(c) $\frac{v_{\text{N}_2}}{V_T} = \frac{6 \text{ liters}}{12 \text{ liters}} = 0.5$

If the total pressure is 1 standard atmosphere (760 torr), what are the partial pressures of each gas in the mixture in frame 45?

(a) torr for O_2 gas = _____

(b) torr for H₂ gas = _____

(c) torr for N_2 gas = _____

Answer: $p_{gas} = mole fraction \times P_T$

(a) 127 (0.167 \times 760 = 127 torr); (b) 253 (0.333 \times 760 = 253 torr); (c) 380 (0.5 \times 760 = 380 torr)

Let's review. A mixture of N₂ gas, NO gas, and NO₂ gas was analyzed by the selective absorption of nitrogen oxides. The initial volume of the sample is 300 mL. After treatment with water to remove NO₂, the volume is 220 mL. An iron(II) sulfate solution is used to remove NO, after which the volume left is 27 mL. Ignoring water vapor, determine the volume of each gas in the original mixture. The pressure remained constant at 1 standard atmosphere.

| (a) | $v_{\rm NO}$ | = | |
|-----|--------------|---|--|
| (4) | VNO. | | |

(b)
$$v_{NO} =$$

(c)
$$v_{N_2} =$$

Answer: $V_T = v_{NO_2} + v_{NO} + v_{N_2}$

(a)
$$v_{NO_2} = 80 \text{ mL} (300 - 220 = 80 \text{ mL})$$

(b)
$$v_{NO} = 193 \text{ mL} (220 - 27 = 193 \text{ mL})$$

(c) $v_{N_2} = 27 \text{ mL}$ (left over after removal of NO₂ and NO)

What is the mole fraction (to the nearest thousandth) of each gas in the mixture described in frame 47?

Answer:

(a)
$$\frac{v_{NO_2}}{V_T} = \frac{80 \text{ mL}}{300 \text{ mL}} = 0.267$$

(b)
$$\frac{v_{NO}}{V_T} = \frac{193 \text{ mL}}{300 \text{ mL}} = 0.643$$

(c)
$$\frac{v_{\text{N}_2}}{V_T} = \frac{27 \text{ mL}}{300 \text{ mL}} = 0.090$$

Determine the volume percentage of the gas mixture in frames 47 and 48.

- (a) volume percentage of NO₂ = _____
- (b) volume percentage of NO =
- (c) volume percentage of N₂ = _____

Answer: Volume percentage = mole fraction x 100%

- (a) volume percentage of $NO_2 = 0.267 \times 100\% = 26.7\%$
- (b) volume percentage of NO = 0.643 × 100% = 64.3%
- (c) volume percentage of $N_2 = 0.090 \times 100\% = 9.0\%$

The total pressure of the mixture prior to analysis was 1 standard atmosphere. Determine the partial pressure (to the nearest tenth) of each gas in the mixture in frames 47 and 48.

(a)
$$P_T =$$
_____torr

(b)
$$p_{NO_3} =$$

- (c) $p_{NO} =$ _____
- (d) $p_{N_2} =$ _____

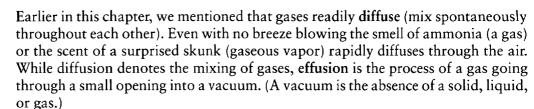
Answer:

- (a) $P_T = 760$ torr (1 standard atmosphere = 760 torr)
- (b) $\rho_{NO_2} = P_T \times 0.267 = 760 \text{ torr} \times 0.267 = 202.9 \text{ torr}$
- (c) $p_{NO} = P_T \times 0.643 = 760 \text{ torr} \times 0.643 = 488.7 \text{ torr}$
- (d) $\rho_{N_2} = P_T \times 0.090 = 760 \text{ torr} \times 0.090 = 68.4 \text{ torr}$

You have just learned to determine the volumes, partial pressures, and mole fractions of individual gases within a gas mixture. In the next section, you will learn how to determine the formula weight of an unknown gas.

GRAHAM'S LAW

51



Diffusion indicates one gas mixing into another gas. Effusion indicates a gas moving into a vacuum. A scientist named Graham noted a relationship between the formula weight of a gas and the velocity or speed with which it effuses. Such a relationship is very useful for determining the formula weights of unknown gases. It is also useful in the separation of two gases of different formula weights. Although Graham's Law predicts accurately the velocity of a gas during effusion, the same law can be used as a reasonable approximation of the velocity of a gas during diffusion.

According to Graham's Law, at a constant temperature, the rate (velocity) of effusion of a gas is inversely proportional to the square root of its formula weight. In the equation, a gas of known molecular weight is compared to an unknown gas. In all calculations with Graham's Law, it is assumed that the temperature and pressure are the same for both gases.

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

 v_1 = velocity or rate of effusion of the first gas

 M_1 = formula weight of the first gas

 v_2 = velocity or rate of effusion of the second gas

 M_2 = formula weight of the second gas

Here is a practical example using Graham's Law. Let oxygen gas (O_2) be the known gas. Oxygen has an effusion rate (v_{O_2}) of 10 milliliters (mL) per second and a formula weight of 32 amu. An unknown gas has an effusion rate (v_x) of 5 milliliters per second. Determine the formula weight (M_X) of the unknown gas. (Note that the equation can be modified as follows.)

$$\frac{v_{\text{O}_2}}{v_X} = \sqrt{\frac{M_X}{M_{\text{O}_2}}} \quad \text{or} \quad \left(\frac{v_{\text{O}_2}}{v_X}\right)^2 = \frac{M_X}{M_{\text{O}_2}}$$

Answer:

$$\left(\frac{v_{O_2}}{v_X}\right)^2 = \frac{M_X}{M_{He}}$$

$$\left(\frac{10 \text{ mL per second}}{5 \text{ mL per second}}\right)^2 = \frac{M_X}{32 \text{ amu}}$$

$$(2)^2 = \frac{M_X}{32 \text{ amu}}$$

 $M_X = 4 \times 32 \text{ amu} = 128 \text{ amu}$

In another situation involving the use of Graham's Law, helium gas (He) has a 52 fairly high velocity of effusion, 50 mL per second, and has a formula weight of 4 amu. An unknown gas has a slower velocity of effusion, 10 mL per second. Using the appropriate equation from the previous frame, determine the formula weight of the unknown gas.

Answer:

$$\left(\frac{v_{He}}{v_X}\right)^2 = \frac{M_X}{M_{He}}$$

$$M_{He} = 4 \text{ amu}$$

$$v_{He} = 50 \text{ mL per so}$$

 $v_{\rm He} = 50 \, \text{mL per second}$

 $v_X = 10 \text{ mL per second}$

$$\left(\frac{50 \text{ mL per second}}{10 \text{ mL per second}}\right)^2 = \frac{M_X}{4 \text{ amu}}$$

$$(5)^2 = \frac{M_X}{4 \text{ amu}}$$

 $M_X = 25(4 \text{ amu}) = 100 \text{ amu}$

- In a different situation, hydrogen (H₂) has an effusion rate of 20 mL per second and 53 its formula weight is 2 amu. Oxygen (O₂) has a formula weight of 32 amu.
 - (a) What is the expected effusion rate of O₂ in this situation?

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Answer:

(a) Note that either of these equations is correct. We will use the equation on the right for convenience in calculation.

$$\frac{v_{\text{H}_2}}{v_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{H}_2}}} \quad \text{or} \quad \frac{v_{\text{O}_2}}{v_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{O}_2}}}$$

 $v_{\rm H_2} = 20 \text{ mL per second}$

$$M_{\rm H_2} = 2 \text{ amu}$$

$$M_{0_2} = 32 \text{ amu}$$

$$\frac{v_{O_2}}{v_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} = \sqrt{\frac{2 \text{ amu}}{32 \text{ amu}}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$v_{O_2} = \frac{1}{4} \times v_{H_2} = \frac{1}{4} \times 20 \text{ mL per second} = 5 \text{ mL per second}$$

(b) The hydrogen gas has an effusion rate of 20 mL per second and oxygen gas has an effusion rate of only 5 mL per second. The lighter hydrogen has the greater rate of effusion (4 times greater than oxygen).

The heavier the formula weight of a gas, the slower the effusion rate, according to Graham's Law. Arrange the four gases listed below in order from the slowest to the fastest effusion rate.

CO₂ has a formula weight of 44.

N₂ has a formula weight of 28.

F₂ has a formula weight of 38.

O₂ has a formula weight of 32.

Slowest _____, ____, Fastest

Answer: CO₂, F₂, O₂, N₂

The equation for Graham's Law can be modified to deal with the density of gases. The relationship between density and effusion rates will be dealt with in a few frames. First, let's clarify the meaning of density as applied to gases. Density is a measure of weight per unit volume. For gases, we will use grams per liter as the measure of density.

You have already learned that the volume of a gas is dependent upon pressure and temperature. In order to have an accurate measure of the density of a gas, we must specify a temperature and pressure. Standard temperature and pressure (abbreviated STP) have been set arbitrarily at 0° Celsius and 1 atmosphere. At STP,

1 mol of *any* gas occupies 22.4 liters. Note that we are still treating every gas as a theoretically ideal gas. The volume of 22.4 liters per mol at STP is a reasonable approximation for real gases.

Assuming that O₂ gas behaves ideally, 1 mol of O₂ at STP occupies what volume?

Answer: 22.4 liters

Unless otherwise stated we will assume that all gases behave ideally. Since oxygen (O₂) has a volume of 22.4 liters per mol at STP, we can calculate its density. The formula weight (the weight of 1 mol) of O₂ is 32.0 grams. The density of O₂ at STP to the nearest hundredth of a gram per liter is:

$$\frac{32.0 \text{ grams}}{1 \text{ mol of } O_2} \times \frac{1 \text{ mol of } O_2}{22.4 \text{ liters}} = 1.43 \text{ grams/liter}$$

Calculate the density of N₂ at STP.

Answer: Using the periodic table, the formula weight of N_2 is 28.0 grams (2 x 14.0 grams)

$$\frac{28.0 \text{ grams}}{1 \text{ mol of } N_2} \times \frac{1 \text{ mol of } N_2}{22.4 \text{ liters}} = 1.25 \text{ grams/liter}$$

(Remember to express the density in grams/liter.)

What is the density of Cl₂ at STP?

Answer: $\frac{70.9 \text{ grams}}{1 \text{ mol of Cl}_2} \times \frac{1 \text{ mol of Cl}_2}{22.4 \text{ liters}} = 3.17 \text{ grams/liter}$

An unknown gas was found to have a formula weight of 128.0 grams. What is its density at STP?

Answer: $\frac{128.0 \text{ grams}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{22.4 \text{ liters}} = 5.71 \text{ grams/liter}$

The equation for Graham's Law can be rewritten to include densities.

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

By eliminating the part that includes formula weights, we have:

$$\frac{\nu_1}{\nu_2} = \sqrt{\frac{d_2}{d_1}}$$

In the equation, d_1 indicates the density of gas 1 and d_2 indicates the density of gas 2. Here is an example using this formula. A known gas (oxygen) has a density

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 (d_{O_2}) of 1.43 grams per liter and an effusion rate of 10.0 mL per second. An unknown gas (X) has an effusion rate of 5.0 mL per second. The density of the unknown gas can be determined as follows.

$$\left(\frac{v_{\rm O_2}}{v_X}\right)^2 = \frac{d_X}{d_{\rm O_2}}$$

$$\left(\frac{10.0 \text{ mL per second}}{5.0 \text{ mL per second}}\right)^2 = \frac{d_X}{1.43 \text{ grams per liter}}$$

$$d_X = 1.43 \text{ grams per liter} \times \left(\frac{10.0}{5.0}\right)^2$$

$$d_X = 1.43 \text{ grams per liter} \times 4$$

$$d_X = 5.72 \text{ grams per liter}$$

Another unknown gas has an effusion rate of 8.0 mL per second. Using oxygen gas as a reference (effusion rate and density are the same as in the previous example), determine the density of the unknown gas.

Answer:

$$\left(\frac{v_{O_2}}{v_X}\right)^2 = \frac{d_X}{d_{O_2}}$$

$$\left(\frac{10.0 \text{ mL per second}}{8.0 \text{ mL per second}}\right)^2 = \frac{d_X}{1.43 \text{ grams per liter}}$$

$$d_X = 1.43 \text{ grams per liter} \times \left(\frac{10.0}{8.0}\right)^2$$

$$d_X = 1.43 \text{ grams per liter} \times (1.25)^2$$

$$d_X = 2.23 \text{ grams per liter}$$

Carbon dioxide (CO₂) is used as a reference gas with a density of 1.96 grams per liter and an effusion rate of 12.0 mL per second. An unknown gas has an effusion rate of 10.0 mL per second. Determine the density of the unknown gas.

Answer:

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$$\left(\frac{v_{\text{CO}_2}}{v_X}\right)^2 = \frac{d_X}{d_{\text{CO}_2}}$$

$$\left(\frac{12 \text{ mL per second}}{10 \text{ mL per second}}\right)^2 = \frac{d_X}{1.96 \text{ grams per liter}}$$

$$d_X = 1.96 \text{ grams per liter} \times \left(\frac{12}{10}\right)^2$$

$$d_X = 1.96 \text{ grams per liter} \times (1.2)^2$$

$$d_X = 2.82 \text{ grams per liter}$$

Once you have found the density of an unknown gas, it is a simple matter to determine its formula weight. Just reverse the procedure used in finding a density from formula weight. For example, the unknown gas in frame 59 had a density of 2.23 grams per liter. Assume STP.

$$\frac{2.23 \text{ grams}}{1 \text{ liter}} \times \frac{22.4 \text{ liters}}{1 \text{ mol}} = 50.0 \text{ grams per mol}$$

In frame 60, you determined that an unknown gas had a density of 2.82 grams per liter. Determine its formula weight to the nearest tenth of a gram per mole. Assume STP.

Answer:
$$\frac{2.82 \text{ grams}}{1 \text{ liter}} \times \frac{22.4 \text{ liters}}{1 \text{ mol}} = 63.2 \text{ grams per mol}$$

THE COMBINED GAS LAW

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Earlier in this chapter, you learned about Boyle's Law and Charles's Law. We will now combine these two laws. To review, Boyle's Law states that PV = constant (at constant temperature). A practical expression of Boyle's Law is $P_1V_1 = P_2V_2$ at constant temperature. Charles's Law states

$$\frac{V}{T}$$
 = constant (at constant pressure).

A practical expression of Charles's Law is

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
 (at constant pressure).

Boyle's and Charles's Laws can be combined into

$$\frac{PV}{T}$$
 = constant.

A practical expression of the combined gas law is

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

In using the combined gas law or any gas law involving temperature, what temperature scale must be used?

Answer: absolute or Kelvin or K (any of these answers is acceptable)

We can modify the combined gas law as follows.

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

Multiplying both sides by T_2 results in $\frac{P_1V_1T_2}{T_1} = P_2V_2$.

Dividing both sides by P_2 results in $\frac{P_1V_1T_2}{T_1P_2} = V_2$.

A sample of helium occupies 1000 liters (V_1) at 15°C (T_1) and 763 torr (P_1) . The temperature is changed to -6°C and the pressure to 420 torr. Use the combined gas law from frame 62 to find the new volume of the gas (V_2) to the nearest liter.

Answer: Change all temperatures to Kelvin scale (add 273° to Celsius scale).

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{1000 \text{ liters} \times 763 \text{ torr} \times 267 \text{ K}}{420 \text{ torr} \times 288 \text{ K}} = 1684 \text{ liters}$$

A sample of oxygen gas occupies 400 mL at 20°C and 740 torr. If the conditions are changed so that the gas is warmed to 30°C and occupies 425 mL, what is its new pressure to the nearest torr?

Answer:
$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2} = \frac{740 \text{ torr} \times 400 \text{ mL} \times 303 \text{ K}}{425 \text{ mL} \times 293 \text{ K}} = 720 \text{ torr}$$

THE IDEAL GAS LAW EQUATION

In using the combined gas law, we have used an equation with six items, five of which are given and one of which is unknown. A simpler equation can be made from the combined gas law by including a constant to represent gases at STP (standard temperature and pressure).

$$PV = nRT$$

In this equation, P, V, and T describe the existing gas conditions. The symbol n represents the number of moles of the gas. The symbol R represents the universal gas constant. This equation is commonly known as the ideal gas law equation. Rewrite the ideal gas law equation so that only R remains on one side of the equation.

$$R = \underline{\qquad}$$
Answer: $\frac{PV}{nT}$ (divide both sides by nT)

The universal gas constant (R) is a numerical value made up of the combination of standard pressure (1 atmosphere or 760 torr), standard temperature (273 K), and the fact that 1 mol of a gas occupies a volume of 22.4 liters at STP.

The following value of R is appropriate for calculations dealing with pressure expressed in *atmospheres*, volume expressed in *liters*, temperature expressed in *Kelvin* degrees, and the quantity of gas expressed in *moles*.

$$R = \frac{PV}{nT} = \frac{1 \text{ atmosphere} \times 22.4 \text{ liters}}{1 \text{ mol} \times 273 \text{ K}} = 0.082 \frac{\text{atmosphere} \times \text{ liters}}{\text{mol} \times \text{ K}}$$

We can also calculate a value of R for use in problems dealing with pressure expressed in *torr*, volume in *liters*, temperature in *Kelvin*, and quantity in *moles*.

$$R = \frac{PV}{nT} = \frac{760 \text{ torr} \times 22.4 \text{ liters}}{1 \text{ mol} \times 273 \text{ K}} = 62.4 \frac{\text{torr} \times \text{liters}}{\text{mol} \times \text{K}}$$

If volume is expressed in *milliliters* (mL), pressure in *torr*, temperature in *Kelvin*, and quantity in *moles*, we have the following value of *R*.

$$R = \frac{PV}{nT} = \frac{760 \text{ torr} \times 22,400 \text{ mL}}{1 \text{ mol} \times 273 \text{ K}} = 62,400 \frac{\text{torr} \times \text{mL}}{\text{mol} \times \text{K}}$$

The appropriate value of R must be selected based upon the units of P or V.

If V is expressed in liters and P in torr, then R is 62.4.

If V is expressed in liters and P in atmospheres, then R is 0.082.

If V is expressed in milliliters and P in torr, then R is 62,400.

It is assumed the temperature is expressed in Kelvin and n is expressed in moles. Here is an example using the ideal gas law equation. Half a mole of gas (n) has a pressure of 2 atmospheres (P) and a temperature (T) of 341 K. We want to calculate its volume in liters using the ideal gas equation. Since V is expressed in liters and P in atmospheres, R must be

$$0.082 \frac{\text{atmosphere} \times \text{liters}}{\text{mol} \times \text{K}}$$

Dividing both sides of the equation PV = nRT by P results in:

$$V = \frac{nRT}{P} = \frac{0.5 \text{ mol} \times 0.082 \frac{\text{atmosphere} \times \text{liters}}{\text{mol} \times \text{K}} \times 341 \text{ K}}{2 \text{ atmospheres}}$$
$$= \frac{0.5 \times 0.082 \text{ liters} \times 341}{2} = 7.0 \text{ liters}$$

In another example, 2 mol of a gas occupy a volume of 4 liters when the temperature is 300 K. What is the pressure (expressed in torr) of the gas?

Answer: Since V is expressed in liters and P in torr, R must be 62.4 $\frac{\text{torr} \times \text{liters}}{\text{mol} \times \text{K}}$

$$P = \frac{nRT}{V} = \frac{2 \text{ mol} \times 62.4 \frac{\text{torr} \times \text{liters}}{\text{mol} \times \text{K}} \times 300 \text{ K}}{4 \text{ liters}} = 9360 \text{ torr}$$

Three moles of a gas are compressed to 10,000 torr. The temperature is 27°C. What is the volume of the gas in milliliters?

Answer:

Since V is expressed in milliliters and P in torr, R must be 62,400 $\frac{\text{torr} \times \text{mL}}{\text{mol} \times \text{K}}$.

Celsius temperature must be changed to Kelvin (27 + 273 = 300 K).

$$V = \frac{nRT}{P} = \frac{3 \text{ mol} \times 62,400 \frac{\text{torr} \times \text{mL}}{\text{mol} \times \text{K}} \times 300 \text{ K}}{10,000 \text{ torr}} = 5616 \text{ mL}$$

If 1.5 moles of gas occupy 41 liters at a pressure of 3 atmospheres, what is the temperature of the gas?

Answer: Since V is expressed in liters and P in atmospheres, R must be

$$0.082 \frac{\text{atmosphere} \times \text{liters}}{\text{mol} \times \text{K}}$$

Divide both sides of the equation by nR.

$$T = \frac{PV}{nR} = \frac{3 \text{ atmospheres} \times 41 \text{ liters}}{1.5 \text{ mol} \times 0.082 \frac{\text{atmosphere} \times \text{ liters}}{\text{mol} \times \text{ K}}} = 1000 \text{ K}$$

We can also use the ideal gas equation to determine formula weights of gases. The formula weight of neon gas (Ne) is 20.18 grams per mol. A sample of Ne gas weighing 201.8 grams represents the weight of how many moles of Ne gas?

Answer: 201.8 grams $\times \frac{1 \text{ mol of Ne}}{20.18 \text{ grams}} = 10 \text{ mol of Ne}$

In the equation PV = nRT, the symbol n represents the number of moles of a gas. The number of moles of a gas is equal to the following, where M is the formula weight of the gas in grams per mole.

weight of gas
$$\times \frac{1}{M} = n$$

The equation PV = nRT can be modified to include the above equation for number of moles. Do so below.

Answer: weight of gas $\times \frac{RT}{M}$

The equation you just wrote can be solved for formula weight.

$$M = \frac{\text{weight of gas} \times RT}{PV}$$

Determine the formula weight of a gas if 20 grams of the gas occupies a volume of 6 liters at a pressure of 2 atmospheres and a temperature of 300 K. Express in grams/mole.

Answer: Since V is in liters and P is in atmospheres, R must be

$$0.082 \, \frac{\text{atmospheres} \times \text{liters}}{\text{mol} \times \text{K}}.$$

$$M = \frac{\text{weight of gas} \times RT}{PV} = \frac{20 \text{ grams} \times 0.082 \frac{\text{atmospheres} \times \text{liters}}{\text{mol} \times \text{K}} \times 300 \text{ K}}{2 \text{ atmospheres} \times 6 \text{ liters}} = 41 \text{ grams per mol}$$

A sample of gas weighing 1.00 gram has a volume of 500 mL at a temperature of 77°C and a pressure of 546 torr. What is the formula weight of the gas?

Answer: Since V is in milliliters and P is in torr, R must be

$$62,400 \frac{\text{torr} \times \text{mL}}{\text{mol} \times \text{K}}$$

Change 77°C to Kelvin (77 + 273 = 350 K).

$$M = \frac{\text{weight of gas} \times RT}{PV} = \frac{1.00 \text{ gram} \times 62,400 \frac{\text{torr} \times \text{mL}}{\text{mol} \times \text{K}} \times 350 \text{ K}}{546 \text{ torr} \times 500 \text{ mL}} = 80 \text{ grams per mol}$$

All of the gas law equations thus far have dealt with theoretically ideal gases. The real gases in the world behave ideally at high temperatures and at low pressures. However, at very high pressures and low temperatures, real gases deviate from the ideal.

In real gases at high pressures, the volume of the gas molecules actually make up a significant part of the gas volume. This causes the real gas to be less compressible than predicted by the ideal gas law.

At very low temperatures, the gas molecules attract one another and the real gas becomes more compressible than predicted by the ideal gas law. These attractive forces between the molecules are known as van der Waals forces.

- (a) In the kinetic molecular theory, what assumption is made about the volume of the molecules of an ideal gas?
- (b) The attraction of gas molecules for each other becomes significant at which range of temperature, very high or very low?

Answer: (a) that the molecules of an ideal gas occupy no volume; (b) very low

At sufficiently low temperatures, the van der Waals forces become strong enough to overcome the kinetic energy of the gas molecules. The result is that gas molecules stick together and form small droplets. These droplets combine to form a liquid. You will learn more about van der Waals forces in a later chapter on liquids (Chapter 10).

Additional constants have been determined to add to the ideal gas law equation, that make the equation more correct for the effects of gas molecule volume at high pressures and van der Waals forces at low temperatures. This equation, known as the van der Waals's equation of state for a real gas, is beyond the scope of this book.

Now you know that gases may be compressed (as in a bicycle pump), exert pressure on the walls of their containers (as in a tire or balloon), have different densities (air versus helium), and effuse or diffuse so you can smell them.

You also know that all gases behave in a similar manner and are affected by changes in temperature and pressure. The laws presented in this chapter apply only to the gaseous state. The remaining states of matter, liquids and solids, behave quite differently than gases. The next two chapters discuss the solid and liquid states. In contrast to gases, solids and liquids do not all behave in a similar manner.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test. Round answers to the nearest tenth.

- A sample of Cl₂ gas occupies a volume of 30.0 mL at 20°C. What volume would it occupy at 50°C? Assume the pressure remains constant and use Charles's Law.
- A sample of CO₂ gas occupies 350 mL at 27°C and 790 torr. What pressure would it exert if it occupied 175 mL and the temperature was changed to 57°C? Use the combined gas law equation.
- 3. What volume would 22.0 g of N₂O occupy at STP? _____
- 4. What is the density of fluorine (F₂) at STP?

| 5. A | Arrange the | following | gases i | in the | order o | of inci | reasing | effusion | rates. |
|------|-------------|-----------|---------|--------|---------|---------|---------|----------|--------|
|------|-------------|-----------|---------|--------|---------|---------|---------|----------|--------|

CO, O₂, SO₂, NH₃, F₂ _____, ____, ____, ____,

- 6. A mixture of CO_2 and O_2 is used to "decompress" deep sea divers to prevent the "bends." If the mixture is 70% O_2 and 30% CO_2 by volume, what is:
 - (a) the volume of O₂ present in 50. 0 liters of the mixture?
 - (b) the mole fraction of O₂ in the mixture?
 - (c) the pressure exerted by the O_2 if the pressure of the mixture is 1000 torr?
- 7. Which of the following can account for the fact that you can smell a skunk even though you may not see it?
 - _____ (a) Gases are in rapid random motion.
 - _____ (b) Gases may be compressed.
 - _____ (c) Gas molecules are far apart.
 - _____ (d) Gas volumes are directly proportional to the absolute temperature.
 - _____ (e) Gas volumes are inversely proportional to the pressure.
- 8. Calculate the formula weight of 1.68 g of a gas that occupies 1.35 liters at STP using the ideal gas law equation.

$$R = 0.082 \frac{\text{atmospheres} \times \text{liters}}{\text{mol} \times \text{K}}$$

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

1.
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{30.0 \text{ mL} \times 323 \text{ K}}{293 \text{ K}} = 33.1 \text{ mL}$$
(frames 25–31)
2. $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = \frac{790 \text{ torr} \times 350 \text{ mL} \times 330 \text{ K}}{175 \text{ mL} \times 300 \text{ K}} = 1738 \text{ torr}$$
(frames 62–64)

3.
$$V_{N_2O} = 22.0 \text{ g} \times \frac{1 \text{ mol } N_2O}{44.0 \text{ g } N_2O} \times \frac{22.4 \text{ liters}}{1 \text{ mol}} = 11.2 \text{ liters } N_2O$$
(frame 55)

5. formula weight CO = 28.01 formula weight O₂ = 32.00 formula weight SO₂ = 64.06 formula weight NH₃ = 17.04 formula weight F₂ = 38.00

Therefore, increasing effusion rate from left to right: SO_2 , F_2 , O_2 , CO, NH_3 (frames 51-54)

- 6. (a) $v_{O_2} = V_T \times \%O_2 = 50.0$ liters $\times 0.70 = 35.0$ liters (frames 39, 40)
 - (b) mole fraction $O_2 = \frac{v_{gas}}{V_T} = \frac{70\%}{100\%} = 0.70$
 - (c) p_{O_2} = mole fraction $O_2 \times P_T = (0.70)(1000 \text{ torr}) = 700 \text{ torr}$ (frames 36, 37)
- 7. (a) and (c) (frames 1, 6, 51)

8.
$$M = \frac{\text{weight of gas} \times RT}{PV}$$

$$M = \frac{1.68 \text{ g} \times 0.082 \frac{\text{atmospheres} \times \text{liters}}{\text{mol} \times \text{K}} \times 273 \text{ K}}{1 \text{ atmosphere} \times 1.35 \text{ liter}}$$

$$M = 27.9 \text{ g/mol}$$
(frames 65–72)

<u>9</u> Solids

Look around you. What do you see? Lots of visible things, such as buildings, tables, chairs, wires, windows, and trees. This chapter is an introduction to the structure and properties of the solid state.

The chapter will let you compare solids and gases and will explore how bonding between particles affects the properties of solids.

We will study the shapes of solids, that is, the different ways atoms, ions, and molecules arrange themselves in three dimensions. Apart from shape, four types of solids have distinctive properties dependent upon the type of bonding between particles. You already know that different substances have different thermal properties. We will show how a specific thermal property may be used to calculate approximate atomic weights of pure metals. Finally, we will discuss the relationship between the size of an ion and its parent atom and the sizes of atoms and ions that contain the same number of electrons.

OBJECTIVES

After completing this chapter, you will be able to

- recognize and apply or illustrate: specific heat, crystal lattice, allotrope, polymorphic, heat of fusion, melting point, sublimation, diffraction, isoelectronic, amorphous;
- explain the differences between "glasses" and crystals;
- explain the differences between gases and solids;
- explain why an ion has a different radius than its parent atom;
- determine if a group of ions and atoms is isoelectronic;
- calculate the approximate atomic weight of a pure metal when given the specific heat of the metal;
- calculate the amount of heat required to melt a solid knowing the heat of fusion of the solid;
- locate the melting point and other properties of a solid on a graph that shows what happens when a solid is heated;
- describe the differences in properties, bonding, and structure among ionic, covalent, molecular, and metallic solids.

In Chapter 8, the kinetic molecular theory of gases described gases as molecules that move rapidly and readily to conform to the shape of the container. A solid, on the other hand, will not conform readily to the shape of its container unless it is forced to do so, for example, if it is crushed to a powder. The atoms or molecules of a solid are fixed in place and do not move; they only vibrate within the confines of their positions in well-defined structures.

Ice cubes and coal lumps need to be crushed to conform to the walls of a container. Are ice cubes and coal lumps gases or solids?

Answer: solids

The forces attracting one gas molecule to another are negligible (except at low temperatures and high pressures). These are the van der Waals forces discussed in Chapter 8. In solids, the forces of attraction between atoms and molecules are relatively strong, and a great deal of energy is required to overcome these forces. In gases, most of the volume (theoretically all of the volume) is the space between the molecules. Gases are easily compressed. Changes in temperature and pressure have comparatively little effect on the volume of a solid. Even extreme pressure causes only a slight reduction in the volume of solids.

We know that there is a lot of space between molecules or atoms in a gas. Based on the above information would you expect a lot or a little space between the molecules or atoms of a solid?

Answer: little

- Melting is defined as changing from the solid state to the liquid state. The temperature at which both the liquid and solid state are present at the same time is known as the melting point of the solid. If a liquid is changing to a solid, this same melting point temperature is also called the freezing point. Each solid has a specific, unique temperature as its melting point.
 - (a) Melting is the change of state from which to which, solid to liquid or liquid to solid?
 - (b) The temperature at which a liquid changes to a solid is which, its melting point or freezing point? ______

Answer: (a) solid to liquid; (b) freezing point

Molecules on the surface of some solids escape from the solid and enter a gaseous state directly without entering the liquid state first. These solids exhibit a measurable vapor pressure. One of the best known examples of this is dry ice, which is solid carbon dioxide. The phenomenon of a solid changing directly to the gaseous state is known as sublimation. The liquid state is bypassed.

Solid mothballs become smaller over a period of time without the appearance of any liquid. The distinctive odor of mothballs in the air indicates that some of the

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solid has vaporized. Wet clothes hung out on a clothesline freeze if the outside temperature remains below the freezing point! Although the temperature remains below the freezing point, the clothes do dry. The ice crystals go directly to the gaseous state over a period of time. You may also have noticed that ice cubes shrink when left in the freezer for a long time. Have the mothballs, ice cubes, and ice crystals in the frozen clothes melted or sublimed?

Answer: sublimed

CRYSTALS AND THEIR SHAPES

Many naturally occurring solids have very distinct geometrical shapes. Table salt, NaCl, looks like cubes. Calcite, CaCO₃, looks like a rectangular solid. Alum, KAl(SO₄)₂ • 12H₂O, looks like two pyramids base to base. A solid that exists in a definite three-dimensional geometrical shape is known as a crystalline solid or crystal. Crystalline solids have a characteristic shape regardless of the size of the piece. There are seven basic crystal shapes that have been identified in naturally occurring solids. They are shown on page 171, along with some variations of the basic shapes, giving a total of 14 arrangements, or crystal lattices, in which crystalline solids occur.

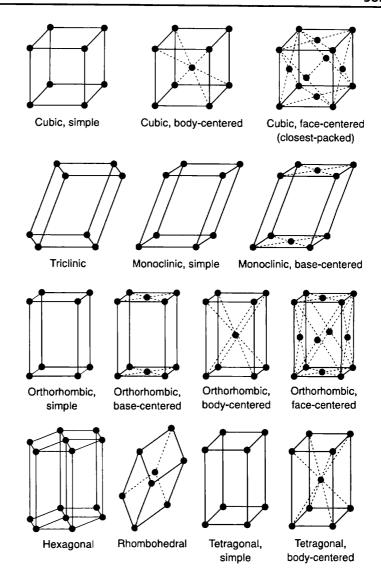
If a large crystal is cleaved (split), would the smaller pieces still be crystals?

Answer: yes (Crystalline solids have a characteristic shape regardless of the size of the pieces. This is how a jeweler cuts a large diamond into several smaller ones.)

The seven crystal systems and their variations are determined by the arrangement of atoms, ions, and molecules within the crystals. The arrangement of atoms within the crystal is known as the crystal lattice. We can determine this arrangement by a process called X-ray diffraction. Planes of atoms and ions that make up the crystal diffract X-rays similar to the way a mirror reflects light. X-ray diffraction analysis of crystals is possible because the wavelengths of X-rays are very close in size to the diameters of the atoms. Visible light has much longer wavelengths than X-rays, therefore the individual atoms within the crystal lattice will not diffract normal light. When X-rays are used, the resulting diffraction may be photographed or sent directly to a computer for analysis and mathematical determination of the structure.

We now discuss some more properties of crystalline and noncrystalline solids.

Some substances can assume more than one crystalline shape. Sulfur, for example, can be found as rhombic crystals or monoclinic crystals. A substance is polymorphic if it exists in more than one crystalline form. Calcium carbonate, CaCO₃,



occurs in nature with either the hexagonal structure or the rhombic structure. Is CaCO₃ an example of a polymorphic solid? _____ Explain why or why not.

Answer: yes; It exists in more than one crystalline form.

When a chemical element is found to be polymorphic, the different crystalline forms of the element are known as allotropes (or allotropic forms) of the element. Carbon is a polymorphic element. Graphite and diamond are both allotropic forms of carbon.

| | (a) Sulfur is an element that occurs in two forms. Thus, rhombic sulfur and monoclinic sulfur are of sulfur. |
|----|--|
| | (b) White phosphorus, red phosphorus, and yellow phosphorus are crystalline forms of phosphorus; therefore, phosphorus is called asubstance. |
| | Answer: (a) allotropes; (b) polymorphic |
| 8 | Not all solids are crystalline. A solid that does not have a definite crystalline shape is said to be amorphous. Glass is a common example of an amorphous solid. It is a solid, but it is not crystalline. If a piece of glass were broken into smaller pieces, could you predict the shape of those pieces? Why or why not? |
| | Answer: No, because glass is not crystalline, it has no definite geometrical form, such as one of the basic crystal shapes. |
| 9 | The entire category of solid substances that appear to be crystalline but are not is called glasses. Glasses have several characteristics that differ from crystals. Crystals have sharp melting points. Melting destroys the attractions that give solids their rigid structure. Below the sharp melting point, crystals are solids. Above the sharp melting point, crystals become liquids. Glasses have relatively large melting ranges instead of a sharp melting point. Glasses generally soften over several degrees of increasing temperature before finally becoming liquid. Ice melts at 0°C. It does not become soft before melting. Is ice more likely to be a glass or a crystalline solid? |
| | Answer: crystalline solid |
| 10 | Crystals cleave (split) along planar (flat) surfaces when struck. Even when broken, crystals retain their basic structural shape. Glasses, on the other hand, fracture to form uneven surfaces when struck. Breakage is not along any definite pattern. A jeweler can split a gemstone with a jeweler's chisel. The surfaces along the split are flat and the cut is clean. Is the gemstone a crystal or a glass? |
| | Answer: crystal |
| 11 | When heated, a solid substance becomes soft and pliable several degrees before actually melting. Is the substance likely to be crystalline? |
| | Answer: no (Crystals have sharp melting points and do not soften before melting.) |
| 12 | In crystals, the strengths of the chemical bonds between the atoms, ions, or molecules are all the same. This accounts for their very sharp melting point. In glasses, the strengths of the bonds vary throughout the solid. This accounts for the wide |

melting point range of glasses. In which class of solids (glasses or crystals) would it be possible for some bonds to be broken at one temperature while other bonds would not be broken until a slightly higher temperature was reached?

Answer: glasses (With bonds of varying energies, some bonds would be broken at lower temperatures than other bonds.)

HEAT OF FUSION

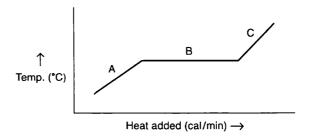
When crystalline solids melt, the crystal lattice is broken down. The solids lose their shape and become fluid. The energy required to change a solid to a liquid while remaining at the melting point temperature is called the heat of fusion. The energy required to change a block of ice at 0°C to water at 0°C is known as the ______ for H₂O.

Answer: heat of fusion

Heat of fusion can be expressed as either calories per gram or calories per mole. The calorie is a unit of energy in the form of heat. The heat of fusion of H₂O is 80 calories per gram. The energy required to melt a 1 gram ice cube at 0°C to water at 0°C is

Answer: 80 calories (Since the heat of fusion for H₂O is 80 calories per gram, it takes 80 calories to melt 1 gram of ice.)

The heat of fusion can be graphically shown by plotting temperature against the energy requirement.

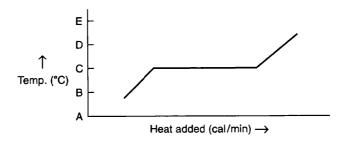


Remember that the heat of fusion is the energy required to liquefy a solid at the melting point. When a solid is heated, its temperature rises *until* the melting point. At the melting point the temperature remains constant until all the solid has melted. After melting is completed, the temperature of the substance (now totally liquid)

rises as more heat is applied. Which part of the graph shows the heat of fusion? (A, B, C) _____

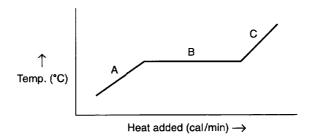
Answer: B (because the temperature remains constant at the heat of fusion)

If the graph below represented H₂O, at what point on the temperature scale should the melting point (0°C) be placed? (A, B, C, D, E) _____



Answer: C (the temperature at which the heat of fusion is observed)

The graph below represents heat applied to a substance such as H_2O or some other crystalline substance.

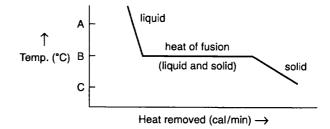


For each of the indicated points, tell whether the substance is solid, liquid, or both solid *and* liquid.

- (a) at point C _____
- (b) at point B _____
- (c) at point A _____

Answer: (a) liquid; (b) both solid and liquid (energy as the heat of fusion is being used to melt the solid); (c) solid

The graph at the top of page 175 represents the reverse process. Heat is removed from a system and a liquid freezes into a solid. In this case, the heat of fusion energy must be removed for the liquid at the freezing point to become solid at the freezing point.



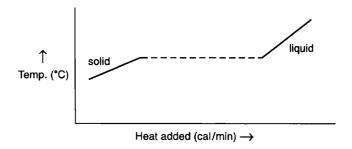
The freezing point (same temperature as the melting point) is indicated by which letter on the temperature scale? (A, B, C) _____

Answer: B

Remember that the heat of fusion for H₂O is 80 calories per gram, with the temperature remaining at the melting point. Based on this information, how many calories of heat do you think must be removed to freeze 1 gram of water if the temperature remains at the freezing point?

Answer: 80 calories (The heat of fusion applies to both melting and freezing.)

For the moment, ignore the heat of fusion in the graph below. Before the heat of fusion, what happens to the temperature of the solid when heat is added—is it increased, decreased, or unchanged?



Answer: increased

SPECIFIC HEAT

Each solid substance as well as each liquid requires a different quantity of heat added to increase the temperature by a given amount. To raise the temperature of 1 gram of solid iron 1° on the Celsius scale requires 0.108 calories. To raise the temperature of 1 gram of solid lead 1° on the Celsius scale requires 0.0306 calories.

Which substance requires more heat, as measured in calories, to raise its temperature 1°: solid lead or solid iron?

Answer: solid iron (Iron requires more than three times as much heat as lead to raise the temperature 1° Celsius for each gram.)

The calories required to raise the temperature of 1 gram of a substance by 1° Celsius is called the specific heat of the substance. The specific heat of copper is 0.093 calories per gram. The specific heat of aluminum is 0.219 calories per gram. Which has the lower specific heat, aluminum or copper?

Answer: copper

Specific heat is useful because it is related to atomic weight.

atomic weight = 6.2 ÷ specific heat

The atomic weight found by this formula is a reasonable approximation of the actual atomic weight of solid elements. The formula shows a relationship between and _______.

Answer: atomic weight; specific heat

The formula is useful for determining approximate atomic weights and identifying unknown substances.

atomic weight (g/mol) =
$$\frac{6.2 \text{ cal/mol}}{\text{specific heat (cal/g)}}$$

For example, the specific heat for iron is 0.108 cal/g.

atomic weight of iron (g/mol) =
$$\frac{6.2 \text{ cal}}{\text{mol}} \div \frac{0.108 \text{ cal}}{\text{g}}$$

= $\frac{6.2 \text{ cal}}{\text{mol}} \times \frac{\text{g}}{0.108 \text{ cal}} = \frac{6.2 \text{ g}}{0.108 \text{ mol}} = 57.4 \text{ g/mol}$

Since the actual atomic weight of iron is 55.8 grams/mol, the result is an approximate atomic weight.

What is the approximate atomic weight (to the nearest tenth) of nickel if it has a specific heat of 0.105 cal/g?

Answer: atomic weight of nickel = $\frac{6.2 \text{ cal/mol}}{0.105 \text{ cal/g}} = 59.0 \text{ g/mol}$

(The actual atomic weight of nickel is 58.71 g/mol.)

A solid element is found to have a specific heat of 0.0565 cal/g. Determine the approximate atomic weight of the element (to the nearest tenth).

Answer: atomic weight = $\frac{6.2 \text{ cal/mol}}{0.0565 \text{ cal/q}}$ = 109.7 g/mol

atomic weight = 109.7 g/mol

Look at the periodic table and determine which solid element is closest in atomic weight to 109.7 g/mol. _____

Answer: silver (The closest element to an atomic weight of 109.7 is silver, Ag, with an actual atomic weight of 107.868 g/mol. Another possibility is cadmium, Cd, with an atomic weight of 112.41 g/mol. Further chemical analysis is necessary to positively identify the element. This is a good approximation, however, and limits the choices.)

Now that you have learned some of the properties of solid substances, we will examine the properties of four general types of solids and cite commonly occurring examples of each.

TYPES OF SOLIDS

27

The melting points of different solids vary with the differences in interparticle attraction found among the various solids. Crystalline solids are classified in four categories based upon differences in interparticle attraction and in the nature of the particles (atoms, ions, or molecules) that make up the crystals. The four categories are: ionic solids, covalent solids, molecular solids, and metallic solids. (You should remember the terms *ionic* and *covalent* as two types of chemical bonds discussed in Chapter 3.)

Ionic solids are made up of ions held together by ionic bonds. Negative and positive ions are bonded together in a regular arrangement of negative to positive to negative to positive and so on, throughout the neatly stacked arrangement within the crystal lattice. The strong electrostatic attraction between the ions is responsible for the hardness and generally high melting points of ionic solids. Examples of ionic solids are NaCl and KCl.

- (a) In an ionic solid is the attraction between ions weak or strong?
- (b) Would you expect an ionic solid to have a low or high melting point?
- (c) Would you expect an ionic solid to be hard or soft?

Answer: (a) strong; (b) high; (c) hard

Ionic solids do not conduct electricity when solid but when heated to the liquid state, the molten ionic compounds conduct electricity well. In the liquid state, the crystal lattice is broken and the ions are free to move about and carry the electric current. Most ionic solids dissolve easily in water. The aqueous solutions of ionic solids also conduct electricity well.

| | A very hard solid with a high melting point dissolves in water, but the aqueous solution does not conduct electricity. Would you expect the solid to be ionic? |
|----|--|
| | Answer: no (lonic solids dissolve readily in water and conduct electricity.) |
| 29 | Covalent solids (also known as network solids) consist of atoms held together completely by covalent bonds extending from atom to atom throughout the crystal lattice. The entire crystal lattice is interlocked in a series of such covalent bonds. Covalent bonds are very strong, and such solids are very hard with very high melting points. A relatively large amount of energy is required to break the bonds. |
| | A solid substance with a high melting point could be (an ionic solid, a covalent solid, either an ionic solid or a covalent solid) |
| | Answer: either an ionic solid or a covalent solid (Covalent solids often have higher melting points than ionic solids, but both have relatively high melting points.) |
| 30 | Covalent solids are nonconductors of electricity in either the solid or the molten (liquid) state. Most covalent solids are not soluble in water. Typical examples of covalent solids are diamond (made of carbon), silicon carbide (SiC, better known as Carborundum), and aluminum nitride (AlN). All of these examples are useful as industrial abrasives for grinding and polishing because of their hardness. A solid is heated until it melts at a high melting point. The molten substance conducts electricity. This solid is likely to be (an ionic solid, a covalent solid, either |
| | an ionic or covalent solid) Answer: an ionic solid (Ionic solids conduct electricity when molten, while covalent solids do |
| | not.) |
| 31 | Molecular solids are made up of either polar or nonpolar molecules. (See Chapter 3 if you need to review polar and nonpolar compounds.) Nonpolar molecules are held together by weak van der Waals forces. Note that the atoms within a molecule may be covalently bonded, but in a molecular solid the molecules themselves are not interconnected with covalent bonds. Both ionic and covalent solids are relatively hard and have high melting points because of the strong bonds within the solids. Try some predictions about the hardness and the melting points of nonpolar molecular solids. Would you expect nonpolar molecular solids with their weak interconnecting forces to: |
| | (a) be relatively hard or relatively soft? |
| | (b) have melting points that are high or low? |
| | Answer. (a) relatively sort, (b) low meiting points |

Two examples of nonpolar molecular solids are dry ice (CO₂) and naphthalene 32 (mothballs). Polar molecular solids such as ice (H_2O) , solid ammonia (NH_3) , and solid sulfuric acid (H₂SO₄) have melting points and degrees of hardness between those of nonpolar molecular solids and ionic solids. There is some electrostatic attraction between polar molecules. As a group, polar and nonpolar molecular solids are generally soft, have comparatively low melting points, and do not conduct electricity. A solid is very hard but does not conduct electricity in the solid or liquid state. The solid is probably (molecular, ionic, covalent) ______. Answer: covalent A fourth category of crystalline solids is the metallic solids. Examples are elemental 33 iron, copper, and silver. Solid metals have been described as made up of positive ions held together by highly mobile electrons or as positive ions in a "sea" of electrons. These electrons move freely, with the result that the metals are excellent conductors of electricity. The melting points and hardnesses of various metals vary over wide ranges. Which of the four types of crystalline solids conducts electricity as a solid — ionic, covalent, molecular, or metallic? Answer: metallic (Ionic solids must be melted or dissolved before they will conduct electricity.) In metallic solids, each metal atom is surrounded by eight other atoms as its nearest 34 neighbors in a cubic closest-packed crystalline structure, or 12 other atoms in a hexagonal closest-packed structure. The outer shell electrons are loosely held in each atom. The mobility of these electrons accounts for the fact that metals are excellent conductors of both electricity and heat. Metallic solids generally assume two closest-packed crystalline structures. What are these geometric structures? _____ Answer: cubic and hexagonal As you should recall, metallic solids also have certain characteristics such as mal-35 leability (can be rolled or beaten into fine sheets), ductility (can be drawn into fine wires), and luster (shine) in both the solid and molten states. Which two of the following characteristics of metallic solids best explain the use of some metallic

solids in electrical wiring? (luster, malleability, ductility, cubic or hexagonal closest-

packed crystal structure, mobility of outer shell electrons)

Answer: ductility and mobility of outer shell electrons

- You have just learned the properties of these types of solids: ionic, covalent, molecular, and metallic.
 - (a) Which are the hardest, so that some examples of these solids are used for industrial drilling and abrasives?
 - (b) Which solids are the softest?
 - (c) Which are the best conductors of electricity and heat?
 - (d) Which solids are held in a crystalline structure by strong electrostatic attractions?

Answer: (a) covalent; (b) molecular; (c) metallic; (d) ionic

In the next section we will discuss how X-ray diffraction has been used to determine the sizes of atoms and ions and how the sizes vary from group to group and period to period in the periodic table.

ATOMIC AND IONIC RADII

37

An important use of X-ray diffraction analysis has been the determination of atomic and ionic sizes. Atomic and ionic sizes are usually listed in angstrom units, Å (1 angstrom unit = 1×10^{-8} centimeters). The radii of some typical atoms and their ions are listed below.

| | Radius | | Radius |
|------|--------|------------------|--------|
| Atom | (Å) | lon | (Å) |
| Li | 1.23 | Li ⁺ | 0.60 |
| Na | 1.57 | Na⁺ | 0.95 |
| K | 2.03 | K ⁺ | 1.33 |
| Rb | 2.16 | Rb ⁺ | 1.48 |
| Cs | 2.35 | Cs+ | 1.69 |
| Ве | 0.89 | Be ²⁺ | 0.31 |
| Mg | 1.36 | Mg ²⁺ | 0.65 |
| Ca | 1.74 | Ca ²⁺ | 0.99 |
| Sr | 1.91 | Sr ²⁺ | 1.13 |
| Ba | 1.98 | Ba ²⁺ | 1.35 |
| | | | |

Using this chart, locate the Na atom. What is the atomic radius of a Na atom?

Answer: 1.57 Å (Remember to express atomic radii in angstrom units, Å.)

Using the same chart, find the radius of the sodium ion, Na⁺.

Answer: 0.95 Å

The positive ion Na⁺ has a smaller radius than its parent atom Na. Look at all the positive ions listed on the chart and compare the positive ions to their parent atoms. How do the radii of positive ions compare with the radii of their parent atoms?

Answer: Positive ions are all smaller than their parent atoms.

Positive ions are smaller than their parent atoms because a positive ion has *lost* one or more electrons. The protons now outnumber the electrons, so the protons (which are in the nucleus) exhibit more attraction for the remaining electrons. The protons thus draw the remaining electrons closer to the nucleus, resulting in a smaller radius than the original atom. In addition, electrons are lost from the outermost shell. Loss of these outermost shell electrons also makes the ion smaller than the original atom.

A negative ion has *gained* one or more electrons. Based upon what you have just learned about positive ions how should the radius of a negative ion compare with the radius of its parent atom?

Answer: The negative ion radius should be larger than the radius of the parent atom.

| SIZES OF NEGATIVE IONS AND THEIR PARENT ATOMS | | | | |
|---|---------------|------------------|------|--|
| Atom | Radius (Å) | | | |
| F | 0.72 | F- | 1.36 | |
| Cl | 0.99 | Cl- | 1.81 | |
| Br | 1.14 | Br - | 1.95 | |
| 1 | 1.33 | I- | 2.16 | |
| 0 | 0.74 | O ²⁻ | 1.40 | |
| S | 1.04 | S ²⁻ | 1.84 | |
| Se | 1.17 | Se ²⁻ | 1.98 | |
| Te | 1.37 | Te ²⁻ | 2.21 | |

| 41 | Look at the ch | art of sizes o | f negative ions | and their | parent atoms. |
|----|----------------|----------------|-----------------|-----------|---------------|
| 4 | LOOK at the ch | art or sizes o | i negative ions | and then | parent atoms. |

- (a) What is the radius of an O²⁻ ion?
- (b) How many centimeters is it?

Answer:

(a) 1.40 Å

(b)
$$1.40 \text{ Å} \times \frac{1 \times 10^{-8} \text{ cm}}{1 \text{ Å}} = 1.40 \times 10^{-8} \text{ cm}$$

Ions and atoms that have the same number of electrons are called isoelectronic. The ion Na⁺ has the same number of electrons as an atom of Ne. All of the following have the same number of electrons and are isoelectronic.

Do any two of these isoelectronic ions or atoms have the same number of protons?

Answer: no (Remember that only the number of electrons is changed. The number of protons in the nucleus remains unchanged and is a fixed number for each element, its atomic number.)

An increase in the positive charge per electron results in a decrease in the radius. All of the following have ten electrons, so they are isoelectronic. Their atomic numbers (shown below the isoelectronic ions) range from 7 to 14.

$$N^{3-}$$
 O^{2-} F^{-} N^{2-} N^{4-} N^{2+} N^{3+} $N^$

In the negative ions, the electrons outnumber the protons. In the positive ions, the protons outnumber the electrons. Would you expect the radii of these isoelectronic species to increase from left to right or to decrease from left to right?

Answer: decrease from left to right (The number of protons increases while the number of electrons remains constant, therefore increasing the attraction on the electrons and making each successive ion smaller.)

When an atom has more protons than electrons, the increase in the positive charge per electron results in a decrease in the radius. When an atom has fewer protons than electrons, the decrease in the positive charge per electron results in an increase in the radius.

Iron, Fe, has an atomic number of 26. A neutral atom of Fe has 26 electrons. An Fe²⁺ ion has 24 electrons. An Fe³⁺ ion has 23 electrons. List the Fe atom and its two ions in order of decreasing size (largest first).

Answer: Fe, Fe2+, Fe3+

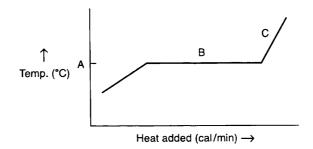
You have just learned some of the properties of solids and how they compare with gases. Our knowledge of the structures of solids and their properties helps us to develop new uses for solids and new combinations of solids that are stronger, better conductors of heat and electricity, and more resistant to chemical attack.

In Chapter 10 we will discuss the liquid state and its properties. A comparison of liquids to the solid and gaseous states is also presented.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test.

- 1. State at least two basic differences between crystals and glasses.
- 2. Which type of solid(s) (ionic, covalent, molecular, or metallic) are:
 - (a) nonconductors of electricity in the solid state? _____
 - (b) generally soft but not malleable or ductile?
 - (c) held together by positive ions in a sea of mobile electrons?
- 3. Which one of each of the following sets will have the larger radius?
 - (a) Mg or Mg²⁺ _____
 - (b) S or S²⁻ _____
 - (c) F⁻ or Ne _____
 - (d) Ca²⁺, K⁺, F⁻, or O²⁻
- Which of the following ions and atoms are isoelectronic with argon (Ar)? (Cl⁻, S²⁻, P, K, Ca²⁺, Kr)
- 5. The graph below represents the heating of a solid. Indicate what is happening or what is represented by each of the labeled points.



| | A |
|----|---|
| | B |
| | C |
| 6. | Sulfur exists in more than one crystalline form. Is it amorphous or polymorphic? |
| 7. | Graphite and diamond are two forms of carbon. What are they called? (amorphous, allotropes, isotopes) |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. (1) Crystals have sharp melting points, while glasses have broad melting point ranges.
 - (2) Crystals cleave along planar surfaces, while glasses fracture to form rounded or uneven surfaces.
 - (3) Crystals have equal bond strengths in all directions, while glasses have variable bond strengths.
 - (4) Crystals diffract X-rays, but glasses do not.

(frames 9-12)

- 2. (a) ionic, covalent, molecular (frames 27, 30)
 - (b) molecular (frame 31)
 - (c) metallic (frame 33)
- 3. (a) Mg, (b) S²⁻, (c) F⁻, (d) O²⁻ (frames 37-40, 43)
- 4. Cl⁻, S²⁻, Ca²⁺ (frame 42)
- 5. A melting point
 - B heat of fusion (solid and liquid present while the solid is melting)
 - C—only liquid present, while temperature is increasing

(frames 15-20)

- 6. polymorphic (frame 6)
- 7. allotropes (frame 7)

10 The Liquid State

Liquids are easily recognized by comparison with the most widely known liquid, water. You know from experience that water flows when we pour it, boils when heated enough, freezes when cooled enough, disappears when left in the open, does not mix with oil or gasoline, supports "water bugs" on its surface, and cools when it evaporates, as when perspiration leaves your skin. These properties of water are characteristic of all liquids. Every liquid has its own boiling point, freezing point, flow, surface, and "heat" properties.

This chapter will acquaint you with the characteristics of the liquid state. Every gas becomes a liquid when it is cooled to a sufficiently low temperature. This is the result of intermolecular attractions. The properties of liquids are largely determined by the magnitude of these intermolecular forces. The forces most often encountered are van der Waals forces or hydrogen bonds, formed by polar molecules, and very weak forces called London forces, which are primarily of interest in the behavior of nonpolar molecules.

Every liquid becomes a solid when sufficiently cooled. This happens at the temperature at which kinetic energy of the molecules becomes so small that intermolecular attraction brings about a complete loss of fluidity. The solid that results has a rigid structure that is characterized by its own unique type of crystal shape.

Liquids fall between gases and solids in their "ordering." Remember, gases fill their container and take its shape, and are in rapid random motion with no order. Solids, on the other hand, are very highly ordered and do not fill or take the shape of their container unless forced to do so.

OBJECTIVES

After you have completed this chapter, you will be able to

- recognize and apply or illustrate: boiling point, vapor pressure, viscosity, surface tension, miscible, immiscible, volatility, density, hydrogen bonding, polar compounds, heat of vaporization, equilibrium, and Le Chatelier's Principle;
- state the effect of temperature on the surface tension, viscosity, and volatility of a liquid;
- give an explanation of why the vapor pressure of a liquid changes with temperature and how this relates to boiling point and critical temperature;

- explain what properties are necessary for a good refrigerant;
- given a graph representing what happens to the temperature of a substance as heat is added to it, locate the melting point, the boiling point, the states of matter that are present, and the regions representing heats of fusion and vaporization;
- given the graph of the vapor pressure versus temperature of a liquid, determine: the vapor pressure of the liquid at a specific temperature and the boiling point of the liquid at a specific atmospheric pressure;
- calculate the amount of heat that must be supplied to vaporize a certain amount of a liquid when given its heat of vaporization;
- predict whether or not two liquids will mix when put together.
- We begin this chapter with a brief comparison of the states of matter based upon the kinetic molecular theory. The kinetic molecular theory was first encountered in explaining the behavior of gases. When cooled to a sufficiently low temperature, the average kinetic energy drops and every gas becomes a liquid. The molecules of liquid substances still move in random motion according to the kinetic molecular theory. However, the molecules in the liquid state move more slowly, and there is very little space between molecules.

When a gas is compressed, the space between the molecules of a gas is actually compressed. Since there is very little space between the molecules of a liquid, would you expect liquids to be readily compressed? _____

Answer: no (In reality, even large pressures have very little effect on the volume of a liquid.)

- The molecules of a liquid are not as structured as those in the solid state. The liquid molecules are free to slide over one another and to flow and assume the shape of the container. The molecules of a solid can vibrate and bend but cannot flow and slide over one another. The three states of matter (gaseous, liquid, and solid) differ in terms of the freedom of movement of molecules.
 - (a) Molecules have the greatest freedom of movement in which state?

| (b) | Molecules | have the | least | freedom | of movement | in | which state? | |
|-----|-----------|----------|-------|---------|-------------|----|--------------|--|
|-----|-----------|----------|-------|---------|-------------|----|--------------|--|

Answer: (a) gaseous; (b) solid

Many of the properties of liquids are determined by the attraction of molecules for each other. These intermolecular attractive forces cause the molecules to stick together and coalesce into a liquid. The intermolecular attractions affect the flow rate of a liquid. Heavy oils, syrup, and molasses flow more slowly than water or gasoline. Compared to liquids that flow rather quickly, liquids of slower flow rate would have (stronger, weaker) _______ intermolecular attractive forces.

Answer: stronger (The stronger the intermolecular attraction, the more the molecules stick to each other and the slower the flow rate of a liquid.)

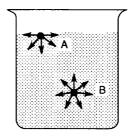
The viscosity of a liquid refers to its resistance to flow. A liquid with a high resistance to flow such as heavy oils or molasses would exhibit high viscosity. A liquid with very little resistance to flow would exhibit low viscosity. High viscosity is associated with relatively (strong, weak) ______ intermolecular attractive forces.

Answer: strong

A liquid with relatively weak intermolecular forces would probably exhibit low _____(use the term that refers to resistance to flow).

Answer: viscosity

Razor blades and certain insects that are heavier than water can float on top of the water due to surface tension. Remember that the molecules of a liquid attract each other through intermolecular attractive forces. Surface tension is caused by a difference in direction of intermolecular attractive forces between those molecules at the surface of a liquid and those in the body of the liquid.



A molecule in the body of the liquid (molecule B) is surrounded by attraction from other liquid molecules. There is equal attraction from all sides. A molecule at the surface of the liquid (molecule A) is attracted only toward the interior of the liquid. It is *not* balanced by an attraction from above. Which molecule (A or B) is involved in surface tension?

Answer: molecule A

Because molecule A and all other molecules making up the surface of the liquid are pulled inward by intermolecular attraction, the liquid tends to form as small a surface as possible. This inward pull of the surface molecules is known as surface tension.

A sphere is the three-dimensional figure with the smallest surface area. Water and other liquids tend to form droplets or small spheres because the inward pull

on the surface molecules tends to produce as small a surface area as possible. A falling raindrop is actually a small sphere that is distended somewhat by the pull of gravity.

Liquids tend to form spherical droplets because of the inward pull on surface molecules, which is called ______.

Answer: surface tension

The inward pull of surface molecules depends upon intermolecular attractive forces. Strong intermolecular attractive forces provide a strong inward pull. Compared to a liquid with relatively weak intermolecular attractive forces, a liquid with relatively strong intermolecular forces could be expected to show:

| (a) | (greater, | lesser) | surface | tension. |
|-----|-----------|---------|---------|----------|
| | | | | |

(b) (higher, lower) _____ viscosity.

Answer: (a) greater; (b) higher

VAPOR PRESSURE

- Vapor pressure is the pressure exerted by the vapor (gaseous) phase of a liquid in a closed container. To understand vapor pressure, you must understand several other concepts. You may already be familiar with evaporation. Evaporation means passing from the liquid state to the gaseous (vapor) state. Remember that all of the molecules in a liquid together have an average kinetic energy that is a measure of the temperature of the liquid. However, not all individual molecules have the same kinetic energy. Some have above average and some have below average kinetic energy. Some molecules with greater kinetic energy will escape from the liquid if they are located near the surface. These molecules evaporate and enter the gaseous (vapor) state.
 - (a) The molecules of liquid that evaporate first are those of (higher, lower) _____ than average kinetic energy.
 - (b) If a saucer of water is uncovered and not touched for a day or two, some of the water "disappears." In terms of the kinetic molecular theory, explain what happened to the water that is missing.

Answer: (a) higher; (b) Some of the water has evaporated. Those molecules with greater than average kinetic energy that are located near the surface of the liquid have escaped and entered the vapor state.

The molecules of greatest kinetic energy evaporate first, while the molecules of lower kinetic energy remain. The result is a drop in temperature of the remaining molecules. (Temperature is simply a measurement of the average kinetic energy of the molecules. As the average kinetic energy drops, so does the temperature.)

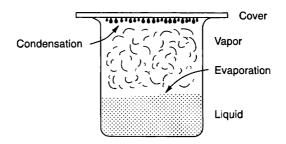
A liquid in a well-insulated container has a rapid rate of evaporation. Its temperature is measured prior to evaporation. After evaporation of a portion of the liquid, would you expect the temperature of the remaining liquid to be higher or lower than the original temperature?

Answer: lower (because the average kinetic energy of the remaining liquid molecules is also lower)

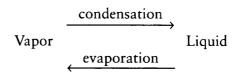
To make up for the loss of kinetic energy through evaporation, a liquid undergoing evaporation will draw heat from its surroundings. That is why rubbing alcohol feels cold on your skin as it evaporates. Heat is removed from the skin during evaporation. Sweating is a means used by your body to control its temperature. A natural breeze or the breeze from a fan can increase the rate of evaporation. As a result, your skin temperature is (warmed, cooled) _______.

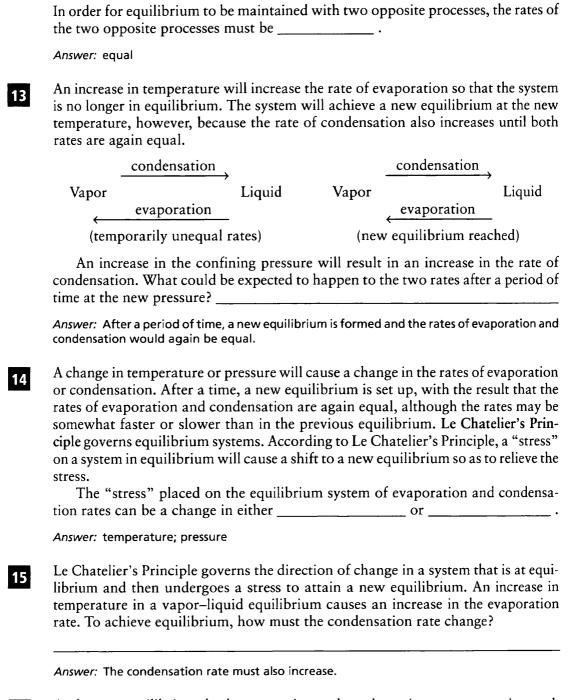
Answer: cooled (The evaporating sweat draws away heat and cools the skin.)

If a container of liquid has a cover, the liquid will continue to evaporate, but after a time, some of the vapor (gaseous) molecules will return to the liquid state in a process called condensation, which is essentially the opposite of evaporation. After a longer time, the rate of condensation will equal the rate of evaporation. When an equal rate of evaporation and condensation is reached, the pressure exerted by the vapor molecules is known as the vapor pressure.



When the rate of evaporation is equal to the rate of condensation, the liquid and vapor are said to be in equilibrium. Liquid molecules continue to evaporate when equilibrium is reached, but just as many vaporized molecules condense into liquid. Both processes continue at equal rates. The processes are opposite but equal in rate.





At the new equilibrium, both evaporation and condensation rates are again equal, although both rates are increased when compared to the previous equilibrium. Remember that vapor pressure is the pressure that a vapor exerts when a liquid and

its vapor (evaporation and condensation) are at equilibrium (at a specified temperature). According to Le Chatelier's Principle, an increase in temperature can shift the equilibrium to increase the rates of evaporation and condensation to form a new equilibrium. The average kinetic energy of the liquid molecules is also increased according to the temperature increase. Similarly, a decrease in temperature can shift the equilibrium to decrease the rates of evaporation and condensation (and decrease the average kinetic energy). The greater the rate of evaporation, the greater the vapor pressure.

Would you expect the vapor pressure of a liquid to increase or decrease if the temperature is increased?

Answer: increase (An increase in average kinetic energy allows more higher energy molecules to evaporate. The increased evaporation rate would increase the amount of vapor and the pressure it exerts.)

BOILING POINT

Water is the most widely known liquid. We have seen water freeze, flow when poured, or boil when the temperature is high enough. The boiling point of water is usually listed as 100°C. This is true only if the atmospheric pressure is 1 atmosphere (which equals 760 torr or 101.325 kilopascals, kPa). At higher pressure, the boiling point of water is raised. At pressures lower than 1 atmosphere, the boiling point of water is below 100°C.

When water is boiled in a pressure cooker, the pressure inside is greater than 1 atmosphere. The boiling point of water could be expected to be (100°C, below 100°C, above 100°C) ______.

Answer: above 100°C

The boiling point of a liquid is the temperature at which the vapor pressure of a liquid equals the surrounding pressure. Based upon this definition, water would boil at 100°C at 1 atmosphere pressure because its vapor pressure was also equal to ______ at that temperature.

Answer: 1 atmosphere

The surrounding pressure of an open pan of boiling water is usually 1 atmosphere. In the pressure cooker, the surrounding pressure is greater than 1 atmosphere. In order for water to boil in a pressure cooker, the vapor pressure must equal this greater surrounding pressure.

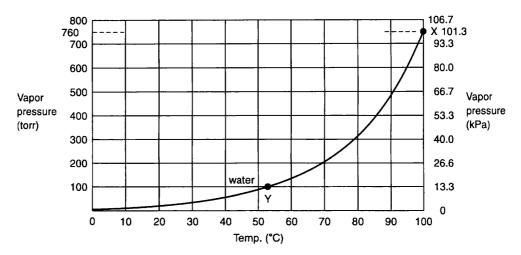
Suppose that instead of increasing the surrounding pressure as with a pressure cooker, we attempted to boil water at a pressure of less than 1 atmosphere, for example on a high mountain. Would you expect water to boil at 100°C, below 100°C, or above 100°C?

Answer: below 100°C (In fact, the boiling point of water on a high mountain, where the atmospheric pressure is less than 1 atmosphere, is below 100°C.)

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The higher the temperature, the greater the vapor pressure. When the vapor pressure of a liquid equals the surrounding pressure (pressure of the outside atmosphere or in some vessel such as a pressure cooker), the liquid will boil. The graph below plots the vapor pressure of water against temperature.



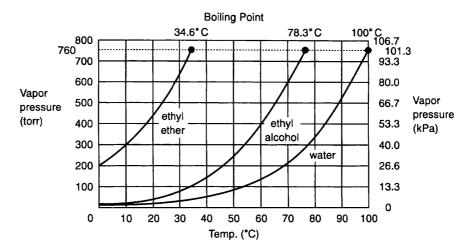
Change of Vapor Pressure with Temperature for Water

| (a) | At the normal boiling point of water (100°C), what is its vapor pressu | ire? (See |
|-----|--|-----------|
| | point X on the graph.) | |

- (b) Water can be made to boil at various temperatures, provided that the vapor pressure is equal to the surrounding or confining pressure. If the surrounding pressure is only 350 torr (46.7 kPa), at what vapor pressure would the water boil?
- (c) Using the graph, at what temperature (approximate) would water boil if the surrounding pressure was only 100 torr (13.3 kPa)? (See point Y on the graph.)

Answer: (a) 760 torr or 1 atmosphere or 101.3 kPa; (b) 350 torr or 46.7 kPa (remember that, at boiling, the vapor pressure of the liquid equals the surrounding pressure); (c) slightly more than 50°C (At that temperature, the vapor pressure is 100 torr or 13.3 kPa. If the surrounding pressure and vapor pressure are equal, water boils.)

The question of the boiling points of other liquids may have occurred to you. Do all liquids have the same boiling points? Look at the graph on the following page.



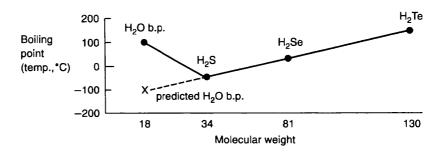
Vapor Pressure and Temperature for Three Common Liquids

At a standard pressure of 1 atmosphere (760 torr, 101.3 kPa), what is the boiling point of:

- (a) water? _____
- (b) ethyl alcohol? _____
- (c) ethyl ether?

Answer: (a) 100°C; (b) 78.3°C; (c) 34.6°C

As a general rule, compounds of elements in the same family on the periodic table increase in boiling point with increasing molecular weight if all other factors are equal.



However, all factors are not always equal. Water (H₂O), for example, has a predicted boiling point of below 0°C when only molecular weights are considered. Another factor must account for the much higher than predicted boiling point of water.

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| (a) | What is the | approximate | boiling | point | of | water | as | pred | icted | by ' | the | graph |
|-----|---------------|----------------|----------|-------|----|-------|----|------|-------|------|-----|-------|
| | above? (See] | point X on the | e graph. |) | _ | | | | | | | |

(b) What is the actual boiling point of water at 1 atmosphere?

Answer: (a) -100°C (approximately); (b) 100°C

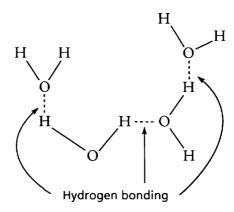
The boiling point of a liquid is affected by the strength of the intermolecular attractive forces. Several kinds of forces can be classified as intermolecular attractions. One type of intermolecular attractive force is caused by polar molecules (first encountered in Chapter 3). Polar molecules have small electrostatic charges on opposite ends of the molecules. As a result, the molecules attract each other. There are also other types of intermolecular attractive forces such as van der Waals forces and London forces. You have already encountered van der Waals forces. London forces are much weaker intermolecular attractions in nonpolar compounds. They are caused by electrons from one molecule affecting the orbit of electrons in another molecule at very specific and constantly changing moments in time. Polar compounds have much stronger intermolecular attractions than nonpolar compounds. Stronger intermolecular attractions tend to keep molecules within the liquid form, with the result that the boiling point is higher than that predicted by molecular weight comparisons.

Compound A and compound B have approximately the same molecular weight. However, compound A has a much higher boiling point than compound B. Based upon what you have just learned, which compound (A or B) could be expected to have the stronger intermolecular attractive forces?

Answer: compound A

Water is a polar compound. The other hydrogen compounds of Group VIA elements such as H₂S, H₂Se, and H₂Te are compounds that are much less polar than H₂O. This explains why water has a much higher boiling point than predicted on the basis of molecular weight alone.

Besides water, certain other hydrogen compounds such as HF and NH₃ are also highly polar compounds with especially strong intermolecular attraction. Because elements such as O, F, and N are strongly electronegative, a high degree of polarity is found in these compounds. The result is that the positively charged hydrogen atom of one molecule may be strongly attracted to the negatively charged atom of another molecule. These intermolecular attractions occur throughout the liquid. Because the attractions are especially strong in certain compounds that are made up of hydrogen and electronegative elements, this type of intermolecular attraction is known as hydrogen bonding.



- (a) Two compounds have similar molecular weights. Hydrogen bonding occurs in one compound but not in the other. Which compound would probably have the higher boiling point, the one with hydrogen bonding or the one without?
- (b) Hydrogen bonding, polarity between molecules of a liquid, and van der Waals forces can all be classified as what kind of forces?

Answer: (a) the one with hydrogen bonding; (b) intermolecular attractive forces

Besides affecting the boiling point, intermolecular attractive forces also affect the evaporation of liquids. A liquid with relatively weak intermolecular forces will evaporate more readily than a liquid with relatively strong intermolecular forces. Volatility is a measure of the tendency of liquids to evaporate. A highly volatile liquid evaporates readily.

At room temperature, ether (diethyl ether) is highly volatile. Glycerin is very low in volatility. Assume that an equal quantity of each liquid is allowed to evaporate.

- (a) Which liquid would you expect to evaporate first?
- (b) Would you expect a liquid with strong intermolecular attractive forces to be highly volatile or low in volatility?

Answer: (a) Ether will evaporate first because of its high volatility. (b) low in volatility

Suppose we have two liquids with similar molecular weights. The liquid with stronger intermolecular attractive forces could be expected to have:

- (a) (greater, lesser) _____ viscosity.
- (b) (greater, lesser) _____ surface tension.
- (c) (higher, lower) ______ boiling point.

| (d) | (higher, lower) | volatility. | |
|-----|-----------------|---------------------|--|
| (e) | (higher, lower) | vapor pressure. | |

Answer: (a) greater; (b) greater; (c) higher; (d) lower; (e) lower

MISCIBILITY

The attraction of polar covalent molecules in liquids is one type of intermolecular attraction that affects characteristics such as boiling points, surface tension, volatility, vapor pressure, and viscosity. The polarity of molecules in liquids also affects miscibility, the ability of liquids to mix. Two liquids will mix if both are polar or both are nonpolar. If one liquid is polar and the other is nonpolar, the two liquids will not mix.

Oil and water do not mix. We have learned that water is a polar molecule. Therefore, would you expect oil to be polar or nonpolar?

Answer: nonpolar

Two polar liquids are miscible; two nonpolar liquids are miscible. However, a polar liquid and a nonpolar liquid are *not* miscible.

Water is a polar compound. Water and oil are not miscible. Gasoline and oil are miscible. Is gasoline polar or nonpolar? ______

Answer: nonpolar (Since water and oil are not miscible, oil must be nonpolar. Gasoline is nonpolar because it mixes with oil.)

Immiscible liquids (those not capable of being mixed) generally separate as two layers, with the more dense liquid on the bottom. Gasoline, jet fuel, or oil usually float on top of water because they are less dense than water and are not miscible with water. Based on this information, would you recommend water as a means for putting out gasoline, jet fuel, or oil fires? ______ Why or why not?

Answer: no; Since these liquids float on top of water, adding water might simply spread the fire. (A more appropriate means for putting out a fire of this type is foam or carbon dioxide, to cut off oxygen to the fire. Foam floats on top of oil or jet fuel.)

We can predict whether liquids are miscible or immiscible by knowing if the liquids are composed of polar or nonpolar molecules. The following table lists some common polar and nonpolar compounds. Read the table carefully and then answer the questions.

| Polar Molecules | |
|---|---|
| Compounds | Examples |
| H bonded to O, N, F, Br, Cl, and I | H₂O, NH₃, HF, HCl |
| O bonded to C, F, Cl, Br, I, and other elements | Alcohols (C_2H_5OH , CH_3OH), glycerine ($C_3H_5(OH)_3$), ethylene glycol ($C_2H_4(OH)_2$), HOCl, HOBr, HOI, acetone (CH_3COCH_3) |
| Nonpolar Molecules | |
| Compounds | Examples |
| Linear, planar, or symmetrical compounds with more than 2 atoms | CCl_4 , CF_4 , CO_2 , BF_3 , ether $(C_2H_5-O-C_2H_5)$ |
| Containing only C and H | Gasoline (mixture of C_7H_{16} [heptane], C_8H_{18} [octane], C_6H_6 [benzene], and $C_6H_5CH_3$ [toluene]) |
| Oils, fats (higher molecular weight containing C, H, and O). | Waxes, lipids, cooking oils |

- (a) Is benzene (C_6H_6) miscible with water (H_2O) ?
- (b) A liquid compound made of just C and H is added to a liquid binary compound with strong electronegativity differences. Will the two liquids mix?
- (c) Is ethylene glycol ($C_2H_4(OH)_2$) miscible with water (H_2O)?

(Note: Ethylene glycol has the structure shown here. H—C—C—H
The O atoms are bonded to C atoms.)

H

(d) Is the symmetrical compound CCl₄ miscible with an oil made up of carbon and hydrogen? _____

Answer:

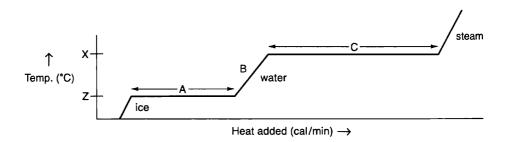
(a) no (Benzene is a nonpolar compound because it is composed of only carbon and hydrogen. Water is polar since it is composed of H bonded to O.)

- (b) no (Compounds made of just carbon and hydrogen are nonpolar. Binary compounds with strong electronegativity differences between the two atoms are polar.)
- (c) yes (Both H₂O and C₂H₄(OH)₂ are polar molecules. A mixture of ethylene glycol and water is commonly found in automobile radiators to protect against freezing. These liquids must be miscible in order for the cooling system to be protected.)
- (d) yes (Both liquids are nonpolar. The CCl₄ compound can be used to dissolve oil and grease stains in cloth.)

HEAT OF VAPORIZATION

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Recall that the heat of fusion is the energy necessary to melt a solid completely to the liquid state (see Chapter 9). While a solid is melting at the melting point through addition of heat of fusion, its temperature does not change. At the boiling point of a liquid, a similar process occurs. In H₂O, the boiling point is 100°C at 1 atmosphere pressure. When heated, the temperature of water increases until it reaches 100°C. After water reaches its boiling point, the temperature does not increase until all the liquid has vaporized to steam. The heat required to vaporize water at the boiling point is called the heat of vaporization. The following graph represents the heating of ice cubes until all of the H₂O is vaporized.



- (a) What letter represents the heat of vaporization?
- (b) What letter represents the boiling point?
- (c) Does the water temperature change while the heat of vaporization is being applied?

Answer: (a) C; (b) X (remember the boiling point is a temperature); (c) no

The graph on the next page represents H_2O . At each of the indicated points, tell whether the H_2O is solid (ice), liquid (water), gaseous vapor (steam), a mixture of ice and water, or a mixture of water and steam.

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Heat added (cal/min) →

- (a) Point A _____
- (b) Point B
- (c) Point C _____
- (d) Point D _____

Answer: (a) ice and water (or solid and liquid); (b) water (or liquid); (c) water and steam (liquid and vapor); (d) steam (vapor)

В

The heat of vaporization of water is 540 cal per gram. It takes how many calories to convert 1 gram of liquid H₂O at 100°C to steam at 100°C?

Answer: 540 cal (This is simply a restatement of the definition of the heat of vaporization.)

The heat of vaporization for water is 540 cal for each gram of H₂O. Two grams of water would require twice as many calories.

$$2 \text{ grams} \times \frac{540 \text{ cal}}{1 \text{ gram}} = 1080 \text{ cal}$$

How many calories of heat would be needed to completely vaporize 10 grams of water at the boiling point (100°C)?

Answer: $10 \text{ grams} \times \frac{540 \text{ cal}}{1 \text{ gram}} = 5400 \text{ cal}$

The heat of vaporization is the energy needed to break the intermolecular attractive forces that keep a liquid in liquid form. It takes 540 cal of heat energy to break the intermolecular attractive forces and vaporize 1 gram of liquid H₂O at 100°C. It is important to remember that vaporization is a reversible process. When H₂O condenses from steam at 100°C to liquid at 100°C, it releases an amount of energy equal to the heat of vaporization.

When 1 gram of steam at 100°C condenses to liquid H₂O at 100°C, it releases how many calories of heat?

Answer: 540 cal

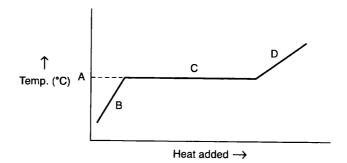
| 36 | A burn suffered from contact with steam at 100°C is much more severe than a burn suffered from contact with the same quantity of boiling water. Can you explain why, in terms of vaporization? |
|----|--|
| | Answer: This more severe burn from steam is caused by the release of 540 cal of heat energy per gram when the steam condenses. |
| 37 | Just as a liquid has a characteristic boiling point, each liquid also has a characteristic heat of vaporization. Certain gases that are readily condensed and have high heats of vaporization are useful in such refrigeration systems as air conditioners, refrigerators, or freezers. Refrigeration systems take advantage of the fact that a liquid which is vaporized at its boiling point requires heat. The resulting vapor (gas) releases heat when it condenses again at the boiling point. In a refrigeration system, a gas is compressed to the point where condensation takes place. The heat released by condensation is given off to the surroundings. The coils behind a refrigerator become warm to the touch because heat is being released after condensation. After the liquid releases its heat to the surroundings, it is piped inside the refrigerator and allowed to vaporize and expand very rapidly. |
| | (a) Vaporization is a process that (requires, releases) heat. |
| | (b) Condensation is a process that (requires, releases) heat. |
| | Answer: (a) requires; (b) releases |
| 38 | Because the vaporization of the liquid inside the refrigerator piping is a process that requires heat, the heat inside the refrigerator is removed and the food and air inside the refrigerator are cooled. After the gas has removed heat from the inside of the refrigerator, the gas is piped outside and compressed again. The cycle of condensation and vaporization is continued. Refrigeration depends upon the requirement of heat for the process of and the release of heat for the process of |
| | Answer: vaporization; condensation |

The condensation-vaporization cycle is important for refrigeration because heat is taken from one place (inside the refrigerator) through vaporization and released at another place (outside the refrigerator) through condensation. Condensation takes place because the gas is compressed through a mechanical compressor. The compressor forces the gas into less space so that the intermolecular attractive forces are strong enough to overcome the kinetic energy of the gas molecules. The molecules then coalesce and the gas is liquefied.

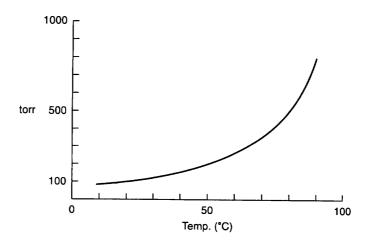
It is possible, however, for the kinetic energy of the molecules to be so great that the intermolecular attractive forces cannot overcome the kinetic energy and the gas will not liquefy no matter how great the pressure. If the coolant gas molecules in a refrigerator possessed so much kinetic energy that the intermolecular attractive

| | forces could not cause the gas to be liquefied no matter how great the pressure, could the refrigerator continue working through the vaporization-condensation cycle? Explain |
|------|--|
| | Answer: no; The gas could not be liquefied under such conditions, and no condensation and therefore no vaporization could take place. |
| 40 | Remember that the temperature is a measure of the average kinetic energy of a gas. The temperature above which the intermolecular attractive forces can no longer overcome the kinetic energy in order to liquefy a gas is known as the critical temperature. At any temperature above the critical temperature, a gas will not liquefy no matter how much pressure is applied. If you were selecting a coolant gas for a refrigerator, would you select one with a critical temperature that is well below room temperature or well above? |
| | Answer: well above room temperature (The refrigerator will no longer function at any temperature above critical temperature because condensation cannot take place at any temperature above critical temperature. The critical temperature should therefore be well above the normal temperature of the surroundings in which the refrigerator must operate.) |
| 41 | The critical temperature is different for each gas. For example, hydrogen has an extremely low critical temperature of -240°C. In order to liquefy hydrogen gas, the temperature must be (above, at, below)240°C. |
| | Answer: at or below |
| LF-1 | This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test. |
| | 1. If we increase the temperature of a liquid, what happens to its vapor pressure? |
| | Acetone is a polar compound. Are water and acetone miscible? |
| | 3. Water has a normal boiling point of 100°C and ethyl alcohol (46 g/mol) has a normal boiling point of 78°C. Which has the lower intermolecular attractive forces? |
| | 4. Containers of three different liquids, A, B, and C, were opened to the air. All three had the same volume to begin with, but the contents of A disappeared very rapidly while the contents of C were the last to disappear. Which liquid has the lowest vapor pressure? |

- 5. A liquid was vaporized in a closed container at a temperature of 200°C. The container was such that one end could be pushed in to increase the pressure on the vapor. While maintaining the temperature of the vapor at 200°C, the pressure on the vapor was increased to 1000 atmospheres but none of the vapor condensed (liquefied). The 200°C temperature is most likely above the ______ temperature of the gas.
- 6. Which would be more serious, a burn from water at 100°C or a burn from steam at 100°C? _____ Why? _____
- 7. Below is a graph representing a liquid being heated at a constant rate. What is happening at B and C?



8. Below is a graph representing how the vapor pressure of a liquid changes as the temperature increases.



(a) What would be the approximate vapor pressure of the liquid at 50°C?

| | (b) If the pressure on the surface of the liquid is only 500 torr, at what approximate temperature would the liquid boil? |
|----|--|
| 9. | Water bugs walk on water, some razor blades can float on water, and water forms droplets. Are these examples of viscosity, surface tension, or vapor pressure? |
| | |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. Vapor pressure will increase. (frames 16, 20)
- 2. Yes, because H₂O is also a polar compound. Since likes mix with likes, they will be miscible. (frames 28–30)
- 3. alcohol (It has the lower boiling point.) (frame 23)
- 4. C. The containers held three liquids with different boiling points, vapor pressures, and degree of volatility. Container A held the liquid that was most volatile and had the highest vapor pressure and lowest boiling point. Container C held the liquid that was least volatile and had the lowest vapor pressure and highest boiling point. Container B held a liquid with properties somewhere between those of A and C. (frame 25)
- 5. critical (frames 40, 41)
- 6. steam; Steam has 540 cal more heat per gram at 100°C (heat of vaporization) than water does at 100°C. (frames 31, 36)
- 7. At B the temperature of the liquid is increasing as heat is being added. At C the liquid is boiling while the temperature remains constant. The flat portion represents heat of vaporization. (frames 31, 32)
- 8. (a) approximately 200 torr; (b) approximately 80°C (frame 20)
- 9. surface tension (frames 6, 7)

11 Solutions and Their Properties

You have just been introduced to the three states of matter — solids, liquids, and gases — and their "observable" properties. Most substances that you encounter in your daily existence are mixtures of these states of matter. The mixtures may be solids in liquids, liquids in liquids, gases in liquids, gases in gases, or any combination of the three states. The most common mixtures are solids in liquids.

This chapter deals with the most common of all liquids, water, and the properties of mixtures of water with other states of matter, particularly solids. This chapter also is concerned with the ways of expressing the *quantitative* relationships between mixtures of states of matter.

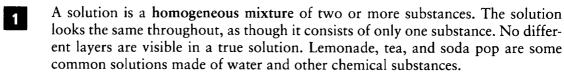
OBJECTIVES

After you have completed this chapter, you will be able to

- recognize and apply or illustrate: solute, solvent, dilute, concentrated, molarity, molality, mole fraction, weight percent, solubility, hydrate, hydration, solvation, saturated, unsaturated, supersaturated, electrolyte, nonelectrolyte, hygroscopic, Raoult's Law, acid anhydride, and basic anhydride;
- given all but one of the following data, calculate the remaining unknown data: molecular weight of the solute, number of grams of the solute, number of grams of solvent (or density and volume), and molality of the solution;
- given all but one of the following data, calculate the remaining unknown data: the molality of a solution (or the data needed to find it), the molal freezing point depression constant, and the lowering of the freezing point of the solution (or the data needed to find it);
- given all but one of the following data, but with the molal boiling point elevation constant, calculate: the rise in the boiling point of the solution, the molality of a solution (or the data needed to find it), the molal freezing point depression constant, and the lowering of the freezing point of the solution (or the data needed to find it);

- given all but one of the following data, calculate the remaining unknown data: number of moles of solute, molarity of the solution, and volume of the solution;
- be able to write balanced chemical equations for the reaction of water with oxides of the alkali metals and oxides of the alkaline earth metals.

SALTS AND OXIDES



A solution is composed of one or more solutes and one solvent. A solute is a substance that is dissolved and is usually the substance of lesser quantity in a solution. The solvent is the substance doing the dissolving and of greater quantity in a solution.

Suppose a teaspoon of table salt is dissolved in a glass of water.

| | (a) Which is the solute, water or salt? |
|---|---|
| | (b) Which is the solvent? |
| | (c) From your experience, is the resulting mixture a solution? |
| | Answer: (a) salt; (b) water; (c) yes (it appears the same throughout and has no visible layers) |
| 2 | In a sugar and water solution, sugar is the and water is the |
| | Answer: solute; solvent |
| 3 | Various types of solutions can include gases dissolved in liquids, liquids in liquids, or solids in liquids. A salt-water solution is an example of a solution involving a solid dissolved in a liquid. |
| | In a fish aquarium, an electric pump is often used to bubble air in the aquarium |
| | water. Some of the oxygen remains dissolved in the water. This solution is an |
| | example where a is the solute and a is the solvent. |

The most common solvent is water. The most common solutes dissolved in water are the soluble solids encountered in Chapter 6.

Answer: gas; liquid (The solution consists of a gas dissolved in a liquid.)

A soluble ionic solid in aqueous solution is called an electrolyte because such a solution conducts electricity. In aqueous (water) solution, the ions of an ionic compound dissociate and are free to move about to conduct electricity. A nonelectrolyte may also dissolve, but the solute remains in molecular form and will not conduct electricity.

- (a) An aqueous solution of NaCl conducts electricity. Is the solute NaCl an electrolyte or nonelectrolyte?
- (b) A solute made up of dissociated positive and negative ions is a(n) (electrolyte, nonelectrolyte)
- (c) Does a solute that remains in molecular form conduct electricity?

Answer: (a) electrolyte; (b) electrolyte; (c) no

Instead of a solute just dissolving in water, it may react with water to form a different compound. Oxides of alkali metals (Na₂O, K₂O, Li₂O) and of alkaline earth metals (MgO, CaO, BaO) react with water to form metal hydroxide solutions. For example:

$$Na_2O + H_2O \rightarrow 2NaOH$$

 $CaO + H_2O \rightarrow Ca(OH)_2$

Sodium hydroxide, NaOH, ionizes to yield Na⁺ and OH⁻. Calcium hydroxide, Ca(OH)₂, ionizes to yield Ca²⁺ and 2OH⁻.

A compound that ionizes to form OH⁻ in aqueous solution is called a base. After the metal oxide has reacted with the water, there is actually a new solute in the solution, the metal hydroxide. In the equations above, what compounds are the solutes once the reaction has occurred?

Answer: NaOH (or Na⁺ and OH⁻) and Ca(OH)₂ (or Ca²⁺ and 2OH⁻)

The general equation for the reaction of an alkali metal oxide with water is as follows. (Substitute any alkali metal for "M.")

$$M_2O + H_2O \rightarrow 2MOH$$

(MOH is a base since it dissociates to form OH ions.)

When K₂O is mixed with an excess of water, the resulting aqueous solution contains what base as the solute?

Answer: KOH (K+, OH-)

The general equation for the reaction of any alkaline earth metal oxide with water is as follows. (Substitute any alkaline earth metal for "M.")

$$MO + H_2O \rightarrow M(OH)_2$$

When MgO is mixed in an excess of water, the resulting aqueous solution contains _____ as the solute.

Answer: Mg(OH)₂ (Mg²⁺, 2OH⁻). Note that the oxidation number of the metal ion does not change in going from metal oxide to metal hydroxide.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

 $H_2SO_3 \rightarrow 2H^+ + SO_3^{2-}$

In the above reaction the resulting solution contains _____ as the solute.

Answer: H₂SO₃ (2H⁺, SO₃²⁻)

The oxides of a number of nonmetals such as carbon, sulfur, nitrogen, and phosphorus react with water to form acids. When the nonmetal oxides are mixed in water, the resulting solute is an acid because of the reaction of the oxide with the water.

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

What is the new solute in this reaction?

Answer: HNO₃ (H⁺ and NO₃⁻ ions)

What is the resulting solute in the following mixture of carbon dioxide and water?

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Answer: H₂CO₃ (2H⁺, CO₃²⁻)

Nonmetal oxides (such as N₂O₅, SO₂, SO₃, P₂O₃, P₂O₅, CO₂, and so on) react with water to form acids. Note that the nonmetal does not change oxidation number in going from the oxide to the acid. The formulas of some of the acids are obtained simply by "adding" the atoms together. Here are some obvious examples.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

 $CO_2 + H_2O \rightarrow H_2CO_3$

Others are not as easy to see.

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

We must rely upon the formulas and names of the common acids you learned in Chapter 5.

What acid is formed when SO₃ reacts with H₂O?

Answer: H_2SO_4 ($H_2O + SO_3 \rightarrow H_2SO_4$)

An unexpected product is sometimes formed when an automobile is equipped with a catalytic converter. The catalytic converter allows sulfur dioxide and sulfur trioxide and water vapor to mix together and react. The reaction of water and sulfur

and calculate.)

| | trioxide produces a pollutant, which is then sprayed out of the automobile exhaust system. Identify the pollutant. |
|---------------|---|
| | Answer: H ₂ SO ₄ (sulfuric acid) |
| 13 | Nonmetal oxides are known as acid anhydrides (acids without water) because they form acids when added to water. Metal oxides are known as basic anhydrides (bases without water) because they form bases when added to water. Identify the following as either acid anhydrides or basic anhydrides. |
| | (a) MgO |
| | (b) P ₂ O ₅ |
| | (c) N ₂ O ₃ |
| | (d) BaO |
| | Answer: (a) basic anhydride; (b) acid anhydride; (c) acid anhydride; (d) basic anhydride |
| 14 | Acid anhydride + $H_2O \rightarrow$ Basic anhydride + $H_2O \rightarrow$ |
| _ | Answer: acid; base |
| | |
| HYDRAT | ES AND WATER OF HYDRATION |
| 15 | Certain compounds actually contain water within the structure of their crystal lattices. Those compounds are called hydrates. The water they contain is known as the water of hydration. Probably the best known hydrate is copper sulfate pentahydrate, which has a characteristic deep blue color and is symbolized as CuSO ₄ • 5H ₂ O. The dot between CuSO ₄ and 5H ₂ O means that water is actually a part of the hydrate molecule, and the formula weight of the hydrate must include the water. A hydrate is a compound containing what as a part of its crystal lattice? |
| | Answer: water (H ₂ O) |
| 16 | Determine the formula weight in grams (to the nearest tenth) of copper sulfate pentahydrate. (You might want to make a table like the ones we used in Chapter 4 to determine formula weights. If so, use a separate sheet of paper to set up the table |

Formula weight of CuSO₄ • 5H₂O = _____

| Element | Number of atoms | Gram atomic weigh | t Atoms × weight |
|---------|-----------------|-------------------|-----------------------------|
| Cu | 1 Cu | 63.5 | 1 × 63.5 = 63.5 |
| S | 1 S | 32.1 | $1 \times 32.1 = 32.1$ |
| 0 | 9 O | 16.0 | $9 \times 16.0 = 144.0$ |
| Н | 10 H | 1.0 | $10 \times 1.0 = 10.0$ |
| | | Fo | ormula weight is 249.6 gran |

It is possible to determine the percentage that the water contributes to the total weight of a hydrate. Just divide the weight of the water molecules by the entire formula weight of the hydrate and multiply the result by 100. For copper sulfate pentahydrate, divide the weight of 5 mol of water by the formula weight of the entire hydrate and multiply by 100.

$$\frac{\text{weight of } 5\text{H}_2\text{O}}{\text{formula weight of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}} \times 100 = \frac{\text{percentage of weight}}{\text{contributed by water}}$$

The percentage of weight contributed by water in $CuSO_4 \cdot 5H_2O$ is ______. (Round this and all other answers in this chapter to the nearest tenth unless otherwise indicated.)

Answer: 249.6 grams
The weight of 5H₂O is:

| Element | Number of atoms | Gram atomic weigh | t Atoms | × weight | |
|---------|-----------------|-------------------|-------------------|------------------------|--|
| Н | 10 H | 1.0 | 10 × 1.0 = | = 10.0 | |
| 0 | 5 O | 16.0 | 5 × 16.0 = | $5 \times 16.0 = 80.0$ | |
| | | | Formula weight is | 90.0 grams | |

percentage weight of water =
$$\frac{\text{weight of } 5\text{H}_2\text{O}}{\text{formula weight of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}} = \frac{90.0 \text{ g}}{249.6 \text{ g}} \times 100 = 36.1 \%$$

Another hydrate is magnesium sulfate heptahydrate, more commonly known as Epsom salts. Determine the formula weight in grams of this hydrate: MgSO₄ • 7H₂O.

Answer: 246.4 g

The percentage by weight of water in Epsom salts (MgSO₄ · 7H₂O) is $\frac{19}{2}$ %. (The weight of 7 mol of H₂O is $7 \times 18.0 = 126.0$ grams.)

Answer:
$$\% H_2O = \frac{126.0 \text{ g}}{246.4 \text{ g}} \times 100 = 51.1\%$$

When heated sufficiently, a hydrate will release all of its water molecules. Copper sulfate pentahydrate (CuSO₄ • $5H_2O$) is a deep blue color. Upon heating (symbolized by \triangle), it loses its water molecules and becomes white.

CuSO₄ •
$$5H_2O$$
 $\stackrel{\triangle}{\longrightarrow}$ CuSO₄ + $5H_2O$ (white anhydrous salt)

Upon heating, 1 mole of $CuSO_4 \cdot 5H_2O$ yields 1 mole of $CuSO_4$. How many mole(s) of H_2O result?

Answer: 5

The white CuSO₄ is the anhydrous (waterless) salt of the CuSO₄ • 5H₂O hydrate. In the presence of water, the white anhydrous CuSO₄ absorbs water into its crystal lattice and returns to the blue hydrate (CuSO₄ • 5H₂O). Every mole of CuSO₄ absorbs 5 mol of H₂O to form 1 mol of CuSO₄ • 5H₂O hydrate. One mole of water weighs 18.0 grams. One mole of CuSO₄ absorbs how many grams of H₂O to form 1 mol of CuSO₄ • 5H₂O hydrate?

Answer: 90.0 (5 x 18.0)

Suppose you had 3 mol of CuSO₄ • 5H₂O and heated it. Three moles of CuSO₄ • 5H₂O hydrate produces how many moles of H₂O when heated?

How many grams of H₂O?

Answer: 15; 270.0 (15 x 18.0)

If 1 kilogram of CuSO₄ • 5H₂O hydrate is heated, how many grams of water are produced? (Hint: Convert the kilogram of CuSO₄ • 5H₂O to moles of CuSO₄ • 5H₂O.)

Answer:

mol of
$$CuSO_4 \cdot 5H_2O = 1000 \text{ g} \times \frac{1 \text{ mol}}{249.6 \text{ g}} = 4.0 \text{ mol}$$

 $4.0 \text{ mol } CuSO_4 \cdot 5H_2O \text{ yield } (4.0 \times 5) = 20.0 \text{ mol } H_2O$
 $g H_2O = 20.0 \text{ mol } \times \frac{18 \text{ g}}{1 \text{ mol}} = 360.0 \text{ g}$

Suppose we know that Epsom salt is a hydrate, but we don't know the number of molecules of water that are part of the hydrate formula. In the following equation, a known weight of Epsom salt hydrate is heated. The resulting anhydrous MgSO₄ is weighed.

$$MgSO_4 \cdot ?H_2O \xrightarrow{\Delta} MgSO_4 + ?H_2O$$

Upon heating, the hydrate loses its water. To determine the weight of water lost, subtract the weight of ______ from the weight of _____.

Answer: MgSO₄; MgSO₄·?H₂O

In our equation from frame 24, if the weight of H₂O is known and the weight of anhydrous MgSO₄ is known, both weights can be converted to moles. The resulting mole fractions can be converted to simple whole numbers to determine the proper formula. Suppose that 3.5 mol of H₂O and 0.5 mol of MgSO₄ were produced when MgSO₄ · ?H₂O was heated. The appropriate formula for the hydrate would be MgSO₄ · ____ H₂O. (Divide each mole result by the smallest mole result to convert both to simple whole numbers.)

Answer:
$$\frac{0.5}{0.5} = 1$$
 and $\frac{3.5}{0.5} = 7$

The formula is MgSO₄ · 7H₂O.

The hydrate $BaCl_2 \cdot ?H_2O$ is heated to give:

$$BaCl_2 \cdot ?H_2O \xrightarrow{\Delta} BaCl_2 + ?H_2O.$$

A sample of the hydrate weighed 488.6 g before heating. After heating, the anhydrous BaCl₂ weighed 416.6 g. Determine:

- (a) the weight of the water formed.
- (b) the moles of water formed.
- (c) the moles of BaCl₂ formed.
- (d) the true hydrate formula.

Answer:

- (a) wt. of $H_2O = 488.6 \text{ g} 416.6 \text{ g} = 72.0 \text{ g} H_2O$
- (b) mol H₂O = 72.0 g × $\frac{1 \text{ mol}}{18.0 \text{ g}}$ = 4 mol H₂O
- (c) mol BaCl₂ = 416.6 g × $\frac{1 \text{ mol}}{208.3 \text{ g}}$ = 2 mol BaCl₂

(d)
$$\frac{\text{mol H}_2\text{O}}{\text{mol BaCl}_2} = \frac{4}{2} = 2$$

The formula is BaCl₂ · 2H₂O.

What does the dot (•) between BaCl₂ and 2H₂O in the BaCl₂ • 2H₂O hydrate indicate?

Answer: that water is an integral part of the crystal lattice of the hydrate (See frame 15 for review.)

Some chemical substances have the ability to absorb moisture from the atmosphere. Such substances are said to be hygroscopic. Flour and table salt are hygroscopic. White anhydrous CuSO₄ absorbs water to form the blue hydrate CuSO₄ • 5H₂O. Because of this very distinct color change, solid anhydrous CuSO₄ is used to detect the presence of water in other liquids. If the solid turns from white to blue when added to a liquid, water is present.

Some anhydrous salts absorb enough water to dissolve themselves in their own water of hydration. They are called **deliquescent**. Anhydrous CaCl₂ is such a substance and is often used on dusty dirt roads or race tracks to control the dust by keeping it moist.

Substances that absorb moisture from the atmosphere are _____.

Answer: hygroscopic (deliquescent if they absorb enough to dissolve in it)

KINDS OF SOLUTIONS

29

There is an upper limit to the amount of substance that a quantity of solvent can dissolve depending upon the type of solvent, the substance to be dissolved, and the temperature. A solution containing the maximum amount of solute at a given temperature is said to be saturated. Additional solute material will not dissolve in a saturated solution. An unsaturated solution contains less than the maximum amount of solute at a given temperature. Additional solute material will dissolve in an unsaturated solution.

Half a gram of NaCl, table salt, is added to an aqueous solution of NaCl. The added salt dissolves. What kind of solution is it, saturated or unsaturated?

Answer: unsaturated

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A solution can also be supersaturated, that is, made to hold more dissolved solute than normally expected at a given temperature. This can occur when a saturated solution is slowly cooled. The cooler solution then holds more dissolved solute than normal. If an additional crystal of solute is added to a supersaturated solution, the excess dissolved solute will quickly crystallize and come out of solution. After the excess solute comes out of solution, the remaining solution is saturated at the new temperature.

A crystal of NaCl is added to an aqueous solution of NaCl. The crystal will not dissolve but has no effect on the solution. What kind of solution is it — unsaturated, saturated, or supersaturated? ______

Answer: saturated

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A crystal of sodium thiosulfate is added to an aqueous sodium thiosulfate solution. Immediately, some of the solute crystallizes out of solution.

- (a) What kind of solution was it before the crystal was added?
- (b) What kind of solution is it after the solute crystallizes?

Answer: (a) supersaturated; (b) saturated

A solution with a relatively large amount of solute in a given amount of solvent is considered to be a concentrated solution. Concentrated is not a very precise term. It simply means that a relatively large proportion of the solution is made up of solute.

A solution with a relatively small amount of solute in a given amount of solvent is considered to be a dilute solution. Dilute means that a relatively small proportion of the solution is made up of solute.

Would a saturated solution of NaCl be considered concentrated or dilute?

Answer: concentrated (because it contains the maximum amount of NaCl)

A small amount of concentrated aqueous sodium chloride solution is added to a very large amount of solvent (water). The resulting aqueous solution is probably (concentrated, dilute) _______.

Answer: dilute

From this point on in this chapter, we do a great deal of manipulation of mathematical formulas and continue to use dimensional analysis in our problem solving. We suggest you obtain assistance if you have difficulty.

PROPORTIONS IN SOLUTIONS

It is useful to know precisely how dilute or concentrated a solution is. There are several methods of showing the proportion of solute to the solvent. One method of showing precise proportions is to give percent by weight. For example, a 10% solution of NaCl in water indicates that 10% of the solution weight is attributed to NaCl and 90% of the solution weight is attributed to the solvent.

In 100 grams of solution that is 10% NaCl by weight there are how many grams of NaCl? ______ How many grams of water? ______

Answer:

g NaCl = 10% NaCl
$$\times \frac{100 \text{ g solution}}{100\%}$$
 = 10 g NaCl g H₂O = g solution - g NaCl = 100 - 10 = 90 g H₂O

Our NaCl solution from frame 34 gives us the following:

solution percent by weight =
$$\frac{\text{weight of solute}}{\text{weight of solution}} \times 100\%$$

10% NaCl solution =
$$\frac{10 \text{ grams of NaCl}}{100 \text{ grams of solution}} \times 100\%$$

Determine the percent by weight of a solution of NaCl if there are 30 grams of NaCl dissolved in water to yield a total solution weight of 200 grams. Remember, in this case, the "part" is the solute weight and the "whole" is the total weight of the solution.

percent =
$$\frac{\text{part}}{\text{whole}} \times 100\%$$

Answer: % NaCl =
$$\frac{30 \text{ g NaCl}}{200 \text{ q solution}} \times 100\% = 15\% \text{ NaCl}$$

Twenty-five grams of NaOH (solute) are added to 175 grams of water (solvent).

What is the % NaOH in the solution? _____ (Note: The total solution weight includes the weight of both solvent and solute.)

Answer: total solution weight = 25 g solute + 175 g solvent = 200 g

% NaOH =
$$\frac{25 \text{ g NaOH}}{200 \text{ g solution}} \times 100\% = 12.5\% \text{ NaOH}$$

In 100 grams of an aqueous solution that is 15% NaCl by weight, there are how many grams of NaCl? _____ How many grams of water? _____

Answer:

g NaCl = 15% NaCl
$$\times \frac{100 \text{ g solution}}{100\% \text{ solution}} = 15 \text{ g NaCl}$$

g H₂O = g solution - g NaCl = 100 - 15 = 85 g H₂O

Concentrated HCl is actually an aqueous solution. Concentrated HCl is 37.9% by weight HCl. How many grams of concentrated 37.9% HCl solution does it take to yield 10 grams of HCl (solute)? (The grams of solution is the unknown.)

Answer: g solution = 10 g HCl
$$\times \frac{100 \text{ g solution}}{37.9 \text{ g HCl}}$$
 = 26.4 g solution

Let's try another one. What weight of dilute nitric acid solution contains 20 grams of HNO₃? The solution is 19% HNO₃ by weight. The total weight of the solution is _____ grams.

Answer: g solution = 20 g HNO₃ ×
$$\frac{100 \text{ g solution}}{19 \text{ g HNO}_3}$$
 = 105.3 g solution

It is also possible to determine the volume of the solution if both the weight and the density of the solution are known.

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

Weight is usually expressed in grams and volume in milliliters.

If a solution has a density of 1.5 grams per milliliter, how much volume would 3 grams of the solution occupy?

Answer:

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

volume = $\frac{\text{weight}}{\text{density}} = \frac{3 \text{ g}}{1.5 \text{ g/mL}} = 2 \text{ mL}$

In frame 39, it was determined that a weight of solution of 105.3 grams contained 20 grams of HNO₃ in a 19% aqueous HNO₃ solution. The total solution weighs 105.3 grams. The density of 19% HNO₃ solution is 1.11 grams per milliliter. The volume occupied by 105.3 grams at 1.11 grams per milliliter is ______ mL.

Answer: volume =
$$\frac{\text{weight}}{\text{density}}$$
 = 105.3 g × $\frac{1 \text{ mL}}{1.11 \text{ g}}$ = 94.9 mL

A liter of milk weighs 946 grams. What is the density of the milk in grams/milliliter (to the nearest thousandth)?

Answer: density =
$$\frac{946 \text{ g}}{\text{liter}} \times \frac{1 \text{ liter}}{1000 \text{ mL}} = 0.946 \text{ g/mL}$$

Instead of using weight percentage of solute in the solution and converting to volume, it is possible to determine volume percentage of the solute in the solution. Volume percentage is most often used when dealing with a solution involving two liquids, such as alcohol and water. Finding the volume percentage of the solute involves the familiar percentage formula.

$$\% = \frac{\text{part}}{\text{whole}} \times 100\%$$

solute percent by volume =
$$\frac{\text{solute volume}}{\text{total volume}} \times 100\%$$

A certain brand of homogenized milk contains 35 milliliters of butterfat in a total volume of 1 liter. What is the percent by volume of butterfat? ______

Answer: solute percent by volume

$$= \frac{\text{solute volume}}{\text{total volume}} \times 100\% = \frac{35 \text{ mL}}{1000 \text{ mL}} \times 100\% = 3.5\% \text{ butterfat}$$

The drugstore sells a solution of 3% hydrogen peroxide (H₂O₂) by volume. In a 150 milliliter quantity of this solution, there are how many milliliters of H₂O₂? (Hint: The volume of the solute is the unknown.)

Answer: volume $H_2O_2 = 150 \text{ mL solution} \times \frac{3 \text{ mL } H_2O_2}{100 \text{ mL solution}} = 4.5 \text{ mL } H_2O_2$

MOLARITY

Instead of the percentage by weight or volume of a solute within the solution, we may wish to deal with moles of solute within the solution. Molarity describes the moles of a solute within a total solution of 1 liter. A solution that is 0.3 molar means that 0.3 mol of solute are contained in 1 liter of solution. One liter of 0.5 molar NaCl solution contains how many moles of NaCl?

Answer: 0.5

Molarity (abbreviated by the italicized capital letter M) indicates the moles of solute contained within 1 liter of solution. If 3 mol of sugar were dissolved in enough water to make a total solution of 1 liter, the solution would be ______ M sugar.

Answer: 3

Again, molarity indicates moles of solute per liter of solution. The molarity specifies the concentration of solute within the solution. All of the 3 M sugar solution from frame 46 is a 3 M sugar solution, even the last few drops, because molarity is the concentration of the solute. If you took 1 liter of 3 M sugar solution and poured half of it (500 mL) in another container, what would be the molarity (concentration) of sugar solution in each container?

Answer: 3 M (The concentration of sugar solute remains the same — 3 mol per liter.)

We could also say that each container had $1\frac{1}{2}$ mol per half liter concentration. It is easier to use a standard such as moles per liter, however. An analogy is miles per hour as a designation for speed. If you were driving at a steady 50 miles per hour for half an hour, you would expect to have driven 25 miles. You were also driving at a speed of 25 miles per half hour, but it is more convenient to use miles per hour as a standard for speed rather than miles per half hour. If you took $1\frac{1}{2}$ mol of sugar and added enough water to make a total of 500 milliliters of solution, the

concentration of sugar solute would be _____ M. (Remember, molarity = moles per liter.)

Answer:
$$M = \frac{\text{mol}}{1 \text{ liter}} = \frac{1.5 \text{ mol}}{0.5 \text{ liter}} = 3 M$$

If 0.1 mol of NaCl was dissolved in water to make 100 milliliters of solution, the concentration of NaCl in the solution will be ______ M.

Answer:
$$M = \frac{\text{mol}}{\text{liter}} = \frac{0.1 \text{ mol}}{0.1 \text{ liter}} = 1 M$$

The weight of a solute can be changed to moles to determine the molarity of a solution.

mol of solute =
$$\frac{\text{weight of solute}}{\text{formula weight}}$$

molarity = $M = \frac{\text{mol of solute}}{\text{liters}}$

The two formulas can be combined as follows:

$$M = \frac{\text{wt. solute} \times \left(\frac{1 \text{ mol solute}}{\text{formula wt. solute}}\right)}{\text{liters of solution}}$$

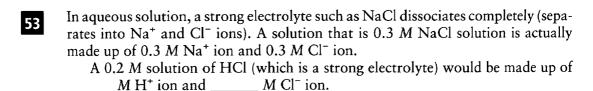
The formula weight for NaCl is 58.4 grams. (To review, see Chapter 4.) If 87.8 grams of NaCl solute is dissolved in enough water to make 3 liters of solution, what molarity would the resulting NaCl solution have?

Answer:
$$M = \frac{87.8 \text{ g NaCl} \times \left(\frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}}\right)}{3.0 \text{ liters solution}} = \frac{1.5 \text{ mol NaCl}}{3.0 \text{ liters solution}} = 0.5 M$$

Answer:
$$M = \frac{37.5 \text{ g Ba}(\text{MnO}_4)_2 \times \left(\frac{1 \text{ mol Ba}(\text{MnO}_4)_2}{375.1 \text{ g Ba}(\text{MnO}_4)_2}\right)}{1 \text{ liter solution}} = 0.1 \text{ M Ba}(\text{MnO}_4)_2$$

The formula weight of NaCl is 58.4 grams per mol. How many grams of NaCl are needed to make 2 liters of a 0.3 M NaCl solution?

Answer: g NaCl = 2 liters solution
$$\times \frac{0.3 \text{ mol NaCl}}{1 \text{ liter solution}} \times \frac{58.4 \text{ g NaCl}}{1 \text{ mol NaCl}} = 35.0 \text{ g NaCl}$$



Answer: 0.2; 0.2

 H_2SO_4 is also a strong electrolyte that dissociates into two H⁺ ions and one SO_4^{2-} ion.

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

That is, one molecule of H_2SO_4 yields two H^+ ions and one SO_4^{2-} ion in aqueous solution. One mole of H_2SO_4 molecules would yield 2 mol of H^+ ions and 1 mol of SO_4^{2-} ions. Two moles of H_2SO_4 would yield 4 mol H^+ ions, and so on. So a 0.1 M solution of H_2SO_4 results in 0.2 M H^+ ions and 0.1 M SO_4^{2-} ions.

Assume that H₃PO₄ is a strong electrolyte and dissociates completely.

$$H_3PO_4 \to 3H^+ + PO_4^{3-}$$

A solution of H_3PO_4 that is 0.1 M results in _____ M H^+ ions and ____ M PO_4^{3-} ions.

Answer: 0.3; 0.1

A liter of 0.1 M solution of H₃PO₄ contains how many times the concentration of hydrogen ions as does a liter of 0.1 M solution of HCl?

$$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$$

 $HCl \rightarrow H^+ + Cl^-$

Answer: three times as much

A liter of 0.1 M solution of NaOH, which is a strong electrolyte, produces a _____ M concentration of OH⁻ ions and a _____ M concentration of Na⁺ ions.

Answer: 0.1; 0.1

What would be the OH⁻ ion concentration in a 0.1 M Ba(OH)₂ solution? Assume Ba(OH)₂ is a strong electrolyte.

Answer: 0.2 M OH

We will use H⁺ ion and OH⁻ ion molar concentrations later in Chapter 13, when we further discuss acids and bases.

COLLIGATIVE PROPERTIES OF SOLUTIONS AND MOLALITY

abbreviated kg.)

| _ | |
|---|--|
| | The physical properties of a solution are somewhat different from the properties of the pure solvent. The amount and kind of solute in the solution affects such properties as boiling point, freezing point, and vapor pressure. These properties that vary according to the ratio of the weights of the solute and solvent are known as colligative properties. In general, as solute is added the resulting solution will have a lower freezing point, lower vapor pressure, and higher boiling point than the pure solvent. What happens to the freezing point of the water in an automobile cooling system when radiator antifreeze (the solute) is added to water (the solvent)? |
| | Answer: The freezing point decreases or lowers (The typical automobile radiator antifreeze solution is made up of half water as the solvent and half ethylene glycol as the solute. The freezing point is typically about –37° Celsius. The boiling point of the solution is increased.) |
| | When dealing with solutions for chemical reactions such as neutralization, it is practical to use molarity (M) as the standard for the concentration of the solute in the solution. Molarity indicates moles of solute within each liter of solution. When working with colligative properties, however, it is more useful to deal with a different standard of the concentration of solute in the solution. This standard is molality. Molality, abbreviated by the small letter m, indicates the moles of solute in each kilogram of solvent. When dealing with physical properties such as the boiling point elevation of a solution, it is more practical to use moles of solute per (liter of solution, kilogram of solvent) |
| | Answer: kilogram of solvent |
| | Molarity is abbreviated by and indicates moles of solute per of Molality is abbreviated by and indicates moles of solute per of |
| | Answer: M; liter; solution; m; kilogram; solvent |
| | Here is the equation for determining molality. |
| | |
| | $m = \frac{\text{mol of solute}}{\text{kilogram solvent}}$ |

Three moles of sugar are added to 1000 grams of H_2O solvent. The molality of the resulting solution is _____ m. (Hint: Change weight of solvent to kilograms,

Answer:
$$m = \frac{3 \text{ mol of solute}}{1 \text{ kg solvent}} = 3 m$$

Two moles of sugar are added to 500 grams of H_2O solvent. The molality of the resulting solution is _____ m.

Answer:
$$m = \frac{2 \text{ mol of solute}}{0.5 \text{ kg solvent}} = 4.0 \text{ m}$$

Molality can also be determined from the number of grams of solute by substituting the formula for moles in the formula for molality.

$$mol = \frac{\text{weight (grams)}}{\text{formula weight}}$$
$$m = \frac{\text{mol of solute}}{\text{kilogram solvent}}$$

The new formula becomes:

$$m = \frac{\text{weight of solute in grams} \times \left(\frac{1 \text{ mol solute}}{\text{formula wt. solute}}\right)}{\text{kilograms of solvent}}$$

Let's use this formula to determine the molality of a glucose solution. Fifty grams of glucose ($C_6H_{12}O_6$) are added to 0.250 kilograms of water. Assume the formula weight of glucose ($C_6H_{12}O_6$) is 180 grams. The molality of this glucose solution is m.

Answer:
$$m = \frac{50 \text{ g glucose} \times \left(\frac{1 \text{ mol}}{180 \text{ g}}\right)}{0.250 \text{ kg of solvent}} = 1.1 \text{ m}$$

Determine the molality of a solution involving 22.5 grams of glucose dissolved in 500 grams of water. The formula weight of glucose is 180 grams. The molality of this glucose solution (to the nearest hundredth) is _____ m. (Note: Be sure to change grams of solvent to kilograms.)

Answer:
$$m = \frac{22.5 \text{ g glucose} \times \left(\frac{1 \text{ mol glucose}}{180 \text{ g glucose}}\right)}{0.500 \text{ kg of solvent}} = 0.25 \text{ m}$$

Determine the molality of a solution involving 116.8 grams of NaCl dissolved in 500 grams of water. The molality of this NaCl solution is _____ m.

Answer:
$$m = \frac{116.8 \text{ g NaCl} \times \left(\frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}}\right)}{0.500 \text{ kg of solvent}} = 4.0 \text{ m}$$

How many grams of solute are necessary to produce a 2.50 m solution of CaCl₂ dissolved in 500 grams of water? The formula weight of CaCl₂ is 111 grams.

Answer: $g CaCl_2 = 0.500 \text{ kg solvent} \times \frac{2.50 \text{ mol } CaCl_2}{1 \text{ kg solvent}} \times \frac{111 \text{ g } CaCl_2}{1 \text{ mol } CaCl_2} = 138.8 \text{ g } CaCl_2$

In dealing with liquid solutes in liquid solvents, the amount of solute and sometimes the solvent is given in terms of volumes such as liters or milliliters. Volumes must be converted to weights in order to determine the molality of the resulting solution. If we are given the volume of a liquid, we also need the density of the liquid in order to determine its weight. Density is usually expressed as grams per cubic centimeter or grams per milliliter. To find the weight in grams of a liquid, multiply the density times the volume (density × volume = weight). The density of ethyl alcohol is found to be 0.80 grams per milliliter. Determine the weight in grams of 23.75 milliliters of ethyl alcohol.

Answer: wt. of alcohol = 0.80 g/mL × 23.75 mL = 19.0 g alcohol

Determine the weight in grams of 300 mL of benzene (C₆H₆) if the density of benzene is 0.90 grams per milliliter.

Answer: wt. of benzene = 0.90 g/mL × 300 mL = 270 g benzene

A solution is made up of 23.75 mL of ethyl alcohol solute added to 300 mL of benzene solvent. In frames 67 and 68 you have just determined the weight of the ethyl alcohol to be 19.0 grams and the weight of benzene to be 270 grams. The formula weight of C₂H₅OH (ethyl alcohol) is 46 grams. Determine the molality of this solution.

Answer:
$$m = \frac{19 \text{ g alcohol} \times \left(\frac{1 \text{ mol alcohol}}{46 \text{ g alcohol}}\right)}{0.270 \text{ kg benzene}} = 1.5 \text{ m}$$

MOLE FRACTION AND VAPOR PRESSURE

Placing a solute in a solvent lowers the vapor pressure of the solvent. If both the solvent and the solute are liquids, the vapor pressure of the solution is due to both solute and solvent. The amount contributed to the vapor pressure by either solute or solvent depends upon the mole fraction of each within the solution.

total mol in a solution = mol of solute + mol of solvent

The mole fraction is simply the number of moles of one of the components of the solution (either solute or solvent) divided by the total number of moles in the solution.

mole fraction of solute =
$$\frac{\text{mol of solute}}{\text{mol of solute + mol of solvent}}$$
mole fraction of solvent =
$$\frac{\text{mol of solvent}}{\text{mol of solute + mol of solvent}}$$

A solution contains 3 mol of solute and 12 mol of solvent. What is the mole fraction of solute?

Answer:
$$\frac{3}{3+12} = \frac{1}{5}$$
 or 0.2

A solution contains 3 mol of solute and 12 mol of solvent. What is the mole fraction of the solvent?

Answer:
$$\frac{12}{3+12} = \frac{4}{5}$$
 or 0.8

- All mole fractions in a solution must add up to 1. A solution is made up of 23 grams of ethyl alcohol (C_2H_5OH) and 156 grams of benzene (C_6H_6). The formula weight of C_2H_5OH is 46 grams per mol. The formula weight of C_6H_6 is 78 grams per mol.
 - (a) What is the mole fraction of ethyl alcohol?
 - (b) What is the mole fraction of benzene?
 - (c) What is the sum of the mole fractions of ethyl alcohol and benzene?

Answer:

(a) mol of
$$C_2H_5OH = \frac{23 \text{ grams}}{46 \text{ grams/mol}} = 0.5 \text{ mol}$$

mol of $C_6H_6 = \frac{156 \text{ grams}}{78 \text{ grams/mol}} = 2.0 \text{ mol}$
mole fraction of $C_2H_5OH = \frac{0.5}{0.5 + 2.0} = 0.2$

- (b) mole fraction of $C_6H_6 = \frac{2.0}{0.5 + 2.0} = 0.8$
- (c) The combined mole fractions are equal to 1 (0.2 + 0.8 = 1).
- A solution can be made of more than two components. To determine the mole fraction of one component in a solution made up of several components, just divide the moles of the component by the total moles in the solution.

In a solution made up of A, B, and C, suppose you wish to know the mole fraction of A.

mole fraction A =
$$\frac{\text{mol A}}{\text{mol A + mol B + mol C}}$$

In this same solution, what is the mole fraction of B?

Answer: mole fraction
$$B = \frac{\text{mol } B}{\text{mol } A + \text{mol } B + \text{mol } C}$$

A solution is made up of 92 grams of ethyl alcohol (C₂H₅OH), 54 grams of H₂O, and 29 grams of acetone (CH₃COCH₃). The formula weight of C₂H₅OH is 46 grams. The formula weight of H₂O is 18 grams. The formula weight of CH₃COCH₃ is 58 grams. Determine the mole fraction of acetone in the solution (to the nearest hundredth).

Answer:

mol of
$$C_2H_5OH = \frac{92 \text{ grams}}{46 \text{ grams/mol}} = 2 \text{ mol of } C_2H_5OH$$

mol of $H_2O = \frac{54 \text{ grams}}{18 \text{ grams/mol}} = 3 \text{ mol of } H_2O$
mol of $CH_3COCH_3 = \frac{29 \text{ grams}}{58 \text{ grams/mol}} = 0.5 \text{ mol of } CH_3COCH_3$
mole fraction of $CH_3COCH_3 = \frac{0.5}{2 + 3 + 0.5} = 0.09$

A solution made of two or more liquids has a vapor pressure that is determined by the mole fractions of the liquids that make up the solution. This general statement leads to Raoult's Law. Raoult's Law is expressed mathematically as:

$$P_A = X_A P_A^0$$

 P_A is the vapor pressure contributed by liquid A in the solution. X_A is the mole fraction of liquid A in the solution. P_A^0 is the vapor pressure of liquid A in its pure form.

A solution is made up of toluene and benzene. Toluene is present in a mole fraction of 0.6 and has a vapor pressure of 70 torr in the pure form. We want to find the vapor pressure contributed by toluene in the solution.

$$P_{\text{toluene}} = X_{\text{toluene}} P_{\text{toluene}}^0$$

That is, the vapor pressure contributed by toluene equals the mole fraction of toluene multiplied by the vapor pressure of pure toluene. The vapor pressure contributed by toluene = ______ torr.

Answer:

$$P_{\text{toluene}} = X_{\text{toluene}} P_{\text{toluene}}^{0}$$

 $P_{\text{toluene}} = (0.6)(70 \text{ torr}) = 42 \text{ torr}$

| 76 | In the same solution of benzene and toluene, benzene also contributes to the vapor |
|-----------|--|
| 70 | pressure of the solution. |

$$P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^{0}$$

To determine the vapor pressure contributed by benzene, we must know the mole fraction of benzene in the solution and the vapor pressure of pure benzene. There are only two liquids in the solution. All mole fractions in a solution add up to equal 1. If toluene accounts for a mole fraction of 0.6, what is the benzene mole fraction?

Answer: 0.4 (1 - 0.6)

In the solution of toluene and benzene, the benzene has a mole fraction of 0.4 and the vapor pressure of benzene in pure form is equal to 190 torr. Use Raoult's Law to calculate the vapor pressure contributed by benzene in this solution.

Answer:

$$P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^0$$

 $P_{\text{benzene}} = (0.4)(190 \text{ torr}) = 76 \text{ torr}$

In our solution made up of toluene and benzene, toluene contributes 42 torr to the vapor pressure of the solution and benzene contributes 76 torr to the vapor pressure of the solution. The total vapor pressure above the solution is the sum of all of the partial vapor pressures (from Dalton's Law of partial pressures, discussed in Chapter 8). The total vapor pressure of the solution is _______ torr.

Answer: 118 (42 + 76)

- Raoult's Law predicts *ideal* vapor pressures. The actual vapor pressure may be slightly more or less than predicted. Another toluene and benzene solution is prepared with a mole fraction of 0.7 for toluene. Assume the vapor pressure of pure toluene liquid to be 70 torr and the vapor pressure of pure benzene liquid to be 190 torr.
 - (a) What is the ideal vapor pressure contributed by toluene in the solution?
 - (b) What is the total ideal vapor pressure of this solution?

Answer:

(a)
$$P_{\text{toluene}} = X_{\text{toluene}} P_{\text{toluene}}^0$$

 $P_{\text{toluene}} = (0.7)(70 \text{ torr}) = 49 \text{ torr}$

(b) The mole fractions of all components in the solution add up to 1. Since toluene accounts for 0.7 mole fraction, the remainder must be attributed to benzene.

$$1 - 0.7 = 0.3$$

$$P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^{0}$$

$$P_{\text{benzene}} = (0.3) (190 \text{ torr}) = 57 \text{ torr}$$

The total vapor pressure is the sum of all partial vapor pressures in the solution. The total vapor pressure is 49 torr + 57 torr = 106 torr.

Raoult's Law also applies to solutions in which the solute is a solid with no vapor pressure. If solid sugar is dissolved in water, the vapor pressure of the water is lowered according to its mole fraction as predicted by Raoult's Law. The solid sugar had almost no measurable vapor pressure, so the entire vapor pressure of the sugar—water solution is contributed by the water. The vapor pressure of pure water is 23.8 torr at 25°C. Sugar is added to the water until the water makes up a mole fraction of 0.75 in the solution.

- (a) What is the vapor pressure of the water in the solution?
- (b) Since the sugar has no measurable vapor pressure, what is the total vapor pressure of the solution?

Answer:

- (a) $P_{\text{water}} = X_{\text{water}} P_{\text{water}}^{0}$ $P_{\text{water}} = (0.75)(23.8 \text{ torr}) = 17.9 \text{ torr}$
- (b) The total vapor pressure of the solution is the same as the vapor pressure contributed by the water since the sugar has no vapor pressure. Total vapor pressure = 17.9 torr.

BOILING POINT ELEVATION

The vapor pressure of a solvent (such as water) is reduced when a solute with no vapor pressure of its own is added to the solvent. Remember that the boiling point of a liquid is the temperature at which the vapor pressure equals the confining pressure. If a nonvolatile solute (one with no vapor pressure of its own) is added to a solvent, the boiling point of the solvent is raised because the vapor pressure is reduced. The more solute added, the more the vapor pressure is reduced, and the more the boiling point is increased.

Adding 1 mol of a nonvolatile solute that is also a nonelectrolyte to 1 kg of water raises the boiling point by 0.51°C. If the boiling point of pure water is 100.00°C, then adding 1 mol of nonvolatile and nonelectrolytic solute to 1 kg of water raises the boiling point of the solution to the new temperature of

Answer: 100.51 (100.00°C + 0.51°C)

The presence of 1 mol of any nonvolatile nonelectrolyte such as sugar added to 1 kg of water raises the boiling point of the water by 0.51°C. This 0.51°C is known as the molal boiling point constant for water.

A sugar-water solution that is 1 m boils at 100.51°C at standard pressure. A sugar-water solution of 1 m raises the boiling point of water by 0.51°C. A sugar-water solution of 2 m raises the boiling point by twice the molal boiling point constant (2 × 0.51 = 1.02°C). A sugar-water solution of 3 m raises the boiling point by 3 times as much, or _____°C.

Answer: 1.53 (3 × 0.51°C)

The molal boiling point constant is usually abbreviated as K_b . The K_b for water is 0.51°C/m. (The K_b varies for other solvents.) A useful formula for predicting the boiling point of solutions is:

$$\Delta T_b = K_b \times m.$$

The increase in the boiling point (ΔT_b) equals the molal boiling point constant (K_b) multiplied by the molality (m) of the solution. For example, if the molality of a sugar-water solution is 3 m, then the increase in boiling point (ΔT_b) equals 0.51°C multiplied by 3, or 1.53°C. Calculate the increase in the boiling point if a sugar-water solution has a molality of 5 m.

$$\Delta T_b =$$

Answer: $K_b \times m = 0.51^{\circ}\text{C} \times 5 = 2.55^{\circ}\text{C}$

A sugar-water solution of 7.0 m would increase the boiling point by _____ $^{\circ}$ C.

Answer: 7.0×0.51 °C = 3.57°C

We can also modify the formula to determine the molality of a solution, by solving for m.

$$m = \frac{\Delta T_b}{K_b}$$

What is the molality of a sugar-water solution that increases the boiling point by 0.255°C?

Answer:
$$m = \frac{\Delta T_b}{K_b} = \frac{0.255^{\circ}\text{C}}{0.51^{\circ}\text{C/m}} = 0.5 \text{ m}$$

FREEZING POINT DEPRESSION

A nonvolatile solute not only raises the boiling point of the solution, but it also lowers the freezing point of the solution. Each mole of any nonvolatile nonelectrolyte,

such as sugar, in 1 kg of water will lower the freezing point by 1.86°C. Since the normal freezing point of water is 0°C, the new freezing point of a solution of 1 mol of sugar added to 1 kg of water will be ______ °C.

Answer: -1.86

The molal freezing point constant for water is -1.86°C/m. The molal freezing point constant is abbreviated as K_f and varies for different solvents as does K_b . The formula for determining the freezing point decrease is:

$$\Delta T_f = K_f \times m$$
.

Determine the value of ΔT_f (the amount of decrease in the freezing point) of a 3 m sugar-water solution. $\Delta T_f =$ ______.

Answer: -1.86°C × 3 = -5.58°C

The freezing point change for a 2.5 m solution of sugar-water would be _____°C.

Answer: $-4.65 (-1.86^{\circ}C \times 2.5 = -4.65^{\circ}C)$

As with the formula for boiling point increase, the freezing point decrease formula can also be used to determine the molality of a solution.

$$m = \frac{\Delta T_f}{K_f}$$

The molality of a sugar-water solution that freezes at -3.50°C (to the nearest hundredth) is ______.

Answer: The change in freezing point is -3.50°C.

$$m = \frac{\Delta T_f}{K_f} = \frac{-3.50^{\circ}\text{C}}{-1.86^{\circ}\text{C/m}} = 1.88 \text{ m}$$

- The sugar solution has been used in the previous examples because it is a nonelectrolyte and the formulas are valid only for such substances. The formulas involving the molal freezing and boiling point constants are valid for which of the following?
 - ____ (a) NaCl, a strong electrolyte
 - ____ (b) sugar, a nonelectrolyte
 - ____ (c) acetic acid, a weak electrolyte

Answer: only (b)

Every mole of a nonelectrolyte will lower the freezing point and raise the boiling point by an amount equal to K_f and K_b . Each mole has a specific number of particles, so

we can say that the greater the number of solute particles in a solvent the greater will be the freezing point decrease and boiling point increase. A strong electrolyte such as 1 mol of NaCl in a kilogram of water is actually a solution of 1 mol of Na⁺ ions and 1 mol of Cl⁻ ions, or 2 mol of particles. So a solution of 1 m NaCl would have the same effect as a 2 m solution of sugar. What would be the change in freezing point of a 1 m NaCl solution?

Answer: $-1.86^{\circ}C \times 2 = -3.72^{\circ}C$

 K_2SO_4 is a strong electrolyte.

$$K_2SO_4(s) \to 2K^+(aq) + SO_4^{2-}(aq)$$

Calculate the change in the boiling point of a 1 m K₂SO₄ solution.

Answer: $0.51^{\circ}C \times 3 = 1.53^{\circ}C$

A 1 m aqueous solution of carbonic acid, H_2CO_3 , has lowered the freezing point -3.00°C. Is H_2CO_3 a strong electrolyte, weak electrolyte, or nonelectrolyte?

Answer: weak electrolyte (If it were a nonelectrolyte the freezing point would be lowered $-1.86 \times 1 = -1.86$ °C. If it were a strong electrolyte and dissociated as $H_2CO_3 \rightarrow H^+ + HCO_3^-$, the lowering would be $-1.86 \times 2 = -3.72$ °C. It might also dissociate as $H_2CO_3 \rightarrow 2H^+ + CO_3^{2-}$, giving a lowering of $-1.86 \times 3 = -5.58$ °C. The ΔT_f falls between the expected values for a nonelectrolyte and strong electrolyte and is, therefore, presumed to be a weak electrolyte.)

In reality, $1 \, m$ NaCl and $1 \, m \, K_2 SO_4$ do not affect the freezing point and boiling point changes as expected. They do not have 2 or 3 times the effect predicted by their 100% dissociation. They have somewhat less effect because the "activity" of the ions is not ideal, but that activity is beyond the scope of this book. In general, nonelectrolytes conform to the expected molal freezing and boiling point constants. Weak electrolytes decrease the freezing point and increase the boiling point only slightly beyond that of nonelectrolytes. Strong electrolytes (which dissociate completely) come close to having each ion act independently in increasing the boiling point and decreasing the freezing points.

You have just learned several things about solutions that chemists and industries use daily in the laboratory or in the factory to produce desired products or results. We could not operate without understanding the solute-solvent properties and relationships we have discussed. You will encounter the concentration terms in the remaining chapters of this book and most certainly in any other chemistry course you might take.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test. Round answers to the nearest hundredth unless otherwise indicated.

| 1. | Complete and balance the following equations. Indicate if the product(s) of each equation is called an acid or a base. | | |
|----|---|--|--|
| | (a) $CO_2 + H_2O \rightarrow \underline{\hspace{1cm}}$ | | |
| | (b) $Na_2O + H_2O \rightarrow$ | | |
| 2. | How many grams of H_2O could you obtain from 1 kg of $CuSO_4 \cdot 5H_2O$ (to the nearest gram)? | | |
| 3. | A solution contains 58 g of acetone (CH_3COCH_3), 69 g of ethyl alcohol (C_2H_5OH), and 63 g of H_2O . What is the mole fraction of water in this mixture? | | |
| 4. | A solution containing 15 g of an unknown substance dissolved in 100 g of water has a boiling point of 100.255°C. What is the molecular weight of the unknown (to the nearest gram)? | | |
| 5. | A 1 <i>m</i> solution of HCN has a boiling point of 100.72°C. Is it a strong electrolyte, a weak electrolyte, or nonelectrolyte? Defend your answer. | | |
| 6. | What is the molarity of a solution that contains 16.5 g $(NH_4)_2SO_4$ in 100 mL of solution? | | |
| 7. | Ammonia gas is passed into water yielding a solution whose density is 0.93 g/ml and is 18.6% by weight of NH_3 . What is the weight of NH_3 per mL of solution? | | |
| 8. | What is the vapor pressure of an aqueous solution of 30.0 g of urea, $(NH_2)_2CO$ dissolved in 200 g of H_2O at 25°C? The vapor pressure of pure H_2O at 25°C is 23.8 torr. (Round to the nearest tenth.) | | |
| | | | |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

1. H₂CO₃ (acid); (b) 2NaOH (base) (frames 5-11)

2. 1 kg CuSO₄ · 5H₂O =
$$\frac{1000 \text{ g}}{249.6 \text{ g/mol}}$$
 = 4.01 mol CuSO₄ · 5H₂O

1 mol of hydrate would yield 5 mol of H₂O.

 \therefore 4.01 mol of hydrate would yield (4.01)(5) = 20.0 mol H₂O

$$\therefore$$
 g of H₂O obtained = (20.0 mol)(18 g/mol) = 360 g

(frames 16-23)

3. mole fraction water =
$$\frac{n_1}{n_1 + n_2 + n_3}$$

$$n_1 = \text{mol of water} = \frac{63 \text{ g}}{18 \text{ g/mol}} = 3.5 \text{ mol H}_2\text{O}$$

$$n_2$$
 = mol of acetone = $\frac{58 \text{ g}}{58 \text{ g/mol}}$ = 1.0 mol of acetone

$$n_3$$
 = mol of ethyl alcohol = $\frac{69 \text{ g}}{46 \text{ g/mol}}$ = 1.5 mol of ethyl alcohol

:. mole fraction
$$H_2O = \frac{3.5}{1.0 + 1.5 + 3.5} = \frac{3.5}{6.0} = 0.58$$
 mole fraction H_2O (frames 70–74)

4. molecular weight solute =
$$\frac{\text{(weight of solute)}(K_b)}{(\Delta T_b)(\text{kg solvent)}}$$

(Note: Assume substance is a nonelectrolyte.)

:. molecular weight =
$$\frac{(15)(0.51)}{(0.255)(0.100)}$$
 = 300 g (frames 81–93)

5. If it is a nonelectrolyte, 1 m HCN should boil at 100.51°C (100°C + ΔT_b).

$$\Delta T_b = (1)(0.51) = 0.51$$
°C

:. boiling point =
$$100^{\circ}\text{C} + 0.51^{\circ}\text{C} = 100.51^{\circ}\text{C}$$

If it is a strong electrolyte (HCN \rightarrow H⁺ + CN⁻), then a 1 m solution should boil at 101.02°C.

$$\Delta T_b = (2)(0.51) = 1.02$$
°C

$$\therefore$$
 boiling point = 100°C + 1.02°C = 101.02°C

Since the observed boiling point is between these two extremes, we would conclude that it is a weak electrolyte, only partially dissociated. (frames 81–93)

6.
$$M = \frac{\text{mol}}{\text{liter}} = \frac{16.5 \text{ g} \times \left(\frac{1 \text{ mol}}{132 \text{ g}}\right)}{0.100 \text{ liter}} = 1.25 M$$
(frames 45–51)

7. weight NH₃ = density \times % by wt. \times volume = 0.93 g/mL \times 0.186 \times 1 mL = 0.17 g (frames 34-41)

8.
$$P_A$$
 = vapor pressure of solution

$$X_A$$
 = mole fraction of solvent

 P_A^0 = vapor pressure of pure solvent

$$P_A = X_A P_A^0$$

$$X_A = \frac{n_A}{n_A + n_B}$$

$$n_A = 200 \text{ g} \times \frac{1 \text{ mol}}{18 \text{ g}} = 11.1 \text{ mol H}_2\text{O}$$

$$n_A = 30 \text{ g} \times \frac{1 \text{ mol}}{60 \text{ g}} = 0.5 \text{ mol urea}$$

$$X_A = \frac{11.1}{11.1 + 0.5} = 0.96$$

$$P_A = (0.96)(23.8) = 22.8$$

(frames 76-80)

12 Chemical Equilibrium

You have just learned several properties of solutions (mixtures of solids, liquids, and gases). We have discussed reactions that go to completion (reactants totally consumed, leaving only new products) in Chapter 5 and electrolytes that dissociate completely in water in Chapter 11. Both of these concepts imply a one-way reaction, continuous movement towards the product side. However, in Chapter 10 we discussed a dynamic equilibrium where the rate of evaporation equals the rate of condensation, that is, the reactions are "reversible."

Many chemical reactions are reversible. The products formed react to give back the original reactants, even as the reactants are forming more products. After some time, both the forward and reverse reactions will be going on at the same rate. When this occurs, the reaction is said to have reached equilibrium. There is no further change in the *amount* of any reactant or product, though both reactions still go on (forever). Since there are many such reactions that appear to go only partway to completion, their study is of major importance to the chemist.

We will discuss several types of equilibrium in this chapter, along with their associated problems and concepts. You will use the concept of molarity you just learned in Chapter 11 to solve equilibrium problems.

OBJECTIVES

After completing this chapter, you will be able to

- recognize and apply or illustrate: equilibrium, equilibrium constant, equilibrant, equilibrium mixture, homogeneous equilibrium, heterogeneous equilibrium, Le Chatelier's Principle, common ion effect, ion product constant;
- define "reversible reaction" and write an example, and recognize at sight whether
 a chemical equation is written so as to indicate that the reaction is reversible;
- given a chemical equation, write the equilibrium constant expression;
- given the equilibrium constant expression, write the equation for the corresponding chemical reaction;
- given the equilibrium constant expression, state the units of K_{eq} ;
- predict whether changing the temperature of a system in equilibrium will shift the equilibrium to the right or to the left;

- state the effect on a system in chemical equilibrium of removing (or adding) a portion of one reactant (or product) and increasing (or decreasing) the total pressure on a system in equilibrium;
- given the balanced chemical equation for the ionization of a weak acid (or weak base), write the expression for the equilibrium constant;
- given the equilibrium constant expression and all the terms in the equation but one, solve for the unknown;
- given the data needed to calculate concentration terms for the equilibrium calculation, change the data into concentrations;
- given the degree of ionization (percent ionization or fraction ionized) of a weak acid or weak base, calculate K_{eq} , or given K_{eq} and the necessary concentrations, calculate the degree of ionization;
- write the chemical equation and the ion product constant expression for the ionization of water.
- In Chapter 10, you learned about Le Chatelier's Principle in connection with the evaporation and condensation of liquids. Le Chatelier's Principle involved stresses placed upon a dynamic equilibrium. In the case of evaporation and condensation, which are two opposite processes, a dynamic equilibrium occurs when the rate of evaporation and the rate of condensation are equal. Both processes continue, but the rates are equal at equilibrium.

In a dynamic equilibrium, two opposite processes continue to occur, but the rates of the opposite processes must be equal. According to Le Chatelier's Principle, when a system in equilibrium is subjected to a stress, the system will change its conditions, relieving the stress and forming a new equilibrium.

In a covered jar containing a little water, the rates of evaporation and condensation will be equal after a time and equilibrium is achieved. If the covered jar is suddenly pressurized, the rate of condensation will suddenly be increased,

- (a) What is the stress in this example?
- (b) What will happen to the rate of evaporation to restore dynamic equilibrium?

Answer: (a) pressure (the sudden pressurization of the jar); (b) The rate of evaporation will decrease suddenly. After a time it will again equal the rate of condensation, thus reestablishing equilibrium.

The following two reactions are completely opposite processes.

$$CO_2 + H_2 \rightarrow H_2O + CO$$

 $CO + H_2O \rightarrow CO_2 + H_2$

The reactants of the first reaction are the products in the second reaction and vice versa. Both reactions can be written as one reversible reaction.

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

In this reversible reaction, what symbol(s) are used to indicate that the reaction is reversible?

Up to this point we have treated all reactions as if they went to completion and continued until one or more of the reactants was consumed. At that point the reaction stopped. However, the reversible reaction in frame 2 proceeds in one direction or the other until an equilibrium is achieved. At equilibrium, all reactants and products are still available in some concentration. Both of the opposite reactions continue at the same rate at equilibrium, but the proportion of reactants and products remains unchanged as long as the equilibrium is maintained.

When a reversible reaction goes to equilibrium, do the opposite reactions stop?

Answer: no (Both of the opposite reactions continue at equilibrium but the rates of the two reactions are equal.)

The following reversible reaction:

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

can also be written as:

$$H_2O + CO \rightleftharpoons CO_2 + H_2$$

By convention, the starting materials of the reaction are written on the left side of the equation. The substances on the left side are also arbitrarily called the reactants, and those on the right side are called the products. The reaction with the arrow pointing to the right (\rightarrow) is called the forward reaction. The reaction with the arrow pointing to the left (\leftarrow) is called the reverse reaction.

Write a reversible reaction with the starting material of H₂ and I₂ (product would be HI).

Answer: $H_2 + I_2 \rightleftharpoons 2HI$

Indicate whether each of the following is a forward or reverse reaction.

(a)
$$PCl_5 \rightarrow PCl_3 + Cl_2$$

(b)
$$PCl_3 + Cl_2 \leftarrow PCl_5$$

Answer: (a) forward; (b) reverse

Reversible reactions that go to equilibrium (instead of to completion) end up with an equilibrium mixture of reactants and products after equilibrium is reached. The equilibrium mixture contains various concentrations of each reactant and product.

List all the substances found in the equilibrium mixture of the reversible reaction below.

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

Answer: CO₂, H₂, CO, and H₂O (all reactants and products)

When a reversible reaction reaches chemical equilibrium, the concentrations of the components in the equilibrium mixture (the products and reactants) remain constant as long as experimental conditions are not changed. At chemical equilibrium, how does the rate of the forward reaction compare with the rate of the reverse reaction?

Answer: The rates are equal.

EQUILIBRIUM CONSTANT

For most reversible reactions going to equilibrium, equilibrium constants have been determined experimentally. An equilibrium constant is the ratio of the concentration of the products divided by the concentration of the reactants at equilibrium and at a specified temperature. The equilibrium constant (product concentrations divided by reactant concentrations) is valid only at a specified temperature after the reaction has gone to (completion, equilibrium) ______.

Answer: equilibrium

Below is a reversible reaction and the expression for the equilibrium constant for this reversible reaction.

$$H_2O + CO \rightleftharpoons CO_2 + H_2$$

$$K_{eq} = \frac{[CO_2][H_2]}{[H_2O][CO]}$$

The symbol K_{eq} represents the equilibrium constant and the brackets [] represent the concentration (usually in moles per liter) of each product and reactant. Look at the placement of each reactant and product in the equilibrium constant expression. In the equilibrium constant expression for a reversible reaction, the (products, reactants) ______ are located in the numerator or upper part of the fraction and the (products, reactants) _____ are located in the denominator or lower part of the fraction.

Answer: products; reactants

$$K_{eq} = \frac{[product][product]}{[reactant][reactant]}$$

Write the equilibrium constant expression for the following reversible reaction.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Answer:
$$\frac{[PCl_3][Cl_2]}{[PCl_5]}$$

(Since there are two products, they should be placed in the upper part of the fraction. The one reactant belongs in the lower part of the fraction.)

A reversible reaction such as $H_2 + I_2 \rightleftharpoons 2HI$ has the following equilibrium constant expression.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Note that the coefficient in front of HI in the reaction becomes an exponent in the equilibrium constant expression.

Write the equilibrium constant expression for the following reversible reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_{eq} = \underline{\hspace{1cm}}$$

Answer:
$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

It is easy to prove to yourself that the coefficients in the reaction should be exponents in the expression for an equilibrium constant.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

This reaction can also be written as:

$$N_2 + H_2 + H_2 + H_2 \rightleftharpoons NH_3 + NH_3.$$

Write the equilibrium constant expression for this last reaction.

$$K_{eq} = \underline{\hspace{1cm}}$$

Answer:
$$\frac{[NH_3][NH_3]}{[N_2][H_2][H_2][H_2]}$$

The concentrations of the reactants are multiplied together: $[H_2][H_2][H_2] = [H_2]^3$. The concentrations of the products are multiplied together: $[NH_3][NH_3] = [NH_3]^2$.

Therefore,

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Write the correct equilibrium constant expression for the following reversible reaction.

$$ZSO_2 + O_2 \rightleftharpoons 2SO_3$$

$$K_{eq} = \underline{\qquad \qquad }$$

$$Answer: \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

CALCULATING EQUILIBRIUM CONSTANTS

Now let's use this general equation to find some actual equilibrium constants. The equilibrium constant expression for $H_2 + I_2 \rightleftharpoons 2HI$ is:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

At 458°C, the equilibrium mixture consists of:

[HI] =
$$1.5 \times 10^{-2}$$
 mol/liter
[H₂] = 4.6×10^{-3} mol/liter
[I₂] = 1.0×10^{-3} mol/liter

Calculate the value of K_{eq} at 458°C (to the nearest tenth).

$$Answer: \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.5 \times 10^{-2} \text{ mol/liter})^2}{(4.6 \times 10^{-3} \text{ mol/liter})(1.0 \times 10^{-3} \text{ mol/liter})} = 48.9$$

At 458°C, the equilibrium constant (K_{eq}) for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 48.9. If you were to repeat the reaction $H_2 + I_2 \rightleftharpoons 2HI$ using three times as much starting material $(H_2 \text{ and } I_2)$ but kept the temperature at 458°C, what would be the value of K_{eq} ? ______ (Hint: This question is tricky. Remember the meaning of the word constant.)

Answer: 48.9 (Any amount of starting material for this reaction under normal conditions will produce a chemical equilibrium with an equilibrium constant of 48.9. The equilibrium constant for this reaction is a constant at the specified temperature. It does not change.)

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After the equilibrium for a reaction is determined experimentally, it is useful for predicting the amount of products at equilibrium or the amount of reactants needed for a different situation involving the same reaction at the specified temperature.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Determine [HI] (the concentration of hydrogen iodide) at equilibrium if:

$$[H_2] = 1.24 \times 10^{-2}$$
 mol/liter
 $[I_2] = 2.46 \times 10^{-2}$ mol/liter
 $K_{eq} = 48.9$

Answer:
$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

$$\begin{aligned} [HI]^2 &= K_{eq}[H_2][I_2] \\ [HI] &= \sqrt{K_{eq}[H_2][I_2]} = \sqrt{(48.9)(1.24 \times 10^{-2} \text{ mol/liter})(2.46 \times 10^{-2} \text{ mol/liter})} \end{aligned}$$

= 1.22×10^{-1} mol/liter of hydrogen iodide

An equilibrium constant expression is valid only if the reaction is balanced. Write 17 the equilibrium constant expression for the following unbalanced reversible reaction. Make sure to balance the reaction equation first. (Refer to Chapter 6, if necessary, for review.)

$$HCl + O_2 \rightleftharpoons Cl_2 + H_2O$$

$$K_{eq} = \underline{\hspace{1cm}}$$

Answer: Balance the reaction equation first (equal numbers of atoms on both sides).

$$4HCI + O_2 \rightleftharpoons 2CI_2 + 2H_2O$$

$$K_{eq} = \frac{[CI_2]^2 [H_2O]^2}{[HCI]^4 [O_2]}$$

So far, the values of the equilibrium constant (K_{eq}) in all examples have been just 18 numbers because all of the mol/liter concentration terms have cancelled out. In determining the value of K_{eq} for the following expression, all mol/liter terms will cancel and K_{eq} will be a unitless number.

$$K_{eq} = \frac{[\]^2}{[\][\]} = \frac{(\text{mol/liter})^2}{(\text{mol/liter})(\text{mol/liter})}$$

Suppose that for a different reaction, the equilibrium constant expression is as follows.

$$K_{eq} = \frac{[]^2[]}{[]^2} = \frac{(\text{mol/liter})^2(\text{mol/liter})}{(\text{mol/liter})^2}$$

All mol/liter do not cancel in this case. Instead of being just a number, K_{ea} will have a value in terms of _____

Answer: mol/liter

$$K_{eq} = \frac{(\text{mol/liter})^2(\text{mol/liter})}{(\text{mol/liter})^2} = \frac{(\text{mol/liter})^3}{(\text{mol/liter})^2} = \text{mol/liter}$$

For the following equilibrium constant expression, the value of K_{eq} will not be just a number.

$$K_{eq} = \frac{\left[\begin{array}{c}\right]^2 \left[\begin{array}{c}\right]^2}{\left[\begin{array}{c}\right]^3} = \frac{(\text{mol/liter})^2 (\text{mol/liter})^2}{(\text{mol/liter})^3}$$

 K_{eq} will be expressed in terms of ______

Answer: mol/liter

$$K_{eq} = \frac{(\text{mol/liter})^2 (\text{mol/liter})^2}{(\text{mol/liter})^3} = \frac{(\text{mol/liter})^4}{(\text{mol/liter})^3} = \text{mol/liter}$$

For the following equilibrium constant expression, the value of K_{eq} is not just a number. This example is a bit more difficult than the previous examples since the denominator has the larger exponent.

$$K_{eq} = \frac{[]^2}{[]^3} = \frac{(\text{mol/liter})^2}{(\text{mol/liter})^3}$$

The value of K_{eq} will be in terms of ______

Answer: liters/mol

$$K_{eq} = \frac{(\text{mol/liter})^2}{(\text{mol/liter})^3} = \frac{1}{(\text{mol/liter})} = \text{liters/mol}$$

To divide by a fraction, invert the fraction and multiply:

$$1 \div \frac{\text{mol}}{\text{liter}} = 1 \times \frac{\text{liter}}{\text{mol}} = \text{liters/mol}$$

For the following equilibrium constant expression, the value of K_{eq} will not be a pure number.

$$K_{eq} = \frac{\left[\right]^2}{\left[\right]^2 \left[\right]^2}$$

The value of K_{eq} will be in terms of ______.

Answer:
$$K_{eq} = \frac{\text{(mol/liter)}^2}{\text{(mol/liter)}^2(\text{mol/liter)}^2} = \frac{1}{\text{(mol/liter)}^2} = \text{liters}^2/\text{mol}^2$$
.

To divide by a fraction, invert the fraction and multiply:

$$1 \div \left(\frac{\text{mol}}{\text{liters}}\right)^2 = 1 \times \left(\frac{\text{liters}}{\text{mol}}\right)^2 = (\text{liters/mol})^2 = \text{liters}^2/\text{mol}^2$$

For the following equilibrium constant expression, the value of K_{eq} will not be a pure number.

$$K_{eq} = \frac{[\text{Cl}]^2 [\text{H}_2 \text{O}]^2}{[\text{HCl}]^4 [\text{O}_2]}$$

The value of K_{eq} will be in terms of ______

Answer:
$$K_{eq} = \frac{[Cl]^2[H_2O]^2}{[HCl]^4[O_2]} = \frac{(mol/liter)^2(mol/liter)^2}{(mol/liter)^4(mol/liter)} = \frac{(mol/liter)^4}{(mol/liter)^5} = \frac{1}{mol/liter} = liters/mol$$

A value of K_{eq} should include proper units such as mol/liter or liters/mol so that further calculations using K_{eq} will have the correct units. Calculate the value of the equilibrium constant for the following reversible reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The concentrations of the equilibrants (reactants and products) at equilibrium at 400°C are as follows.

$$N_2 = 1.20 \text{ mol/liter}$$

$$H_2 = 0.80 \text{ mol/liter}$$

$$NH_3 = 0.28 \text{ mol/liter}$$

In addition to the numerical value of K_{eq} we must determine the proper units for K_{eq} . After checking the equation for proper balancing, write the expression for the equilibrium constant. After determining the proper expression, you may find it easiest to calculate the numerical value of K_{eq} first and determine the proper units in a separate step.

The value of K_{eq} at 400°C is ______

Answer:
$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.28)^2}{(1.20)(0.80)^3} = \frac{(0.0784)}{(1.20)(0.512)} = 0.128$$

The proper unit can be determined as follows.

$$K_{eq} = \frac{[{\rm NH_3}]^2}{[{\rm N_2}][{\rm H_2}]^3} = \frac{({\rm mol/liter})^2}{({\rm mol/liter})({\rm mol/liter})^3} = \frac{({\rm mol/liter})^2}{({\rm mol/liter})^4} = \frac{1}{({\rm mol/liter})^2} = ({\rm liters/mol})^2 = {\rm liters/mol})^2$$

The actual value of K_{eq} is 0.128 liters²/mol² at 400°C.

TYPES OF EQUILIBRIUM

All of the reversible reactions used as examples have so far included only reactions in which all equilibrants (reactants and products) are of the same state (all gases or all soluble solids). A chemical equilibrium in which all equilibrants are of the same state is called a homogeneous equilibrium. A chemical equilibrium in which the equilibrants are of different states is called a heterogeneous equilibrium.

A chemical equilibrium of a reaction in which a solid and a gas are reactants and a gas is the product is what kind of equilibrium?

Answer: heterogeneous

For the following reaction, an abbreviation has been added to indicate the state of each reactant or product.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The letter "g" following a substance indicates that the substance is a gas. The letter "l" indicates that a substance is a liquid. An "s" indicates that a substance is a solid. And, finally, an "aq" indicates that a substance is an ion in aqueous (water) solution.

- (a) The chemical equilibrium involving the reaction above is what kind of equilibrium?
- (b) An equilibrium involving the following reaction would be what kind of equilibrium?

$$NH_3(g) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Answer: (a) homogeneous; (b) heterogeneous

Some heterogeneous equilibrium reactions are special cases when the equilibrium constant expression is written for them.

$$NH_3(g) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The correct equilibrium constant expression is:

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

What reactant or product has not been included in the above expression for the equilibrium constant?

Answer: H₂O

H₂O was not included in the equilibrium expression in frame 26 because it is a pure liquid whose concentration does not change significantly. Pure liquids as well as pure solids should *not* be included in the expression for an equilibrium constant because the concentration of a pure liquid or pure solid does not change if the temperature does not change.

Because the concentrations of pure solids and liquids stay constant, it would be redundant to include them in the equilibrium constant expression. ("Pure" indicates that the compound or element is not mixed with another compound or element. Water is a pure liquid if some other substance is not dissolved or mixed with it.) Gases, however, change concentration with pressure even if the temperature is

constant. Only those equilibrants whose concentration is variable should be included in the equilibrium constant expression. Unless otherwise stated, any reactant or product that is a liquid (l) or solid (s) should not be included in the equilibrium constant expression.

Write the equilibrium constant expression for the following reversible reaction.

$$CuO(s) + H_2(g) \rightleftharpoons Cu(s) + H_2O(g)$$

(Note that H_2O is a vapor that behaves like a gas and not a liquid in this reaction.)

Answer:
$$\frac{[H_2O]}{[H_2]}$$

(The CuO and Cu are solids, as indicated by the "s" that follows these solids in the equation, and should not be included in the expression.)

Write the equilibrium constant expression for the following reaction.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

 $K_{eq} = \underline{\hspace{1cm}}$

Answer:
$$\frac{[CO]^2}{[CO_2]}$$

(The solid does not appear in the equilibrium constant expression; gases do.)

Write the equilibrium constant expression for the following reaction.

$$Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)$$

(Note that H2O is not a liquid in this reaction.)

$$K_{eq} =$$

Answer:
$$\frac{[H_2O]^4}{[H_2]^4}$$

Write the equilibrium constant expression for the following reaction.

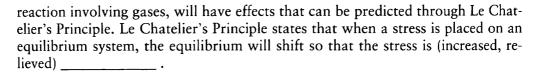
$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

$$K_{eq} = \underline{\hspace{1cm}}$$

Answer: [NH₃][H₂S] (The only reactant is a solid, therefore the denominator is eliminated.)

STRESS IN EQUILIBRIUM

Le Chatelier's Principle is applicable to all chemical equilibria. Such stresses as adding more of a reactant or product to a reaction, or changing the pressure of a



Answer: relieved

The following reaction can serve as an example of what happens when a stress is placed upon a chemical equilibrium.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

First, write the equilibrium constant expression for this reaction.

$$K_{eq} =$$

Answer: $\frac{[PCl_3][Cl_2]}{[PCl_5]}$

Assume that at a certain temperature, the concentration in mol/liter of each equilibrant in the reaction from frame 32 is as follows.

$$PCl_3 = 6 \text{ mol/liter}$$

$$Cl_2 = 6 \text{ mol/liter}$$

$$PCl_5 = 9 \text{ mol/liter}$$

Calculate the value of K_{eq} .

Answer:
$$K_{eq} = \frac{(6 \text{ mol/liter})(6 \text{ mol/liter})}{(9 \text{ mol/liter})} = 4 \text{ mol/liter}$$

To observe the effects of Le Chatelier's Principle, we now add an additional 6 mol/liter of Cl₂ gas to the equilibrium. We suddenly have a total of 12 mol/liter of Cl₂ as well as the original amount of PCl₃ and PCl₅. The system is no longer at equilibrium. Immediately, one of the reaction rates (forward or reverse) increases so as to relieve the stress. Look carefully at the reversible reaction.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Since the concentration of Cl_2 has just doubled, the reaction will try to relieve that stress. As a response to all that extra Cl_2 , which of the following would you expect to happen?

- (a) The forward reaction rate increases (producing even more Cl₂ and PCl₃ while reducing the PCl₅).
- (b) The *reverse* reaction increases (reducing the supply of Cl₂ and PCl₃ while increasing the PCl₅).

Answer: (b) (This is logical since there is a surplus of Cl₂. The reverse reaction rate increases until equilibrium is again restored.)

After relieving the stress, the reaction from frames 32–34 will again be at equilibrium, although the concentration of each equilibrant has changed.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

1. Original K_{eq} :

$$K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(6 \text{ mol/liter})(6 \text{ mol/liter})}{(9 \text{ mol/liter})} = 4 \text{ mol/liter}$$

2. Doubling the Cl₂ concentration, system is no longer at equilibrium:

After doubling the Cl₂ concentration, the system returns to equilibrium.

The concentration of each equilibrant at the new equilibrium has been calculated for you using a mathematical procedure called the quadratic equation. You will not be required to use quadratic equations in this text.

3. New K_{eq} :

$$K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(4.22 \text{ mol/liter})(10.22 \text{ mol/liter})}{(10.78 \text{ mol/liter})} = 4.0 \text{ mol/liter}$$

Note that after equilibrium is restored, the value for K_{eq} remains the same. Since the temperature has remained the same should you have expected the value for K_{eq} to change? _____

Answer: no (If the temperature does not change, K_{eq} will not change because it is a constant for the reaction at equilibrium.)

Compare the new equilibrium concentrations to those of the original equilibrium in frame 35. Besides the doubled Cl₂ concentration (which was the stress applied), which equilibrant:

- (a) increased in concentration?
- (b) decreased in concentration? _____

Answer: (a) The concentration of PCl_5 increased from 9 mol/liter to 10.78 mol/liter; (b) The concentration of PCl_3 decreased from 6 mol/liter to 4.22 mol/liter.

| 37 | Adding more of one of the products (Cl ₂) in the above reaction resulted in a shift of the equilibrium that favored the reverse reaction, as predicted by Le Chatelier's Principle. After equilibrium is again restored, the concentration of the other product (PCl ₃) is (decreased, increased) The concentration of the reactant (PCl ₅) is (decreased, increased) |
|----|--|
| | Answer: decreased; increased |
| 38 | As a general rule (because of Le Chatelier's Principle), increasing the concentration of one of the products of a reaction favors the reverse reaction and results in a decrease in the concentration of any other product and an increase in the concentration of the reactants. This reaction represents an ordinary reversible reaction at equilibrium. |
| | $A + B \rightleftharpoons C + D$ |
| | If the concentration of product D is suddenly increased, label each of the following as increased or decreased. |
| | (a) the concentration of A |
| | (b) the concentration of B |
| | (c) the concentration of C |
| | Answer: (a) increased; (b) increased; (b) decreased (The equilibrium is shifted to favor the reactants.) |
| 39 | The reversible reaction $A + B \rightleftharpoons C + D$ can also be written $C + D \rightleftharpoons A + B$. Suppose the concentration of A were increased suddenly. After equilibrium is again restored, which of the following increases and which decreases? |
| | (a) the concentration of B |
| | (b) the concentration of C |
| | (c) the concentration of D |

Answer: (a) decreases; (b) increases; (c) increases

- According to Le Chatelier's Principle:
 - If the concentration of one reactant is suddenly increased, the equilibrium will shift so that all products are increased and the other reactant will be decreased.
 - If the concentration of one product is suddenly increased, the equilibrium will shift so that all reactants are increased and the other product is decreased.

The brackets [] indicate concentration (in mol/liter).

$$A + B \rightleftharpoons C + D$$

If [C] is increased, then [A] is ______, [B] is ______, and [D] is ______.

Answer: increased; increased; decreased

Decreasing a reactant or product can also be a stress.

$$A + B \rightleftharpoons C + D$$

If C were to be suddenly decreased by removing some from the reaction system, the forward reaction would be favored and more product would be produced until equilibrium was again established. To produce more product would require a decreased concentration of reactants. A decrease in [C] causes the exact opposite of an increase in [C].

- (a) If [A] is increased (by adding some A to the reaction mixture), then [B] is ______, [C] is ______, and [D] is ______.
- (b) If [A] is decreased (by removing some A from the reaction mixture), then [B] is ______, [C] is ______, and [D] is ______.

Answer: (a) decreased; increased (The forward reaction is favored.); (b) increased; decreased; decreased (The reverse reaction is favored.)

Whenever a quantity of a reactant or product is added to or removed from a chemical equilibrium system, the equilibrium responds according to Le Chatelier's Principle. The stress in this case is the addition or removal of some quantity of reactant or product. A chemical equilibrium will also respond to a change in temperature.

A chemical reaction may either require heat to continue the reaction or give off heat during the reaction. A chemical reaction requiring heat (energy) to proceed is called endothermic. A chemical reaction giving off heat (energy) during a reaction is exothermic.

The forward reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ requires heat energy. It is an (exothermic, endothermic) _____ reaction.

Answer: endothermic

The forward reaction of $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is exothermic. It (gives off, requires) _____ heat energy.

Answer: gives off

A forward exothermic reaction can be written to show heat as a product.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

A forward endothermic reaction can be written to show heat as a requirement on the reactant side. The following forward reaction is endothermic. Which equation is correctly written?

____ (a) heat +
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

___ (b)
$$CaCO_3(s) \rightleftharpoons CaO + CO_2(g) + heat$$

Answer: (a)

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The equilibrium constant for an endothermic reaction increases with rising temperature. The equilibrium constant for an exothermic reaction decreases with rising temperature. This means that for an endothermic reaction, increasing the temperature will increase the concentration of products (at the expense of reactants). For an exothermic reaction, the opposite holds true.

A simple way to remember these effects is to treat the heat energy as a reactant or product and apply what you have learned from Le Chatelier's Principle.

heat +
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Treating heat as a required item on the reactant side, apply Le Chatelier's Principle. If the temperature is raised (heat is increased), indicate whether the concentrations of the following reactant and products increase or decrease.

- (a) [CaCO₃] _____
- (b) [CaO] _____
- (c) [CO₂] _____
- (d) Is the reaction endothermic or exothermic?

Answer: (a) decreases; (b) increases; (c) increases; (d) endothermic (Increasing the required heat energy favors the forward reaction.)

Indicate whether increasing the temperature for the reaction expressed below would increase or decrease the concentrations of the reactants and product.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

- (a) [NH₃] _____
- (b) [N₂] _____
- (c) [H₂] _____
- (d) Is this reaction endothermic or exothermic?

Answer: (a) decreases; (b) increases; (c) increases; (d) exothermic (Increasing one of the products would favor the reverse reaction. Since heat energy is being treated as a product, increasing it would have the same effect.)

A decrease in temperature (some of the heat is removed) has an effect opposite that of an increase.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

If the temperature is decreased, indicate whether the concentrations of the reactants and product would increase or decrease.

- (a) [NH₃] _____
- (b) [N₂] _____
- (c) [H₂] _____

Answer: (a) increases; (b) decreases; (c) decreases (Decreasing one of the products favors the forward reaction. Since heat is being treated as a product, decreasing it has the same effect.)

The effects of increasing or decreasing the pressure surrounding a chemical equilibrium involving gases can also be predicted on the basis of Le Chatelier's Principle. Increasing the pressure favors the side of the reaction (reactant side or product side) containing the fewest moles of gas.

For the following reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the reactant side has 4 mol of gas and the product side has 2 mol of gas. If the pressure is increased, which side will be favored and end up with an increase in concentration?

Answer: the product side (Increased pressure favors the reaction side with the fewest moles of gas.)

In this reaction, only the CO₂ product is a gas. The other equilibrants are solids that cannot be compressed.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

An increase in pressure causes the reaction equilibrium to shift in favor of the side of the reaction with the least moles of gas. In this reaction, the reactant side has no moles of gas while the product side has 1 mol of gas. An increase in pressure would favor which side of the reaction?

Answer: the reactant side (Zero moles of gas is less gas than 1 mol of gas.)

Now look at this reaction.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

- (a) The reactant side of this reaction has how many moles of gas?
- (b) The product side has how many moles of gas?
- (c) Which side of the reaction would be favored by an increase in pressure?

(d) Which side of the reaction would be favored by a decrease in pressure? (Remember, decreasing the pressure has the opposite effect of increasing the pressure.)

Answer: (a) 1 mol; (b) 2 mol (PCl₃ and Cl₂ each represent 1 mol of gas, which adds up to 2 mol on the product side.); (c) reactant side; (d) product side

Here's a tricky question. Remember, increasing the pressure favors the side of the reaction with the least moles of gas, provided there *is* a side with the least moles of gas. For the following reversible reaction, increasing the pressure will favor which side of the reaction?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Answer: Neither side is favored because there are 2 mol of gas on each side of the reaction. (Increasing the pressure has no effect if both sides of a reaction have an equal number of moles of gas.)

The reversible reaction below is presently at equilibrium. You desire to shift the equilibrium to favor the product side in order to increase the concentration of CO₂ as much as possible.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + heat$$

To produce an equilibrium with a large concentration of CO₂, indicate whether you would increase or decrease the following conditions.

- (a) pressure _____
- (b) temperature _____
- (c) concentration of O₂(g)

Answer: (a) increase (This favors the product side since it has fewer moles of gas.); (b) decrease (Treating heat as a product, this removes some heat favoring the production of more product.); (c) increase (Increasing the concentration of a reactant results in an increase in products as well as a decrease in other reactants.)

We have discussed the concept of equilibrium and how it applies to those chemical reactions that do not go to completion. You have learned what happens to a reaction at equilibrium when a "stress" is applied to the reaction. Most of the equilibria discussed involved reactants and products that were all in the gaseous state or equilibria between gases and pure solids and liquids.

Chemists have learned that many reactions that occur between ions in aqueous solutions also do not go to completion and reach a state of equilibrium. Ionic equilibria are also affected by stresses according to Le Chatelier's Principle.

We now discuss several special cases of ionic equilibria and how they are used to determine the degree of dissociation of weak electrolytes and the concentration of ions in aqueous solutions. We also discuss how slightly soluble compounds

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behave and how their solubility is determined in aqueous solutions and in the presence of other ions.

IONIC EQUILIBRIA

You have used Le Chatelier's Principle and the equilibrium constant for reversible reactions. Equilibria also exist for such things as salts and their ions in solution, and acids and bases and their dissociated ions. Other substances, even though they may dissociate only very slightly into ions, are at equilibrium with those ions. An ionic equilibrium constant expression is written just like those of the reversible reactions previously encountered. Write the ionic equilibrium constant for the following reaction.

$$\begin{split} HC_2H_3O_2(aq) &\rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \\ K_{eq} &= \underline{\hspace{1cm}} \\ &\text{Answer: } \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \end{split}$$

Instead of K_{eq} , the equilibrium constant may be K_a if it represents the dissociation of an acid, K_b if it represents the dissociation of a base, K_i for a general ionization constant, or K_{sp} for a solubility product constant. We will discuss K_{sp} now and these other constants later. The equilibrium constant expression is the same for any of these as for the reactions dealt with previously. Write the equilibrium constant expression for the solubility product of the very slightly soluble salt AgBr.

$$AgBr(s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$

$$K_{sp} = \underline{\qquad}$$

Answer: [Ag+][Br-] (The solid is not included since its concentration is constant at constant temperature.)

The abbreviation K_{sp} stands for solubility product constant. It represents the solubility of a salt in a saturated solution and is called a product because the negative and positive ion concentrations are multiplied together to determine the value of the constant. Write the solubility product expression for the salt CaF₂.

$$CaF_{2}(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq)$$

$$K_{sp} = \underline{\hspace{1cm}}$$
Answer: $[Ca^{2+}][F^{-}]^{2}$ (Don't forget the exponent.)

The solubility product equation represents the dynamic equilibrium between a solid and its dissociated ions in a saturated solution.

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

Write the solubility product expression for the saturated aqueous solution of Bi_2S_3 . $K_{sp} =$ Answer: $[Bi^{3+}]^2[S^{2-}]^3$

Write the K_{sp} expression for the saturated aqueous solution of AgCl. (AgCl is only slightly soluble.)

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

 $K_{sp} =$

Answer: [Ag+][Cl-]

In a saturated solution of slightly soluble AgCl in water, an equilibrium exists between the AgCl solid and its dissociated aqueous ions.

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

Suppose that extra Cl⁻ ion is added to this equilibrium. From Le Chatelier's Principle, you know that the equilibrium would favor the left side of the equation. This situation is like the general reversible reaction $A + B \rightleftharpoons C + D$. Adding more Cl⁻ ion to the equilibrium is like adding more of product D to the reaction. Adding more of product D causes an increase in the concentration of the reactants and a decrease in the concentration of product C. Indicate whether adding more Cl⁻ ion to the equilibrium causes an increase or decrease in the following.

- (a) the formation of AgCl(s)
- (b) the concentration of Ag⁺

Answer: (a) increase; (b) decrease

The effect of adding more Cl⁻ to the saturated solution of AgCl can also be shown by using the solubility product constant. The solubility of AgCl is 1.2×10^{-5} mol/L.

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

 $K_{sp} = [Ag^{+}][Cl^{-}] = (1.2 \times 10^{-5} \text{ mol/liter}) \times (1.2 \times 10^{-5} \text{ mol/liter})$

Assume the K_{sp} to equal $1.44 \times 10^{-10} \text{ mol}^2/\text{liter}^2$. If the Cl⁻ concentration were to be increased, what must happen to the Ag⁺ concentration? (Remember that K_{sp} is a constant and does not change.)

Answer: The Ag⁺ concentration must decrease. (When the Ag⁺ concentration and Cl⁻ concentration are multiplied together, they must equal the K_{sp} constant. When the concentration of one of the ions is increased, the other must decrease to keep the K_{sp} constant.)

The extra Cl⁻ ion that is added to the saturated solution of AgCl of frames 58 and 59 might have come from NaCl or some other strong electrolyte having a Cl⁻ ion.

This is an example of the common ion effect. The slightly soluble AgCl and the strong electrolyte NaCl both have the Cl⁻ ion in common. Adding some NaCl to a saturated solution of AgCl forces the equilibrium to shift so that some of the Ag⁺(aq) and the extra Cl⁻(aq) come out of the solution and precipitate. In this example of the common ion effect, which is the "common" ion?

Answer: Cl- (from both NaCl and AgCl)

If some of the strong electrolyte AgNO₃ is added to a saturated solution of AgCl, the common ion effect can also be observed.

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

In this example of the common ion effect, which would be the "common" ion?

Answer: Ag+ (from both AgCl and AgNO₃)

If you added some strong electrolyte such as NaNO₃ to a saturated solution of AgCl, would you expect to observe the common ion effect?

Answer: no (There are not two ions alike in AgCl and NaNO3.)

The common ion effect is observed when a strong electrolyte is added to a saturated solution of a very slightly soluble salt, weak acid, or weak base, and one ion of the strong electrolyte is the same as one of the ions in the original solution.

You may have wondered why AgCl is used as an example since we have previously assumed that all of AgCl precipitated out of solution. In actuality, all salts are soluble to some degree. The solubility of some salts such as AgCl is so minimal that very little error is introduced by treating it elsewhere as not soluble at all.

Is there a salt that is absolutely not soluble even to a small degree?

Answer: no (All salts are soluble to some slight degree. For practical purposes in some experiments, we can often ignore the dissolved portion of a very slightly soluble salt. For K_{sp} calculations and the common ion effect, we cannot ignore it.)

The value of the solubility product constant (K_{sp}) can easily be determined if the solubility of a salt is known.

$$PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$$

Lead sulfide (PbS) is a slightly soluble salt. Only 1×10^{-14} mol of the salt will dissolve in a liter of water at 20°C. In pure water, at 20°C, this means that the

concentration of Pb²⁺ ion will be 1×10^{-14} mol/liter and the concentration of S²⁻ ion will also be 1×10^{-14} mol/liter. Calculate K_{sp} .

$$K_{sb} = [Pb^{2+}][S^{2-}] =$$

Answer: $(1 \times 10^{-14} \text{ mol/liter})(1 \times 10^{-14} \text{ mol/liter}) = 1 \times 10^{-28} \text{ mol}^2/\text{liter}^2$

Up to 7×10^{-5} mol of calcium carbonate will dissolve in a liter of pure water at 20° C.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Calculate the K_{sp} of CaCO₃ at 20°C.

$$K_{sp} =$$

Answer: $[Ca^{2+}][CO_3^{2-}] = (7 \times 10^{-5} \text{ mol/liter})(7 \times 10^{-5} \text{ mol/liter}) = 4.9 \times 10^{-9} \text{ mol}^2/\text{liter}^2$

At a certain temperature, up to 2×10^{-4} mol of CaF₂ will dissolve in a liter of pure water. Calculate the K_{sp} of CaF₂ at the temperature.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq)$$

(Note: The fluoride ion has a coefficient of 2 in front of it. This means that two fluoride ions are produced for every calcium ion when CaF_2 dissociates. It also means that the fluoride ion concentration must be squared in the K_{sp} expression.)

$$K_{sp} =$$

Answer: $[Ca^{2+}] = 2 \times 10^{-4}$ mol/liter

Two fluoride ions are formed for every calcium ion.

[F⁻] = (2)(2 × 10⁻⁴ mol/liter) = 4 × 10⁻⁴ mol/liter.

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2 \times 10^{-4} \text{ mol/liter})(4 \times 10^{-4} \text{ mol/liter})^2$$

= (2 × 10⁻⁴ mol/liter)(16 × 10⁻⁸ mol²/liter²) = 32 × 10⁻¹² mol³/liter³
= 3.2 × 10⁻¹¹ mol³/liter³

All of the K_{sp} solubilities calculated in the examples assume that the salts are dissolved in pure water (with no common ions present). Once the K_{sp} is determined, however, we can use the constant to determine the concentration of one ion of the salt if the concentration of the other ion is known.

From a table of K_{sp} values, the value of the K_{sp} for iron sulfide (FeS) is 1×10^{-22} mol²/liter² at a certain temperature.

$$FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$$

First, write the expression for the K_{sp} of FeS.

$$K_{sp} =$$

Answer: $[Fe^{2+}][S^{2-}] = 1 \times 10^{-22} \text{ mol}^2/\text{liter}^2$

A liter of water solution already contains some small quantity of Fe²⁺ in it. The water is at the proper temperature. By experiment, it is determined that a maximum of 1×10^{-3} mol of S²⁻ can be mixed in this liter of water solution before the FeS precipitate is formed. Since the value for K_{sp} is known and the concentration of S²⁻ is 1×10^{-3} mol/liter, we can determine the concentration of Fe²⁺ in the water sample by modifying the K_{sp} expression.

$$[Fe^{2+}] = \frac{K_{sp}}{[S^{2-}]}$$

Calculate the concentration of Fe²⁺.

Answer: $[Fe^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{1 \times 10^{-22} \text{ mol}^2/\text{liter}^2}{1 \times 10^{-3} \text{ mol}/\text{liter}} = 1 \times 10^{-19} \text{ mol/liter}$

The K_{sp} for BaCO₃ is 5×10^{-9} mol²/liter² at 20°C. $K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5 \times 10^{-9} \text{ mol}^2/\text{liter}^2$

An aqueous solution contains a Ba²⁺ concentration of 2×10^{-4} mol/liter. What is the maximum possible ${\rm CO_3}^{2-}$ concentration in that solution just before precipitation of BaCO₃ occurs? The solution temperature is kept at 20°C.

$$[CO_3^{2-}] =$$

Answer: $\frac{K_{sp}}{[Ba^{2+}]} = \frac{5 \times 10^{-9} \text{ mol}^2/\text{liter}^2}{2 \times 10^{-4} \text{ mol}/\text{liter}} = 2.5 \times 10^{-5} \text{ mol}/\text{liter}$

Determine the maximum possible F^- ion concentration in an aqueous solution containing 1×10^{-3} mol/liter of Ca^{2+} ion. The K_{sp} for CaF_2 is equal to 4×10^{-11} mol³/liter³ at the same temperature as the solution. (This one is more difficult. Remember to square the F^- in the K_{sp} expression.)

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq)$$

[F⁻] =

Answer:

$$K_{sp} = [Ca^{2+}][F^{-}]^{2}$$

$$[F^{-}]^{2} = \frac{K_{sp}}{[Ca^{2+}]}$$

 $[F^{-}] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}} = \sqrt{\frac{4 \times 10^{-11} \, \text{mol}^3 / \text{liter}^3}{1 \times 10^{-3} \, \text{mol} / \text{liter}}} = \sqrt{4 \times 10^{-8} \, \text{mol}^2 / \text{liter}^2} = 2 \times 10^{-4} \, \text{mol} / \text{liter}^2$

Water is usually considered to be completely a nonelectrolyte. Even water, however, dissociates to a very small degree. This is called self-ionization and will be

covered in more detail in the next chapter. The dissociation of water is represented by the following equation.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Write the ion product constant expression (K_w) for the dissociation of water.

Answer: [H⁺][OH⁻] (Liquid water is left out since its concentration essentially does not change.)

The actual value of the ion product constant for water (K_w) is 1×10^{-14} mol²/liter² (at 25°C). You should memorize the value of K_w since it is very commonly used in aqueous acid and base calculations. In water with no impurities (at 25°C) the concentration of H⁺ is 1×10^{-7} mol/liter and the concentration of OH⁻ is also 1×10^{-7} mol/liter. Calculate the value of K_w with these concentrations.

$$K_w = (1 \times 10^{-7} \text{ mol/liter})(1 \times 10^{-7} \text{ moles/liter}) =$$

Answer: $1 \times 10^{-14} \text{ mol}^2/\text{liter}^2$

The most common definition of an acid or base depends upon the concentration of the hydrogen ion in an aqueous solution. In pure water, the concentrations of H⁺ and OH⁻ are equal. It is neutral (neither acidic nor basic). If the H⁺ ion concentration is greater than 1×10^{-7} mol/liter, the solution is acidic. If the H⁺ ion concentration is less than 1×10^{-7} mol/liter, the solution is basic.

A water solution is found with $[H^+] = 1 \times 10^{-5}$ mol/liter. The solution is (acidic, basic) ______.

Answer: acidic (A concentration of 1×10^{-5} is greater than 1×10^{-7} .)

If the [H⁺] is 1×10^{-5} mol/liter for a particular solution, the [OH⁻] can be calculated.

$$K_{w} = [H^{+}][OH^{-}] = 1 \times 10^{-14} \text{mol}^{2}/\text{liter}^{2}$$

$$[OH^{-}] = \frac{K_{w}}{[H^{+}]}$$

Calculate the concentration of OH⁻ for this solution.

Answer:
$$\frac{K_w}{[H^+]} = \frac{1 \times 10^{-14} \text{ mol}^2/\text{liter}^2}{1 \times 10^{-5} \text{ mol/liter}} = 1 \times 10^{-9} \text{ mol/liter}$$

In Chapter 13, acids and bases will be covered in greater detail. For now, an acid is considered to be a substance that increases the H⁺ concentration of neutral water. A base is considered to be a substance that decreases the H⁺ concentration of neutral water. The strength of an acid or base depends only upon the extent of

dissociation when in water (aqueous) solution. The same definition is already familiar to you as a strong electrolyte or a weak electrolyte. A strong acid (or base) is a strong electrolyte that dissociates completely into its ions in aqueous solution. A weak acid (or base) is a weak electrolyte that dissociates only partially in aqueous solution.

HCl is an acid that is a strong electrolyte.

$$HCl \rightarrow H^+ + Cl^-$$

Remember that M indicates molarity (moles/liter). If a 0.1 M solution of HCl dissociates, it produces a _____ M solution of H⁺ and a _____ M solution of Cl⁻.

Answer: 0.1; 0.1

HCl is such a strong electrolyte that in an aqueous solution, there are only H⁺ and Cl⁻ ions. The equation for the dissociation of HCl is:

$$HCl \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

In aqueous solution, there is no more HCl; only H⁺ and Cl⁻ ions can be found. The equation for the dissociation of HCl goes to completion. Only the products are left. The reactant (HCl) is completely used up to form products. An equation that goes to completion must be distinguished from an equilibrium equation. In an equilibrium equation, both the products and the reactants are continually present and the forward and reverse reactions continue at equal rates.

An aqueous solution of 0.001 M HCl is actually dissociated into a solution of 0.001 M H⁺ and 0.001 M Cl⁻.

Ignoring the chloride ion, a solution of 0.001 M H⁺ is the same as $[H^+] = 1 \times 10^{-3}$ mol/liter by definition.

- (a) A solution of 0.01 M HCl results in $[H^+] =$
- (b) After being dissociated into ions in an aqueous solution, would you expect to find any undissociated HCl in the 0.01 M solution?

Answer: (a) $0.01~M~or~1\times10^{-2}~M~or~1\times10^{-2}~mol/liter$ (all are correct answers); (b) No, the HCl dissociates completely into ions.

Not all acids are strong electrolytes. Some are weak electrolytes that only dissociate partly into ions. Part of the weak electrolyte remains undissociated. This part establishes equilibrium with the dissociated ions. The equilibrium constant for a weak acid is abbreviated K_a .

Acetic acid is an example of a weak acid. What is the acetic acid equilibrium constant expression?

$$HC_2H_3O_2(aq) = H^+(aq) + C_2H_3O_2^-(aq)$$

$$K_a =$$

Answer:
$$\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

At 0.02 mol/liter concentration, acetic acid is 3% dissociated. Therefore, the hydrogen ion concentration of the solution equals 3% multiplied by 0.02 mol/liter. (The 3% becomes 0.03 in decimal form.)

$$HC_2H_3O_2 \rightleftharpoons H^++C_2H_3O_2^-$$

The acetate ion concentration $[C_2H_3O_2^-]$ equals the hydrogen ion concentration $[H^+]$ since one acetate ion is formed for every hydrogen ion. What is the concentration of the hydrogen ion?

$$[H^+] = (0.03)(0.02 \text{ mol/liter}) =$$

Answer: (The solution is made up of $0.02 \, \text{mol/liter} \, \text{HC}_2\text{H}_3\text{O}_2$ acid. If the acid were to dissociate completely (100%), the value of [H $^+$] would also be 0.02 mol/liter. However, the acid only dissociates 3%. Therefore, the hydrogen ion concentration will be 3% of 0.02 mol/liter.)

$$[H^+] = (0.03)(0.02 \text{ mol/liter}) = 0.0006 \text{ mol/liter} \text{ or } 6 \times 10^{-4} \text{ mol/liter}$$

Acetic acid is 3% dissociated in a 0.02 mol/liter solution. Therefore,

$$[H^+]$$
 = (0.03)(0.02 mol/liter) = 6 × 10⁻⁴ mol/liter
 $[C_2H_3O_2^-]$ = (0.03)(0.02 mol/liter) = 6 × 10⁻⁴ mol/liter

The remaining 97% is molecular acetic acid. The 97% becomes 0.97 in decimal form. The concentration of the remaining molecular acetic acid can be found by multiplying 0.97 times 0.02 mol/liter.

$$[HC_2H_3O_2] = (0.97)(0.02 \text{ mol/liter}) = _____$$

Answer: 0.0194 mol/liter or $1.94 \times 10^{-2} \text{ mol/liter}$

Calculate the ionization constant (K_a) for acetic acid. (Round to the nearest hundredth.)

[H⁺] = (0.03)(0.02 mol/liter) =
$$6 \times 10^{-4}$$
 mol/liter
[C₂H₃O₂⁻] = (0.03)(0.02 mol/liter) = 6×10^{-4} mol/liter
[HC₂H₃O₂] = (0.97)(0.02 mol/liter) = 1.94×10^{-2} mol/liter

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} =$$

Answer:
$$\frac{(6 \times 10^{-4} \text{ mol/liter})(6 \times 10^{-4} \text{ mol/liter})}{1.94 \times 10^{-2} \text{ mol/liter}} = 1.86 \times 10^{-5} \text{ mol/liter}$$

A solution of 0.050 M hydrofluoric acid (HF) is found to be 10% dissociated (or ionized). If the acid were to dissociate completely (100%), the value of [H⁺] would also be 0.050 M. However, the acid only dissociates 10%. Therefore, the hydrogen

ion concentration will be 10% of 0.050 M. The 10% converts to a decimal of 0.10 in the calculation. The portion of HF that dissociates produces one H⁺ ion for each F⁻ ion.

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

Determine the concentrations (expressed as M, molarity) of H⁺ and F⁻ in the solution.

Answer:
$$(0.10)(0.050 M) = 0.005 M \text{ or } 5 \times 10^{-3} M$$

 $(0.10)(0.050 M) = 0.005 M \text{ or } 5 \times 10^{-3} M$

The HF acid solution is 0.050 M. If 90% of the acid remains in molecular form, calculate the concentration of the acid remaining in molecular form. (The 90% becomes 0.90 in decimal form.)

Answer:
$$(0.90)(0.050 M) = 4.5 \times 10^{-2} M$$

Write the ionization constant expression (K_a) for hydrofluoric acid and calculate the value of K_a using the various concentrations just calculated in the previous two frames. (Round to the nearest tenth.)

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

$$K_a =$$

Answer:
$$\frac{[H^+][F^-]}{[HF]} = \frac{(5 \times 10^{-3} M)(5 \times 10^{-3} M)}{(4.5 \times 10^{-2} M)} = 5.6 \times 10^{-4} M$$

Some bases are also weak electrolytes. The ionization constants of weak bases are calculated in the same way as those of weak acids. An ammonium hydroxide solution is 0.05 M. Assume that the ammonium hydroxide is 2% ionized (dissociated).

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Determine the concentration of NH₄⁺ ions and OH⁻ ions in the solution. Also determine the concentration of the NH₃(aq) that did not dissociate.

Answer: The concentrations of NH_4^+ ions and OH^- ions are equal. The solution is 0.05 M but only 2% ionized.

$$[NH_4^+] = (0.02)(0.05M) = 0.001 M \text{ or } 1 \times 10^{-3} M$$

 $[OH^-] = (0.02)(0.05 M) = 0.001 M \text{ or } 1 \times 10^{-3} M$

If 2% is ionized, that leaves 98% in molecular form.

$$[NH_3] = (0.98)(0.05 M) = 0.049 M = 4.9 \times 10^{-2} M$$

Determine the value of the ionization constant (K_b) for the base ammonium hydroxide. (Round to the nearest tenth.)

$$[NH_4^+] = 1 \times 10^{-3} M$$

 $[OH^-] = 1 \times 10^{-3} M$
 $[NH_3] = 4.9 \times 10^{-2} M$

Answer:
$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(1 \times 10^{-3} M)(1 \times 10^{-3} M)}{(4.9 \times 10^{-2} M)} = 2.0 \times 10^{-5} M$$

Calculate the ionization constant (K_a) for formic acid (HCOOH) that ionizes (dissociates) 4% in a 0.10 M solution. (Round to the nearest tenth.)

$$HCOOH \rightleftharpoons H^+ + COOH^-$$

$$K_a = \underline{\hspace{1cm}}$$

Answer: If 4% is ionized, then 96% must be in molecular form.

[H⁺] = (0.04)(0.10 M) = 0.004 M = 4 × 10⁻³ M
[COOH⁻] = (0.04)(0.10 M) = 0.004 M = 4 × 10⁻³ M
[HCOOH] = (0.96)(0.10 M) = 0.096 M = 9.6 × 10⁻² M

$$K_a = \frac{[H^+][COOH^-]}{[HCOOH]} = \frac{(4 \times 10^{-3})(4 \times 10^{-3})}{(9.6 \times 10^{-2} M)} = 1.7 \times 10^{-4} M$$

The weak acid H₃PO₄ is different from previous weak acids because three hydrogen ions are formed for every phosphate (PO₄³⁻) ion. An acid with more than one hydrogen ion for each negative ion is called a polyprotic acid. A polyprotic acid loses its hydrogen ions one at a time. The three steps for the dissociation of H₃PO₄ are:

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(2)
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

(3)
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

Write the equilibrium constant expressions for each of these steps.

 $K_{a_1} = \underline{\qquad}$ $K_{a_2} = \underline{\qquad}$

 $K_{a_3} = \underline{\hspace{1cm}}$

Answer: $K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$ $K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

 $K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$

Up to this point, all solutions involving equilibrium have been aqueous. Solvents other than water are also possible since the solvent makes no difference in the calculations. Gases are also possible solutes. One example could be N_2O_4 in equilibrium with NO_2 in a chloroform solvent. Write the equilibrium constant expression (K_{eq}) for $N_2O_4 \rightleftharpoons 2NO_2$.

K_{eq} = _____

Answer: $\frac{[NO_2]^2}{[N_2O_4]}$

The equilibrium constant (K_{eq}) for the equilibrium of $N_2O_4 \rightleftharpoons 2NO_2$ is equal to 1.1×10^{-5} mol/liter at a specified temperature. A solution of N_2O_4 in chloroform solvent is determined to be 0.02 mol/liter. Determine the concentration of NO_2 at the specified temperature. (Round to the nearest tenth.)

 $[NO_2] =$

Answer: The equilibrium expression found in frame 88 can be modified to solve for [NO₂].

$$\begin{split} [NO_2]^2 &= (K_{eq})[N_2O_4] \\ [NO_2] &= \sqrt{(K_{eq})[N_2O_4]} \\ &= \sqrt{(1.1 \times 10^{-5} \text{ mol/liter})(0.02 \text{ mol/liter})} \\ &= \sqrt{2.2 \times 10^{-7} \text{ mol}^2/\text{liter}^2} \\ &= 4.7 \times 10^{-4} \text{ mol/liter} \end{split}$$

The concepts of chemical and ionic equilibria are very important to you and the chemist. Many useful industrial products, such as NH₃ for fertilizers and

explosives, require the manipulation of an equilibrium situation to achieve their production. Many physiological processes rely upon equilibria between dissolved salts and weak acids and bases that are present in our bodies. Blood cells must be surrounded by solutions with proper electrolyte balance and H⁺ ion concentration similar to that found within the cell, or the cell may be damaged. In the next chapter, we say more about acids and bases and their equilibria.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test.

| 1. | Write the | equilibrium | constant ex | xpression fo | or the f | ollowing | reaction |
|----|-----------|-------------|-------------|--------------|----------|----------|----------|
| | | | | | | | |

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$

- (a) K_{eq} = _____
- (b) What units will K_{eq} have?
- 2. Calculate how many moles of HI would be present at equilibrium when $[H_2] = 1 \times 10^{-2}$, $[I_2] = 2.5 \times 10^{-2}$, and $K_{eq} = 50$ for this equilibrium mixture. Assume system volume is 1 liter. (Round to the nearest hundredth.)

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

3. In what direction will the equilibrium be shifted (left toward the reactant side or right toward the product side) by the following changes?

heat +
$$N_2(g)$$
 + $O_2(g)$ \rightleftharpoons 2NO(g)

- (a) an increase in pressure _____
- (b) a decrease in temperature _____
- (c) a decrease in N₂ concentration _____
- 4. Write the equilibrium constant expression for the following equilibrium reaction.

$$Al_2Cl_6(aq) + 12H_2O(l) \rightleftharpoons 2Al(H_2O)_6^{3+}(aq) + 6Cl^{-}(aq)$$

K_{eq} = _____

- 5. A 0.10 M solution of ammonium hydroxide is found to be 1% ionized. Calculate K_b (to the nearest tenth).
- 6. Calculate (to the nearest hundredth) the molar solubility of $BaSO_4$ if

$$K_{sp}$$
 of BaSO₄ = 1.1 × 10⁻¹⁰

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, you are ready to proceed to the next chapter. If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

1. (a)
$$\frac{[Cl_2]^2[H_2O]^2}{[HCI]^4[O_2]}$$
 (frames 9–13)

(b) liters/mol (frames 18-22)

2.
$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = 50$$

[HI] =
$$\sqrt{50 \times [H_2] \times [I_2]}$$

[HI] =
$$\sqrt{(50)(1 \times 10^{-2})(2.5 \times 10^{-2})} = \sqrt{1.25 \times 10^{-2}} = 1.12 \times 10^{-1} \text{ mol}$$
 (frames 14–16)

- 3. (a) no change (frames 48-51)
 - (b) left toward the reactant side (frames 42-47)
 - (c) left toward the reactant side (frames 34-41)

4.
$$\frac{[Al(H_2O)_6^{3+}]^2[Cl^-]^6}{[Al_2Cl_6]}$$
 (frames 9–13, 25–30)

5.
$$NH_3(g) + H_2O(I) \Rightarrow NH_4^+(aq) + OH^-(aq)$$

 $[NH_4^+] = (0.1)(0.01) = 0.001$

$$[OH^{-}] = (0.1)(0.01) = 0.001$$

 $[NH_3] = (0.10 - 0.001) = 0.099$

$$(0.001)^2$$
 $(1 - 10^{-3})^2$

$$K_b = \frac{(0.001)^2}{0.099} = \frac{(1 \times 10^{-3})^2}{9.9 \times 10^{-2}} = 1.0 \times 10^{-5}$$
 (frames 84, 85)

6.
$$BaSO_4(s) = Ba^{2+} + SO_4^{2-}$$

$$\therefore [Ba^{2+}] = S$$

$$[SO_4^{2-}] = S$$

 $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$
 $\therefore S^2 = 1.1 \times 10^{-10}$

$$\therefore S^2 = 1.1 \times 10^{-10}$$

$$\therefore$$
 S = 1.05 × 10⁻⁵ mol/liter (frames 55, 64, 65)

13 Acids and Bases

Chapters 11 and 12 gave you an indication that all acids have certain properties in common and all bases have certain properties in common. The major common property is that acids react with bases (and vice versa) to produce salts. For example, if solutions of HCl (an acid) and KOH (a base) are mixed, the following reaction occurs.

$$HCl + KOH \rightarrow KCl + H_2O$$

acid + base \rightarrow salt + water

Such a reaction gives a solution that no longer has the acidic or basic properties that were evident before mixing, provided the correct volumes and concentrations were used.

What then is an acid? What is a base? There are three definitions that have been developed through the years. Each has its own particular usefulness, depending upon the nature of the reactants and the conditions of the reaction. In this chapter we will discuss each of the definitions and their particular usefulness.

Our discussion of acids and bases will touch on several other important concepts, including reactions of salts with water, another concentration term specially developed for acid-base solutions, and the importance of acid-base chemistry to physiological and industrial processes.

OBJECTIVES

After completing this chapter, you will be able to

- recognize and apply or illustrate the following: Arrhenius, Brønsted-Lowry, and Lewis acids and bases, neutralization, hydrolysis, pH, buffer solution, titration, conjugate acid or base, amphiprotic, indicator, hydronium ion, and hydrated;
- write a chemical equation for a neutralization reaction between any acid and base;
- predict whether a solution of a given salt will be acidic, basic, or neutral;

- calculate the pH of a solution when given:
 - (a) the degree of ionization of a weak acid or base and vice versa,
 - (b) K_a or K_b of the acid or base and vice versa,
 - (c) the concentration of a solution of a strong acid or base;
- solve titration problems.

ARRHENIUS ACIDS AND BASES

There are several chemical theories of acids and bases. The most familiar is that of Arrhenius. According to the Arrhenius definition, an acid is any substance that produces or increases the H⁺ ion concentration in an aqueous solution (remember, water is the solvent). Both HCl and HC₂H₃O₂ can increase the H⁺ ion concentration of water. Do HCl and HC₂H₃O₂ qualify as acids according to Arrhenius?

Answer: yes (because they increase the H⁺ concentration of water)

An Arrhenius base is any substance that produces or increases the concentration of OH⁻ ion in aqueous solutions. All of the substances that have been named acids and bases so far in this book qualify as Arrhenius acids and bases.

NaOH is a strong electrolyte and NH₄OH is a weak electrolyte. In pure water, they both increase the OH⁻ concentration. Do NaOH and NH₄OH qualify as Arrhenius bases?

Answer: yes (because they both increase the OH⁻ ion concentration in aqueous solution)

A neutralization reaction takes place between an acid and a base in aqueous solution if the moles of H⁺ ion equal the moles of OH⁻ ion. The general equation (net ionic) for such a neutralization is as follows.

$$H^+ + OH^- \rightarrow H_2O$$

Complete and balance the following neutralization reaction, which takes place in aqueous solution. (You may complete the reaction in molecular form.)

$$Ba(OH)_2 + HCl \rightarrow$$

Answer: BaCl₂ + 2H₂O

Here is another typical neutralization reaction.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

| | each of these neutralization reactions, the product that all these equations have common is |
|---------------------------------------|--|
| Ans | wer: H ₂ O |
| one | any neutralization reaction, regardless of the acid-base definition we are using, to of the products is the same as the solvent. In a neutralization reaction taking the between an Arrhenius acid and an Arrhenius base, one product will always be |
| — Ans | wer: H ₂ O |
| contral do soli is utilization. Ans. | the concentration of an acid solution is unknown, a basic solution of known icentration can be added slowly in measured amounts until the solution is neutized. The concentration of the acid can then be determined. It is also possible to the reverse, adding an acid solution to a base. This process of adding a basic ation to an acid or vice versa for neutralization is called titration. An indicator ised in the solution being titrated. The indicator shows one color at a specifical of hydrogen ion concentration and another color at another level of hydrogen concentration. The concentration of a basic solution can be determined by a process called wer: titration |
| | ization to produce water. |
| | $H^+ + OH^- \rightarrow H_2O$ |
| | e ions other than H^+ and OH^- that make up an acid or a base are spectator ions t do not enter the reaction. |
| (a) | Complete and balance the following neutralization reaction. |
| | $HCl + Ca(OH)_2 \rightarrow$ |
| (b) | The complete ionic equation for this reaction is |
| (c) | The spectator ions are and |
| Ans | wer: |
| (a) | CaCl ₂ + 2H ₂ O |

(b) $2H^+ + 2CI^- + Ca^{2+} + 2OH^- \rightarrow Ca^{2+} + 2CI^- + 2H_2O$

(c) Ca²⁺; 2Cl⁻

The net ionic equation for a neutralization reaction is simply:

 $H^+ + OH^- \rightarrow$

Answer: H₂O

In a neutralization reaction, one H⁺ ion reacts with one OH⁻ ion to form one molecule of H₂O. (The ratio of H⁺ to OH⁻ is 1 to 1.)

Remember that M indicates moles/liter. A 1 liter solution of 1 M H⁺ ions could be expected to completely neutralize 1 liter of 1 M OH⁻ ions. (One mole of H⁺ ions completely neutralizes 1 mol of OH⁻ ions.) It would take how many liter(s) of 0.5 M H⁺ ion solution to neutralize 2 liters of 0.5 M OH⁻ ion solution?

Answer: 2 liters (Neutralization of H⁺ and OH⁻ takes an equal number of moles of each. Two liters of 0.5 M H⁺ solution represents 1 mol of H⁺ ions [Chapter 11]. Two liters of 0.5 M OH⁻ solution represents 1 mol of OH⁻ ions.)

The neutralization of H⁺ and OH⁻ to form H₂O is possible when an equal number of moles of each type of ion is present. A 1 liter solution of 0.1 M H⁺ ions represents 0.1 mol of H⁺ ions and can be neutralized (through titration) by any of the following:

1 liter of 0.1 M OH⁻ ion solution, which is 0.1 mol of OH⁻ ions, or 100 milliliters of 1.0 M OH⁻ solution (also 0.1 mol of OH⁻ ions), or 200 milliliters of 0.5 M OH⁻ solution (also 0.1 mol of OH⁻ ions), or 500 milliliters of _____ M OH⁻ ion solution (also 0.1 mol of OH⁻ ions).

Answer: 0.2 $\left(M = \frac{0.1 \text{ mol}}{0.5 \text{ liter}} = 0.2 \text{ mol/liter}\right)$

How many liter(s) of 0.4 M H⁺ solution are needed to neutralize 3 liters of 0.2 M OH⁻ solution?

Answer:

mol H⁺ soln = 3 liters OH⁻ ×
$$\frac{0.2 \text{ mol OH}^-}{1 \text{ liter soln}}$$
 × $\frac{1 \text{ mol H}^+}{1 \text{ mol OH}^-}$ × $\frac{1 \text{ liter soln}}{0.4 \text{ mol H}^+}$ = 1.5 liters H⁺ soln

(As you probably guessed, "soln" is the abbreviation for "solution.")

How many milliliters of 0.6 M H⁺ solution are needed to titrate (neutralize) 250 milliliters of 1.8 M OH⁻ solution?

Answer: mL H⁺ soln = 250 mL OH⁻ soln × $\frac{1 \text{ liter soln}}{1000 \text{ mL soln}}$ × $\frac{1.8 \text{ mol OH}^-}{1 \text{ liter soln}}$ × $\frac{1 \text{ mol H}^+}{1 \text{ mol OH}^-}$

$$\times \frac{1 \text{ liter soln}}{0.6 \text{ mol H}^{+}} \times \frac{1000 \text{ mL soln}}{1 \text{ liter soln}}$$

= 750 mL H⁺ soln

Let's use H₂SO₄ to titrate an OH⁻ solution. H₂SO₄ dissociates to form two H⁺ ions.

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

Therefore, a 1 M solution of H_2SO_4 will dissociate to form a 2 M H⁺ solution. (Ignore the SO_4^{2-} ion since it is a spectator ion.)

How many liters of 1 M H₂SO₄ are needed to neutralize 1 liter of 1 M OH-solution?

Answer: liters
$$H_2SO_4$$
 soln = 1 liter OH^- soln $\times \frac{1 \text{ mol } OH^-}{1 \text{ liter soln}} \times \frac{1 \text{ liter soln}}{1 \text{ mol } H_2SO_4} \times \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol } H^+}$

$$\times \frac{1 \text{ mol } OH^-}{1 \text{ mol } OH^-} = 0.50 \text{ liter } 1 \text{ M } H_2SO_4 \text{ soln}$$

How many milliliters of 0.1 M KOH are needed to titrate (neutralize) 25 milliliters of 0.2 M H₃PO₄ solution?

Answer: mL KOH soln = 25 mL H₃PO₄ ×
$$\frac{1 \text{ liter soln}}{1000 \text{ mL soln}}$$
 × $\frac{0.2 \text{ mol H}_3\text{PO}_4}{1 \text{ liter soln}}$ × $\frac{3 \text{ mol H}^+}{1 \text{ mol H}_3\text{PO}_4}$
× $\frac{1 \text{ mol OH}^-}{1 \text{ mol H}^+}$ × $\frac{1 \text{ liter soln}}{0.1 \text{ mol KOH}}$ × $\frac{1000 \text{ mL}}{1 \text{ liter soln}}$
= 150 mL KOH soln

Titration is a very useful laboratory technique. You will more than likely have to use it to determine the concentration of an unknown acid or base. You may also be required to calculate the formula weight or molar concentration of an acid or base using titration data. With your understanding of moles and molarity, you should be able to calculate them if required to do so.

We now introduce a new concentration term that relates specifically to H^+ and OH^- concentrations in aqueous solutions. It is used to indicate the degree of acidity or alkalinity (or basicity) of an aqueous solution.

Acidity of an aqueous solution is measured by the hydrogen ion concentration of the solution. If you remember the ion product constant for pure water at 25°C, write it below. If not, use the following information to calculate it. Pure water has a H⁺ concentration of $1 \times 10^{-7} M$ (at 25°C). The OH⁻ concentration of pure water is also $1 \times 10^{-7} M$ (at 25°C). The ion product constant for pure water at 25°C is _______.

Answer:
$$K_w = [H^+][OH^-] = 1 \times 10^{-14} M^2$$

The $K_{i\nu}$ for water is usually listed as 1×10^{-14} with no reference to units or temperature. The temperature of 25°C and moles²/liter² (which is the same as M^2) are both assumed.

If the H⁺ concentration is changed to 1×10^{-3} M for an aqueous solution, what is the OH⁻ concentration? (Remember that $K_{\nu\nu}$ is a constant.)

Answer:
$$[OH^{-}] = \frac{K_W}{[H^{+}]} = \frac{1 \times 10^{-14} M^2}{1 \times 10^{-3} M} = 1 \times 10^{-11} M$$

If $[OH^-]$ is equal to 1×10^{-9} M, then the $[H^+]$ must be equal to _____ M.

Answer:
$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14} M^2}{1 \times 10^{-9} M} = 1 \times 10^{-5} M$$

If the hydrogen ion concentration is known, then the hydroxide ion concentration is easily determined, and vice versa. A solution with a hydrogen ion concentration of greater than 1×10^{-7} M is acidic. A solution with a hydrogen ion concentration of less than 1×10^{-7} M is basic.

Is a solution with a hydroxide ion concentration $[OH^-]$ of 1×10^{-10} M acidic or basic? (Find the $[H^+]$ first.)

Answer:
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14} M^2}{1 \times 10^{-10} M} = 1 \times 10^{-4} M$$

Since 1×10^{-4} M is greater than 1×10^{-7} M, the solution is definitely acidic.

pH AND pOH

Instead of writing the hydrogen ion concentration to indicate the acidity (or alkalinity) of a solution, a simple number indicating the pH of a solution is often used. The pH, sometimes called the "hydrogen ion exponent," is defined mathematically as the negative logarithm to the base 10 of the hydrogen ion concentration. For the following H⁺ ion concentrations, compare the power of 10 exponent with the corresponding value of pH.

For
$$[H^+] = 1 \times 10^{-2}$$
 the pH is 2
For $[H^+] = 1 \times 10^{-4}$ the pH is 4
For $[H^+] = 1 \times 10^{-9}$ the pH is 9
For $[H^+] = 1 \times 10^{-6}$ the pH is ______

Answer: 6

If the hydrogen ion concentration is $1 \times 10^{-(e \times ponent)}$, then the pH is equal to the exponent. Or, expressed another way:

$$pH = -log[H^+]$$
 (log to the base 10)

If a solution has a pH of 3, what is the hydrogen ion concentration?

Answer:
$$[H^+] = 1 \times 10^{-3} M$$

What is the pH of pure neutral water?

Answer:
$$[H^+] = 1 \times 10^{-7} M$$

 $\therefore pH = 7$

A solution is acidic if $[H^+]$ is greater than 1×10^{-7} M. A solution is alkaline if $[H^+]$ is less than 1×10^{-7} M. Is a solution with a pH of 6 acidic or alkaline?

Answer: acidic (The [H⁺] = 1×10^{-6} , which is greater than 1×10^{-7} .)

To determine the pH of a solution if the $[H^+]$ is something other than $1 \times 10^{-(exponent)}$ requires use of common logarithms (log to the base 10). Some instructors may arrange problems so that all $[H^+]$ will be $1 \times 10^{-(exponent)}$ to simplify calculations. More often than not, $[H^+]$ is something other than $1 \times 10^{-(exponent)}$. We have chosen such examples and included a log table for your use in the Appendix. You may also use your scientific calculator. In this book, the answers to problems involving logarithms will assume you understand and know how to use logarithms.

To determine the pH of a hydrogen ion concentration of $n \times 10^{-\text{(exponent)}}$, where n is a number other than 1, we must determine the logarithm of the number n.

pH =
$$-\log[H^+]$$

pH = $-\log[n \times 10^{-(exponent)}]$
pH = $-\log n$ + exponent
pH = exponent - $\log n$

Determine the pH of a solution if $[H^+] = 3 \times 10^{-5}$ (to the nearest hundredth). Use the log table in the Appendix.

Determine the pH of a solution with $[H^+] = 6.4 \times 10^{-4}$ (to the nearest hundredth).

Answer: The log of 6.4 is 0.81 (see table).

If
$$[H^+] = n \times 10^{-(exponent)}$$
, then

$$pH = exponent - log n = 4 - log 6.4 = 4 - 0.81 = 3.19.$$

Determine the pH of a 0.002 M aqueous solution of HCl (to the nearest hundredth). (Determine the [H⁺] first. The acid HCl is a strong electrolyte that dissociates completely.)

Answer:
$$[H^+] = 2 \times 10^{-3} M$$

 $pH = exponent - log n$
 $pH = 3 - log 2 = 3 - 0.30 = 2.70$

Conversely, we can determine [H⁺] if the pH is known. A pH of 8.58 indicates a hydrogen ion concentration of $1 \times 10^{-(8.58)}$ M. Such a number is not usable as is; it merely indicates an actual answer of between 1×10^{-9} and 1×10^{-8} M. We must convert it to a usable answer.

$$pH = -log[H^+]$$

 $[H^+] = antilog(-pH)$
 $[H^+] = antilog(-8.58)$

The table of logs reads only positive logs. Therefore, we must change the negative antilog, antilog -8.58, to an expression of the next largest negative integer (-9) and find the antilog of the remainder (-8.58 = -9 + 0.42).

$$[H^+] = \operatorname{antilog}(-8.58) = \operatorname{antilog}(-9 + 0.42) = (\operatorname{antilog} 0.42) \times (\operatorname{antilog} -9)$$

The antilog of 0.42 is 2.6 (from the table). The antilog of -9 is 10^{-9} . Then $[H^+] = (antilog 0.42) \times (antilog <math>-9) = 2.6 \times 10^{-9} M$.

Determine the [H⁺] for a solution with pH of 4.72 (to the nearest tenth).

Answer:
$$[H^+]$$
 = antilog(-pH) = antilog(-4.72) = antilog(-5 + 0.28)
= (antilog 0.28) × (antilog -5)
= $1.9 \times 10^{-5} M$

Determine the $[H^+]$ of a solution if the pH is 10.8 (to the nearest tenth).

Answer:
$$[H^+]$$
 = antilog(-pH) = antilog(-10.8) = antilog(-11 + 0.2)
= (antilog -11) × (antilog 0.2) = $1.6 \times 10^{-11} M$

- Just as the pH is the negative log of [H⁺], we can evaluate pOH, which is the negative log of [OH⁻]. Remember that for pure neutral water, [H⁺] = 1×10^{-7} and [OH⁻] = 1×10^{-7} .
 - (a) What is the pH for pure water?
 - (b) What is the pOH for pure water? _____
 - (c) For pure water, pH + pOH =

Answer: (a) 7; (b) 7; (c) 14

The pH and pOH of any aqueous solution add up to 14. If either the pH or the pOH is known for a solution, the other can quickly be determined. If the pOH is equal to 3, what is the pH?

Answer: pH + pOH = 14pH = 14 - pOH = 14 - 3 = 11

Now that you can determine pH, what is its significance? Many chemical and physiological processes are pH dependent. That is, the pH of the reaction system determines whether or not the reaction will take place. The pH of your blood is normally around 7.6 (slightly basic). If it varies much, either higher or lower, you get sick. Your stomach contains HCl as part of your gastric juices and is normally acidic. What then is an "acid stomach"? The pH of the contents of your stomach has decreased (greater H⁺ concentration), creating a greater than normal acidity. Electrolyte balance inside and outside the cells of our body is also pH dependent. To maintain the proper balance requires a carefully regulated system wherein the pH of the system remains virtually constant within very specific limits. We now discuss this system that is so prevalent in our bodies and that is extensively used in commercial processes to maintain a constant pH.

Buffer Solutions

When a chemist wishes to keep the pH of a solution fairly constant even if some small amount of strong acid or base is added, he will use a buffer solution. A buffer solution involves a chemical equilibrium between either a weak acid and its salt or a weak base and its salt, and shows the common ion effect.

A typical buffer solution is one made up of acetic acid ($HC_2H_3O_2$), which dissociates to a small degree into H^+ and $C_2H_3O_2^-$ ions, and sodium acetate, a salt

of acetic acid that dissociates completely into Na⁺ and C₂H₃O₂⁻ ions. Which ion is common to acetic acid and sodium acetate?

Answer: C₂H₃O₂-, the acetate ion

A buffer solution can consist of a weak acid and its salt or a weak base and its salt, depending upon the desired pH of the buffer solution. A buffer solution with a pH in the acidic range (1-7) can be made from a solution of a weak acid and its salt. A buffer solution with a pH in the basic range (7-14) can be made from a solution of a weak base and its salt. HC₂H₃O₂ and its salt NaC₂H₃O₂ are useful for making a buffer solution with a pH in the ______ range.

Answer: acidic (HC₂H₃O₂ is a weak acid.)

The key to understanding the action of a buffer solution is to remember that a weak acid (or weak base) is only dissociated to a very small degree. Most of the $HC_2H_3O_2$ is still in molecular form when in aqueous solution. The salt, on the other hand, is completely dissociated. All of the $NaC_2H_3O_2$ becomes Na^+ and $C_2H_3O_2^-$.

$$NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^-$$

 $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$

If equal molar quantities of $NaC_2H_3O_2$ and $HC_2H_3O_2$ are mixed in an aqueous buffer solution, almost all of the acetate ion $(C_2H_3O_2^{-1})$ comes from $(HC_2H_3O_2, NaC_2H_3O_2)$

Answer: NaC₂H₃O₂

If just acetic acid is mixed in water, the result is a large amount of molecular $HC_2H_3O_2$ and only a little H^+ and a little $C_2H_3O_2^-$.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

a lot a little a little

If $NaC_2H_3O_2$ is mixed in water, the result is a large amount of Na^+ ion and a large amount of $C_2H_3O_2^-$ ion and no $NaC_2H_3O_2$.

$$NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^-$$

none a lot a lot

If equal molar amounts of HC₂H₃O₂ and NaC₂H₃O₂ were added together in the same aqueous solution, the result would be:

- (a) (a lot, a little) $_$ $HC_2H_3O_2$
- (b) (a lot, a little) $\underline{\hspace{1cm}}$ H^+
- (c) (a lot, a little) $C_2H_3O_2$

Answer: (a) a lot; (b) a little; (c) a lot

The resulting combination of both the weak acid and its fully dissociated salt results in a buffer solution with a large proportion of weak acid ($HC_2H_3O_2$) in molecular form, a large proportion of the common ion from the salt ($C_2H_3O_2^-$), and a small proportion of H^+ ion. We can ignore the large proportion of the positive ion from the salt (Na^+). The addition of extra $C_2H_3O_2^-$ from the salt shifts the equilibrium to increase the $HC_2H_3O_2$ and decrease the H^+ , according to Le Chatelier's Principle.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

a lot a little a lot

According to Le Chatelier's Principle, what would happen to this new equilibrium if some additional H^+ were added to the solution? The concentration of $HC_2H_3O_2$ would (increase, decrease) ______. The concentration of $C_2H_3O_2^-$ would (increase, decrease) ______.

Answer: Adding some H^+ would shift the equilibrium to increase the concentration of $HC_2H_3O_2$ and, in the process, some of the $C_2H_3O_2^-$ would be used up so that its concentration would decrease. The equilibrium would shift to the left.

Answer: HC₂H₃O₂; C₂H₃O₂⁻

If some additional OH⁻ ion is added to the solution, a neutralization reaction would immediately occur.

$$H^+ + OH^- \rightarrow H_2O$$

Some of the H^+ ion from the equilibrium would be used up. The result is a shift in the equilibrium so that more H^+ is produced. The reaction would shift to the right temporarily $(HC_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^-)$ until the extra OH^- ion added had combined with the H^+ ion. At that point, the equilibrium is again restored.

Adding extra OH^- to the solution causes the equilibrium to shift in order to produce more H^+ ion. In order to produce more H^+ ion, the equilibrium shifts so that some $HC_2H_3O_2$ is (produced, used up) _____ and some $C_2H_3O_2^-$ is (produced, used up) ______.

Answer: used up; produced

This chemical equilibrium represents a buffer system.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

a lot a little a lot

- (a) The addition of a little H⁺ from a strong acid such as HCl would shift the equilibrium so that the concentration of HC₂H₃O₂ is (increased, decreased)

 and the concentration of C₂H₃O₂⁻ is (increased, decreased)
- (b) The addition of a little OH $^-$ from a strong base such as NaOH has the opposite effect. It will remove some of the H $^+$ and shift the equilibrium so that the concentration of HC₂H₃O₂ is (increased, decreased) _____ and the concentration of the C₂H₃O₂ $^-$ is (increased, decreased) _____.

Answer: (a) increased, decreased; (b) decreased, increased

In a buffer system such as acetic acid and the acetate ion from sodium acetate, the pH remains relatively constant because extra hydrogen ion (H⁺) undergoes a chemical reaction rather than remaining in the solution. Extra hydroxide ion (OH⁻) is neutralized by additional hydrogen ion produced by the acetic acid as needed. The extra OH⁻ ion also does not remain in solution since it is neutralized. An aqueous buffer system will continue to absorb most of the extra H⁺ or OH⁻ until one of the equilibrants is depleted.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

a lot a little a lot

This buffer system will continue to absorb additional H^+ ion until the $(HC_2H_3O_2, C_2H_3O_2)$ is used up.

Answer: C₂H₃O₂-

A buffer solution useful for maintaining a pH of greater than 7 is made up of a weak base and a salt of the base. Such a buffer system involves an aqueous solution of ammonia (NH₃ • H₂O) and its salt (NH₄Cl).

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

none a lot a lot
 $NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$
a lot a little a little

A buffer solution may be made from equal molar amounts of $NH_3 \cdot H_2O$ and NH_4Cl . Would the resulting solution contain a lot or a little of the following substances? (Ignore the Cl^- ion.)

- (a) $NH_3 \cdot H_2O$
- (b) NH₄⁺_____
- (c) OH⁻_____

Answer: (a) a lot; (b) a lot; (c) a little

The resulting buffer solution equilibrium can be represented as follows if the Clion is ignored.

$$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^- (K_b = 1.8 \times 10^{-5})$$

a lot a little

According to Le Chatelier's Principle, the addition of a small quantity of extra OH-ion from a strong base would shift the equilibrium so that the concentration of $NH_3 \cdot H_2O$ would (increase, decrease) ______ and the concentration of NH_4^+ would (increase, decrease) ______.

Answer: increase; decrease

The addition of more H^+ from a strong acid would cause an immediate neutralization reaction ($H^+ + OH^- \rightarrow H_2O$). The neutralization reaction would remove OH^- ions from the buffer equilibrium system. To compensate for a loss of OH^- ions (according to Le Chatelier's Principle), the equilibrium will shift so that the concentration of $NH_3 \cdot H_2O$ would (increase, decrease) _____ and the concentration of NH_4^+ would (increase, decrease) _____ .

Answer: decrease; increase

Both the acidic and the basic buffer systems react with small additional quantities of H⁺ and OH⁻ to shift a buffer equilibrium. Instead of remaining in solution, the extra H⁺ or OH⁻ ions serve to shift the equilibrium and result in an increase (or decrease) of the weak acid or base and a decrease (or increase) in the salt of the acid or base. The final result is a relatively small change in the pH rather than a large change. Buffering action will continue until so much H⁺ or OH⁻ is added that one of the equilibrants is mostly used up.

A buffer solution is useful for maintaining a relatively constant pH if small quantities of _____ or ____ are added to the solution.

Answer: H+; OH-

Here are other important equilibria involved in physiological processes.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
 (digestive processes)
 $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (digestive processes)
 $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ (cell fluids)

We now examine the situation where just adding a salt to water may change the pH of the water.

Hydrolysis of Salts

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A salt is a product of the neutralization of an acid and a base. Common table salt (NaCl) is a product of the neutralization reaction involving HCl acid and NaOH base.

A salt can be a product of (a) a strong acid and a strong base, (b) a strong acid and a weak base, (c) a weak acid and a strong base, or (d) a weak acid and a weak base. HCl is a strong acid (completely dissociated). NaOH is a strong base (completely dissociated). NaCl is a product of a ______ acid and a _____ base.

Answer: strong; strong

By the Arrh

By the Arrhenius definition of acids and bases, an acid and a base react to yield water and a salt.

NaOH is a strong (completely dissociated) base.

KOH is a strong base.

H₂SO₄ is a strong acid.

HCl is a strong acid.

HC₂H₃O₂ is a weak (partially dissociated) acid.

H₂CO₃ is a weak acid.

NH₄OH is a weak base. (Also written NH₃ • H₂O or NH₃(aq).)

NaCl is a product of a strong acid and a strong base.

- (a) K₂CO₃ is a product of a _____ acid and a _____ base.
- (b) NH₄Cl is a product of a _____ acid and a _____ base.
- (c) Na₂SO₄ is a product of a _____ acid and a _____ base.
- (d) NH₄C₂H₃O₂ is a product of a _____ acid and a ____ base.

Answer:

- (a) weak; strong (H₂CO₃, KOH)
- (b) strong; weak (HCl, NH₄OH)
- (c) strong; strong (H₂SO₄, NaOH)
- (d) weak; weak (HC2H3O2, NH4OH)

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The general formula for the neutralization of Arrhenius acids and bases is:

acid + base
$$\rightarrow$$
 H₂O + salt

The reverse reaction is possible, especially since weak acids or bases usually involved reversible equilibrium reactions. When a salt is mixed with water, it dissociates. The resulting ions may react with water in a reaction known as hydrolysis.

Pure water is ionized (dissociated) to a small degree. The ions of some salts may react with the ions of pure water. What ions result from the ionization of pure water?

Answer: H+ and OH-

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The ions of pure water could possibly react with the ions of the various salts. Table salt (NaCl) is produced by reaction of a strong acid (HCl) and a strong base (NaOH). If NaCl is mixed with water, the equation could be as follows.

Both the acid (HCl) and the base (NaOH) are completely dissociated and can be shown as ions. NaCl is also completely dissociated.

$$Na^+ + Cl^- + H_2O \rightarrow H^+ + Cl^- + Na^+ + OH^-$$

Eliminate the spectator ions in the above reaction and write the net ionic equation.

Answer: $H_2O \rightarrow H^+ + OH^-$

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The net ionic equation of the reaction of NaCl with water is simply $H_2O \rightarrow H^+ + OH^-$, the ionization of water. The addition of a salt from a strong acid and a strong base has no effect on the H^+ concentration or the OH^- concentration. The aqueous solution of such a salt remains neutral.

The salt Na_2SO_4 is the product of H_2SO_4 (a strong acid) and NaOH (a strong base). Would the addition of Na_2SO_4 to pure neutral water have any effect on the H^+ concentration or the OH^- concentration?

Answer: no (because it is a salt of a strong acid and a strong base)

$$2Na^{+} + SO_{4}^{2-} + 2H_{2}O \rightarrow 2Na^{+} + SO_{4}^{2-} + 2H^{+} + 2OH^{-}, \text{ or } 2H_{2}O \rightarrow 2H^{+} + 2OH^{-}$$

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NH₄Cl is a salt of a strong acid and a weak base. The hydrolysis reaction is:

$$NH_4Cl + H_2O \rightarrow HCl + NH_4OH$$

The salt (NH₄Cl) dissociates completely and so does the strong acid (HCl). The H_2O and the weak base (NH₄OH) remain largely in molecular form. The complete ionic equation results in:

$$NH_4^+ + Cl^- + H_2O \rightarrow H^+ + Cl^- + NH_4OH$$

Eliminate the spectator ions in this equation. The net ionic equation is

Answer: $NH_4^+ + H_2O \rightarrow H^+ + NH_4OH$

The hydrolysis of a salt from a strong acid and a weak base produces a solution that is acidic. The net ionic equation of the hydrolysis of such a salt shows the production of additional H⁺ ions. The concentration of H⁺ ions is therefore increased and the solution becomes acidic.

Answer: less than

 $NaC_2H_3O_2$ is the salt of a weak acid and a strong base. The hydrolysis reaction is:

$$NaC_2H_3O_2 + H_2O \rightarrow HC_2H_3O_2 + NaOH$$

The salt $(NaC_2H_3O_2)$ dissociates completely. The strong base (NaOH) also dissociates completely. The weak acid $(HC_2H_3O_2)$ and H_2O remain largely in molecular form. The complete ionic equation becomes:

$$Na^+ + C_2H_3O_2^- + H_2O \rightarrow HC_2H_3O_2 + Na^+ + OH^-$$

The net ionic equation (eliminate spectator ions) is

Answer: $C_2H_3O_2^- + H_2O \rightarrow HC_2H_3O_2 + OH^-$

The hydrolysis of a salt from a weak acid and a strong base results in a solution that is basic. The net ionic equation of the hydrolysis of such a salt shows the production of OH⁻ ions. The concentration of OH⁻ ions is increased, and therefore the solution becomes basic.

The pH of neutral water is 7. The pH of a solution containing a salt from a weak acid and a strong base is (greater than, less than) ________7.

Answer: greater than

The hydrolysis of a salt from:

a strong acid and a weak base yields an acidic solution.

a weak acid and a strong base yields a basic solution.

If the acid is stronger than the base, the salt solution will be acidic. If the base is stronger than the acid, the salt solution will be basic. If the acid and the base are both strong, the solution will be neutral.

NaNO₃ is the salt of HNO₃ (a strong acid) and NaOH (a strong base). Which will an aqueous solution of NaNO₃ be — acidic, basic, or neutral?

Answer: neutral

The only combination not yet covered is the salt of a weak acid and a weak base. In the case of a weak acid or a weak base, both may be weak but one may be slightly stronger than the other. Strength of a weak acid is measured by its K_a (ionization constant of a weak acid). Strength of a weak base is measured by its K_b (ionization constant of a weak base).

Imagine that a salt is produced from a weak acid and a weak base. The weak acid, however, is stronger than the weak base (K_a is larger than K_b). Based upon what you have already learned from the hydrolysis of a salt from a strong acid and a weak base, what would you expect from the hydrolysis of this salt?

Answer: It would be slightly acidic, because the weak acid is stronger than the weak base.

Another salt of a weak acid and a weak base undergoes hydrolysis.

 K_a for the weak acid is 2.0×10^{-6} K_b for the weak base is 2.0×10^{-4}

The weak base is slightly (weaker, stronger) _____ than the weak acid.

Answer: stronger (K_b is larger than K_a , therefore the weak base is somewhat stronger than the weak acid.)

A salt is produced from a weak acid and a weak base.

 K_a for the weak acid is 2.0×10^{-6} K_b for the weak base is 2.0×10^{-4}

Hydrolysis of the salt produces an aqueous solution that is slightly (acidic, basic)

Answer: basic

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NH₄C₂H₃O₂ is a salt of a weak acid (HC₂H₃O₂) and a weak base (NH₄OH).

$$K_a$$
 for HC₂H₃O₂ is 1.8 × 10⁻⁵ K_h for NH₄OH is 1.8 × 10⁻⁵

In this case, the K_a and the K_b are equal. The weak acid and the weak base are equal in strength. You learned earlier that a solution of a salt of a strong acid (completely

dissociated) and a strong base (completely dissociated) would be neutral because the base and acid were equal in strength. If NH₄C₂H₃O₂ undergoes hydrolysis, would you expect the aqueous solution to be slightly acidic, slightly basic, or neutral?

Answer: neutral (Since neither the acid nor the base is stronger than the other, the salt solution will be neutral.)

NH₄CN is a salt of a weak acid (HCN) and a weak base (NH₃(aq)).

$$K_b$$
 for NH₃ = $\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$ = 1.8 × 10⁻⁵
 K_a for HCN = $\frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$ = 4.0 × 10⁻¹⁰

The aqueous solution resulting from the hydrolysis of NH₄CN will be (acidic, basic, neutral) _____

Answer: basic

The aqueous solution of a salt derived from:

- (a) a strong acid and strong base is _____.
- (b) a strong acid and weak base is _____.
- (c) a weak acid and strong base is _____.
- (d) a weak acid and a weak base $(K_a \text{ is larger than } K_b)$ is _____.
- (e) a weak acid and a weak base $(K_b \text{ is larger than } K_a)$ is _____.
- (f) a weak acid and a weak base $(K_a \text{ equals } K_b)$ is _____.

Answer: (a) neutral; (b) acidic; (c) basic; (d) acidic; (e) basic; (f) neutral

The Arrhenius Theory is the most extensively used theory in beginning chemistry classes today. However, many chemists have used solvents other than water in their research. They noticed that strong Arrhenius acids and bases that were 100% ionized in water and therefore considered to be of the same strength did not all ionize to the same extent in other solvents. The strength of the acid or base depended upon the solvent used. The Arrhenius acid-base definitions limit acids to the presence of H⁺ in solution and bases to the presence of OH⁻ in solution. A broader definition is required when using solvents other than water. We now discuss the theory that was developed for use in other solvents (nonaqueous solvents).

BRØNSTED-LOWRY ACIDS AND BASES: LEVELING EFFECT OF THE SOLVENT

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HCl, HNO₃, and H₂SO₄ are all strong acids. They each dissociate completely in an aqueous solution. In aqueous solution, all of these acids are equal in strength because they all dissociate completely.

Perchloric acid (HClO₄) also dissociates completely in aqueous solution. Since acid strength is based upon the extent to which an acid dissociates, HClO₄ is (equal to, stronger than, weaker than) ______ HCl, HNO₃, and H₂SO₄ in aqueous solutions.

Answer: equal to

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For simplicity, the dissociation of HCl in water is written as follows.

$$HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

All strong acids form a positive ion and a negative ion. In reality, however, the H^+ ion from an acid combines with H_2O to form H_3O^+ , which is known as the hydronium ion.

- (a) What is the positive ion from all strong acids?
- (b) In aqueous solutions, this ion combines with H2O to form what ion?

Answer: (a) H⁺ or hydrogen ion; (b) H₃O⁺ or hydronium ion

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The polar nature of H_2O molecules causes the H^+ ion to combine with H_2O and form the H_3O^+ ion. An ion surrounded by H_2O molecules is said to be hydrated. The aqueous solution of any strong acid is actually composed of H_3O^+ ions and a negative ion.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

 $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$
 $H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-}$
 $HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$

What ion is common to all of these strong acids?

Answer: H₃O+ or hydronium ion

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Because they dissociate completely, all strong acids form aqueous solutions that are composed of H_3O^+ ions and a negative ion. The negative ion has no effect on acid strength. The strongest acid that can exist in an aqueous solution is the hydronium ion (H_3O^+). All strong acids that dissociate completely in H_2O are of equal strength because all form the hydronium ion (H_3O^+). Even though $HClO_4$ may be stronger

than HNO₃ in some other solvent, they are of equal strength in H₂O solution because both dissociate completely to form hydronium ions. In aqueous solution, no acid can be stronger than what ion?

Answer: hydronium ion, H₃O⁺

In some solvent other than water, HClO₄ may be stronger than HNO₃. In aqueous solution, both are of equal strength because both form H₃O⁺ equally well. All acids that dissociate completely in H₂O form H₃O⁺ equally well. The strength of acid is limited by the solvent because H₃O⁺ is the actual acid in aqueous solutions. This equalization of acid strength depending upon the solvent is known as the leveling effect of the solvent. Because the H⁺ ion is hydrated when introduced in H₂O solvent, all acids are leveled to the strength of the H₃O⁺ ion. The leveling effect of the solvent holds true also for bases. The strongest base that can exist in aqueous solution is the OH⁻ ion.

The hydroxide ion (OH^-) can be described as a water molecule (H_2O) without a hydrogen ion (H^+) . The hydronium ion (H_3O^+) can be described as a water molecule (H_2O) with a hydrogen ion (H^+) .

- (a) When the hydronium ion and the hydroxide ion combine, what is formed? $(H_3O^+ + OH^- \rightarrow ?)$
- (b) The OH is the strongest base that can exist in what kind of solution?
- (c) All strong bases are leveled to the strength of what ion in aqueous solutions?

Answer: (a) H₂O; (b) aqueous or H₂O; (c) OH⁻ or hydroxide ion

Acids that dissociate completely in water may dissociate only partially in other solvents. A process similar to hydration occurs in such solvents. For solvents other than water this process is called solvation. Acids or bases in solvents other than water are no longer under the Arrhenius definition of acids and bases. Two scientists named Brønsted and Lowry formed a wider definition of acids and bases that includes solvents other than water.

The word "hydration" and the Arrhenius definition of an acid or base are both limited to what kind of solutions?

Answer: aqueous (H₂O or water)

Brønsted and Lowry defined an acid as a substance capable of donating a proton (proton donor) and a base as a substance capable of accepting a proton (proton acceptor). The proton is exactly the same as the H⁺ ion in Arrhenius acid-base equations. (The H⁺ ion is viewed as the hydrogen atom without the electron. The only subatomic particle left after removal of the electron is the proton.)



Answer: H+ (a proton)

Identifying the proton donor (acid) is not very difficult. Brønsted-Lowry bases (proton acceptors), however, include a variety of substances and ions in addition to the OH⁻ ion. In the following equation, the cyanide ion (CN⁻) can act as a proton acceptor in the reverse reaction.

$$HCN \rightleftharpoons H^+ + CN^-$$

The CN⁻ ion is therefore the Brønsted-Lowry base in the equation. Using Brønsted-Lowry definitions, identify the acid, base, and proton in the equation below.

Answer: HCN \rightleftharpoons H⁺ + CN⁻ acid proton base

The Brønsted-Lowry acid (HCN) and the Brønsted-Lowry base (CN⁻) are called a conjugate acid-base pair because the only difference between them is the presence or absence of a proton. HCN and CN⁻ are exactly the same with the exception of the proton (H⁺).

The following substances are Brønsted-Lowry acids or bases. Only one conjugate pair is present, however.

$$NH_3$$
, H_2O , NH_4^+ , Cl^- , SO_4^{2-} , HCN

The conjugate acid-base pair is _____ and _____.

Answer: NH₄+; NH₃ (NH₄+ is the same as NH₃ plus a proton.)

- NH₄⁺ and NH₃ are a conjugate acid-base pair.
 - (a) Which is the acid (proton donor)?
 - (b) Which is the base (proton acceptor)?

Answer: (a) NH_4^+ ; (b) NH_3

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

donor acceptor

Since the proton (H⁺) does not generally exist by itself, Brønsted-Lowry equations usually show two sets of conjugate acid-base pairs and no protons. A Brønsted-Lowry reaction generally shows an acid and a base as reactants and an acid and a base as products.

In the equation below, identify the acids and bases by writing the correct names in the blanks.

$$HCN + NH_3 \rightleftharpoons CN^- + NH_4^+$$

Answer:
$$HCN + NH_3 \rightleftharpoons CN^- + NH_4^+$$

acid base base acid

In the equation in frame 69 identify the two conjugate acid-base pairs.

| and | · <u>·</u> |
|---------|------------|
| and | |

Answer:

HCN (acid); CN- (base)

NH₄+ (acid); NH₃ (base)

(The only difference between the acid and base of a conjugate pair is the proton.)

Identify the acids and bases in the following Brønsted-Lowry equation. Draw a line joining the acid and base of each conjugate pair. For example:

$$A + B \rightleftharpoons C + D$$
acid base acid base

$$HCl + NH_3 \rightleftharpoons Cl^- + NH_4^+$$

Answer:
$$HCI + NH_3 \rightleftharpoons CI^- + NH_4^+$$
acid base base acid

Identify the acids, bases, and conjugate pairs in the following reactions as you did in frame 71.

(a)
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

(b)
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Answer:

(a) HCl +
$$H_2O \rightleftharpoons H_3O^+ + Cl^-$$

acid base acid base

(b)
$$NH_3 + H_2O \Rightarrow NH_4^+ + OH^-$$

base acid acid base

In one reaction above, H_2O accepted a proton to become H_3O^+ . In another reaction, H_2O donated a proton to become OH^- .

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

A substance that can act as both a Brønsted-Lowry acid and a base is said to be amphiprotic. In the above reactions, what substance is amphiprotic?

Answer: H₂O (It can either donate or accept a proton. Donating a proton is the definition for a Brønsted–Lowry acid. Accepting a proton is the definition for a Brønsted–Lowry base.)

Some pure solvents ionize slightly. For example, we have shown that water ionizes $(H_2O \rightleftharpoons H^+ + OH^-)$. The ionization is more correctly written to include the hydronium (H_3O^+) ion $(H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-)$. Whenever a pure solvent ionizes in this manner, the process is called self-ionization or auto-ionization. Identify the acids, bases, and conjugate pairs in the equation of H_2O ionization.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Answer:
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
 or $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ acid base acid base base acid acid base

(It doesn't matter which H₂O is labeled the acid or which is the base as long as the conjugate pairs are correct.)

We have seen that the strongest acid that can exist in an *aqueous* solution is the positive ion formed by the solvent plus a proton $(H_2O + \text{proton} = H_3O^+)$. The strongest base that can exist is the negative ion formed by the solvent minus a proton $(H_2O - \text{proton} = OH^-)$. Other solvents behave in a similar manner.

Liquid ammonia (NH₃) can be used as a solvent for Brønsted-Lowry acid-base reactions. It self-ionizes to produce two ions.

$$NH_3(l) + NH_3(l) = NH_4^+ + NH_2^-$$

- (a) Identify the strongest acid that can exist in a liquid ammonia solution.
- (b) Identify the strongest base that can exist in a liquid ammonia solution.

Answer: (a) NH₄+ (solvent + proton); (b) NH₂- (solvent - proton)

In the self-ionization equation in frame 75, ammonia is acting as both an acid and a base. Since it acts as both a proton acceptor and a proton donor, ammonia can be called .

Answer: amphiprotic

Pure acetic acid (HC₂H₃O₂) can also be used as a solvent for Brønsted-Lowry acid-base reactions. The self-ionization equation for acetic acid is as follows.

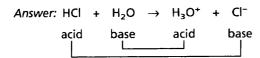
$$HC_2H_3O_2(l) + HC_2H_3O_2(l) \rightleftharpoons H_2C_2H_3O_2^+ + C_2H_3O_2^-$$

- (a) What is the strongest acid that can exist when acetic "acid" is the solvent?
- (b) What is the strongest base that can exist when acetic "acid" is the solvent?

Answer: (a) $H_2C_2H_3O_2^+$ (solvent + proton); (b) $C_2H_3O_2^-$ (solvent - proton)

In the Brønsted-Lowry concept of acids and bases, the stronger the acid, the weaker its conjugate base. Conversely, the stronger the base, the weaker its conjugate acid. In the following Brønsted-Lowry equation, the hydration of HCl produces the hydronium ion and the Cl⁻ ion. The reaction is virtually complete. A negligible amount of HCl remains in molecular form. Identify the acids, bases, and conjugate pairs in the reaction.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$



- In this reaction, HCl is a much stronger acid than H_3O^+ since HCl donates virtually all of its protons to H_2O to form H_3O^+ . On the other hand, H_2O is a much stronger base than Cl^- since it accepts virtually all of the protons while leaving almost none for the Cl^- ion.
 - (a) Is the weaker base (Cl⁻) the conjugate of the weaker acid or the stronger acid?
 - (b) Is the weaker acid (H_3O^+) the conjugate of the weaker base or the stronger base?

Answer: (a) stronger; (b) stronger

Every Brønsted-Lowry acid-base reaction favors the production of the weaker acid and the weaker base. A reaction with the stronger acid and base as reactants and the weaker acid and base as products will proceed favorably to produce a relatively large proportion of products.

stronger acid + stronger base → weaker acid + weaker base

The reverse reaction below is *not* favored and very little product will be formed.

weaker acid + weaker base → stronger acid + stronger base

The following reaction produced a large proportion of products with very little of the reactants left over. Identify the stronger acid and the stronger base.

$$HI + NH_3 \rightarrow NH_4^+ + I^-$$

- (a) The stronger acid is _____.
- (b) The stronger base is _____.

Answer: (a) HI; (b) NH₃ (The weaker acid and base are favored in a reaction. If a large proportion of products results from a reaction, then the reactants are stronger.)

Using solvents other than water, we can differentiate between strengths of those acids that are completely dissociated in water. The leveling effect of water is thus avoided. For example, HCl and HI are both strong acids (dissociate completely) in aqueous solution. However, in a solvent such as liquid ammonia, it has been determined that HI dissociates to a greater degree than HCl. HI is therefore stronger than HCl.

| Name | Formula | Formula | Name |
|----------------------|---|--|----------------------|
| Strongest acid | | | Weakest base |
| perchloric acid | HClO₄ | CIO ₄ - | perchlorate ion |
| hydrogen iodide | HI | I - | iodide ion |
| sulfuric acid | H ₂ SO ₄ | HSO₄⁻ | hydrogen sulfate ion |
| hydrogen chloride | HCl | Cl- | chloride ion |
| nitric acid | HNO ₃ | NO ₃ - | nitrate ion |
| hydronium ion | H ₃ O ⁺ | H ₂ O | water |
| hydrogen sulfate ion | HSO₄ [−] | SO ₄ ²⁻ | sulfate ion |
| acetic acid | HC ₂ H ₃ O ₂ | $C_2H_3O_2^-$ | acetate ion |
| ammonium ion | NH ₄ ⁺ | NH ₃ | ammonia |
| hydrogen cyanide | HCN | CN- | cyanide ion |
| water | H₂O | OH- | hydroxide ion |
| ethyl alcohol | C₂H₅OH | C ₂ H ₅ O ⁻ | ethoxide ion |
| ammonia | NH ₃ | NH ₂ | amide ion |
| Weakest acid | | | Strongest base |

A table of some Brønsted-Lowry acids and bases appears above. The acids are listed in order of decreasing strength. Their conjugate bases are listed in order of increasing strength.

(a) What is the strongest Brønsted-Lowry acid listed?

| (b) | The conjugate ba | ise of the strongest | acid is the w | eakest base. | What is the | weak- |
|-----|------------------|----------------------|---------------|--------------|-------------|-------|
| | est base? | | | | | |

Answer: (a) perchloric acid (HClO₄); (b) perchlorate ion (ClO₄ $^-$)

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The above table of Brønsted-Lowry acid-base strengths can be used to determine whether a reaction will proceed to favor the formation of products. If the product acid and base are weaker than the reactant acid and base, the forward reaction will proceed favorably to form products. If the product acid and base are stronger than the reactant acid and base, the reaction will *not* proceed to favor the products.

Will the following Brønsted-Lowry reaction proceed and favor the formation of products? (Use the table of acid and base strengths to determine the relative strengths of the acids and bases in the reaction.)

$$HI + C_2H_3O_2^- \rightarrow I^- + HC_2H_3O_2$$

acid base base acid

Answer: Yes. HI is a stronger acid than $HC_2H_3O_2$. $C_2H_3O_2^-$ is a stronger base than I^- . Because the acid and base are the reactants, the reaction will proceed to favor the products.

Which does this Brønsted-Lowry reaction favor — the products or the reactants?

$$HSO_4^- + NH_2^- \rightarrow NH_3 + SO_4^{2-}$$

acid base acid base

Answer: the products (HSO_4^- is stronger than NH_3 . NH_2^- is stronger than SO_4^{2-} .)

Will the following Brønsted-Lowry reaction favor the reactants or the products? (Hint: First determine the acids and bases.)

$$C_2H_5OH + Cl^- \rightarrow C_2H_5O^- + HCl$$

Answer:
$$C_2H_5OH + CI^- \rightarrow C_2H_5O^- + HCI$$

acid base base acid

HCl is a stronger acid than C_2H_5OH . $C_2H_5O^-$ is a stronger base than Cl⁻. Since the products are stronger than the reactants, the reactants are favored and only very slight amounts of products are formed.

In the following reaction, are the reactants or the products favored?

$$HCl + CN^- \rightarrow HCN + Cl^-$$

Answer: The products are favored. (HCl is a stronger acid than HCN. CN⁻ is a stronger base than Cl⁻. The weaker acid and base of the products are favored.)

The general term that covers all Brønsted-Lowry acid-base reactions is protolysis. All protolytic reactions favor the production of the (weaker, stronger) ______ acid and base.

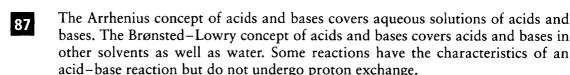
Answer: weaker

Arrhenius defined an acid-base neutralization as a reaction in which $\rm H_2O$ is always a product. Brønsted-Lowry defines an acid-base neutralization as a reaction in which the solvent is always a product, and an acid-base reaction is referred to as protolysis.

The Brønsted-Lowry definition broadens our concepts of acids and bases by permitting more compounds to be considered as acids or bases that are not under the Arrhenius definition. The Brønsted-Lowry definitions are particularly useful to organic chemists, who deal quite often with nonaqueous systems. However, the Brønsted-Lowry idea still requires the presence of a proton that may be transferred from an acid to a base. This is still somewhat limiting in scope, so a third

concept involving something that is present in all substances, electrons, has been developed. We now discuss that third concept.

THE LEWIS ACID-BASE CONCEPT



An "acid" that does not have a proton to donate would not fit the Brønsted-Lowry concept. For all practical purposes, a proton is the same as what ion?

Answer: H+

A scientist by the name of Lewis developed an acid-base theory to include those reactions that seem to behave like acid-base reactions but do not involve proton (H⁺) exchange. According to Lewis, an acid is any substance that can accept a pair of electrons to form a coordinate covalent bond. A base, on the other hand, is any substance that is capable of donating a pair of electrons to form a coordinate covalent bond. To avoid confusion between the Brønsted-Lowry concept and the Lewis concept, remember that the electron and proton are oppositely charged.

| (a) | A Brønsted-Lowry acid is a proton (acceptor, donor) |
|-----|---|
| (b) | A Lewis acid is an electron pair (acceptor, donor) |
| (c) | A proton has what charge? |
| (d) | An electron has what charge? |
| Ans | <i>wer</i> : (a) donor; (b) acceptor; (c) +; (d) – |

Brønsted-Lowry protolysis normally deals with a *single* proton. Lewis acids and bases deal with a *pair* of electrons in coordinate covalent bonds. A Lewis base can be an electron-rich negative ion, such as OH⁻, HSO₄⁻, and O²⁻, or a molecule that has one or more pairs of electrons that are not already part of a covalent bond. Examples include H₂O and NH₃. Lewis acids include positive ions, such as H⁺, Al³⁺, and Ag⁺, as well as molecules that have room for an additional pair of electrons. Examples include BF₃, SO₃, and CO₂.

 HCO_3^- is an ion with a pair of available electrons. This ion is probably a Lewis (acid, base) ______.

Answer: base (A Lewis base is an electron pair donor.)

The reactions of Lewis acids and bases are best depicted by dot symbols that are appropriately known as Lewis symbols. Dot symbols were encountered in Chapter 3. Remember that dots are used to symbolize electrons.

The H⁺ ion is a Lewis acid since it can accept a pair of electrons to share in a coordinate covalent bond. The NH₃ molecule is a Lewis base since it has an unshared pair of electrons.

$$H^{+} + : \ddot{\mathbb{N}} : H \to \begin{bmatrix} H \\ H : \ddot{\mathbb{N}} : H \end{bmatrix}^{+}$$

$$\ddot{H}$$

Look at this Lewis reaction depicted by Lewis symbols. In a coordinate covalent bond, the electron pair forming the bond comes from one substance. In this reaction, both electrons come from what substance?

Answer: NH_3 (Since H^+ has no electrons at all, both bonding electrons must come from the NH_3 molecule.)

The hydrolysis of HCl to form the hydronium ion (H_3O^+) can also be interpreted through the Lewis concept.

$$\begin{array}{c} H^{+}: \ddot{\mathbb{C}} \\ \vdots \\ H \end{array} \rightarrow \begin{bmatrix} H: \ddot{\mathbb{O}}: H \\ H \end{bmatrix}^{+} + \begin{bmatrix} : \ddot{\mathbb{C}} \\ \vdots \end{bmatrix}^{-} \end{array}$$

Remember that HCl dissociates completely in aqueous solutions and that the Clion is a spectator ion.

- (a) Which reactant is the Lewis acid?
- (b) Which reactant is the Lewis base?

Answer: (a) HCI (Actually only the H⁺ ion. It accepts a pair of electrons.); (b) H₂O (It shares a pair of its free electrons to form a coordinate covalent bond.)

One example of a Lewis acid-base reaction has been encountered previously as an example of a coordinate covalent bond. That is the reaction between BF₃ and NH₃ to form NH₃BF₃.

$$\begin{array}{cccc} H & :\ddot{F}: & H : \ddot{F}: \\ H : \ddot{N} : + & \ddot{B} : \ddot{F} : \rightarrow H : \ddot{N} : \ddot{B} : \ddot{F} : \\ \ddot{H} & : \ddot{F} : & \ddot{H} : \ddot{F} : \end{array}$$

- (a) The two electrons that form the coordinate covalent bond come from (NH $_3$, BF $_3$) _____ .
- (b) The Lewis acid in this example is _____.
- (c) The Lewis base is _____.

Answer: (a) NH₃; (b) BF₃ (electron pair acceptor); (c) NH₃ (electron pair donor)

You have just learned three ways chemists use to describe acids, bases, and neutralization reactions while also learning about pH, buffer solutions, and titration. If you take more chemistry courses you will encounter these subjects again. This understanding will provide a firm foundation for further study. In any case, this general knowledge will help you understand the behavior of some common substances and their uses.

SELF-TEST

This self-test is designed to show how well you have mastered this chapter's objectives. Correct answers and review instructions follow the test.

1. One concept of acidity holds that hydrogen is not required to be present in an

| | acid. This concept was proposed by: |
|----|---|
| | (a) Brønsted-Lowry |
| | (b) Arrhenius |
| | (c) Lewis |
| | (d) Lavoisier |
| 2. | According to Brønsted-Lowry concept, only one of the following statements is true. Which one is it? |
| | (a) A base is a neutron acceptor. |
| | (b) H_3O^+ and OH^- are a conjugate acid-base pair. |
| | (c) An acid is a proton donor. |
| | (d) The stronger the acid, the stronger is its conjugate base. |
| 3. | The strongest acid that can exist in substantial amounts in aqueous solution is: |
| | (a) HClO ₄ |
| | (b) H ₂ O |
| | (c) H ₃ O ⁺ |
| | (d) OH ⁻ |
| | (e) O ²⁻ |
| | (f) NH ₃ |

| 4. | In the reaction, $H_3N + BF_3 \rightarrow H_3NBF_3$: |
|-----|---|
| | (a) H₃N is a Brønsted-Lowry acid. |
| | (b) H ₃ N is a Lewis acid. |
| | (c) BF ₃ is a Brønsted-Lowry acid. |
| | (d) BF ₃ is a Lewis acid. |
| 5. | What kind of a solution will the salt of a strong acid and a weak base give when dissolved in H_2O ? (acidic, basic, neutral) |
| 6. | How many milliliters of 0.60 M HNO ₃ are required to neutralize 40 mL of 1.20 M Ca(OH) ₂ ? |
| 7. | Of the acids H_2SO_4 , HCI , HNO_3 , $HCIO_4$, all have the same strength in aqueous solutions. This is an example of what is called the |
| 8. | What is the pH of a solution that is $1.00 \times 10^{-7} M$ HC!? |
| 9. | What is the H ⁺ concentration of a solution whose pH is 4.0? |
| | [H ⁺] = |
| 10. | According to Lewis theory, any negative ion is a |
| 11. | Would a solution of NaC ₂ H ₃ O ₂ be acidic, basic, or neutral? Why? |
| 12. | Use the table on page 287 to predict if the formation of the products is favored. Explain why or why not. |
| | (a) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$ |
| | (b) $C_2H_5OH + H_2O \rightarrow C_2H_5O^- + H_3O^+$ |
| | (c) $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ |
| 13. | Listed below are some statements. Indicate whether they are true or false. |
| | (a) A buffer solution is prepared by mixing solutions of a strong acid and a salt of that acid. |
| | (b) A solution whose H ⁺ concentration is 1×10^{-4} is acidic. |
| | (c) NH₄OH is a typical weak base. |
| | (d) $pH = -log(OH^-)$. |
| | (e) The strongest base that can exist in substantial concentrations in a solvent that can act as an acid is the conjugate base of the solvent acid. |

ANSWERS

Compare your answers to the self-test with those given below. If you answer all questions correctly, congratulations! If you miss any, review the frames indicated in parentheses following the answers. If you miss several questions, you should probably reread the chapter carefully.

- 1. (c) (frames 87, 88)
- 2. (c) (frame 65)
- 3. (c) (frame 62)
- 4. (d) (frame 88)
- 5. acidic (frame 58)
- 6. $Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$ $mL\ HNO_3\ soln = 40\ mL\ Ca(OH)_2\ soln \times \frac{1.20\ mol\ Ca(OH)_2}{1\ liter\ soln} \times \frac{1\ liter}{1000\ mL} \times \frac{2\ mol\ OH^-}{1\ mol\ Ca(OH)_2}$ $\times \frac{1\ mol\ H^+}{1\ mol\ OH^-} \times \frac{1\ liter\ soln}{0.6\ mol\ HNO_3} \times \frac{1000\ mL}{1\ liter} = 160\ mL\ HNO_3\ soln$ (frames 3, 9–14)
- 7. leveling effect (All strong acids are "leveled" to the strength of the H₃O⁺ ion in aqueous solution.) (frame 63)
- 8. $[H^+] = 1 \times 10^{-7} M$ $pH = -\log 1 \times 10^{-7} = 7$ (frames 19-25)
- 9. $[H^+]$ = antilog(-pH) = antilog(-4) = 1 × 10⁻⁴ M (frames 26, 27)
- 10. base (frames 87-92)
- 11. Basic, because it is the salt of a weak acid and a strong base (frames 46–58)
- 12. (a) Yes. A weaker conjugate acid and base formed
 - (b) No. A stronger conjugate acid and base formed.
 - (c) No. A stronger conjugate acid and base formed so the reverse reaction is favored (frames 80–86)
- 13. (a) F (frames 30-35)
 - (b) T (frame 18)
 - (c) T (frame 39, 40)
 - (d) F (frames 19-23)
 - (e) T (frame 63)

Appendix

TABLE OF ATOMIC WEIGHTS

| Element | Symbol | Atomic Number | Atomic Weight | Element | Symbol | Atomic Number | Atomic Weight |
|-------------|--------|------------------|------------------|---------------|--------|------------------|------------------|
| Actinium | Ac | 89 | 227.0278 | Mercury | Hq | 80 | 200.59 |
| Aluminum | Al | 13 | 26.98154 | Molybdenum | Mo | 42 | 95.94 |
| Americium | Am | 95 | (243) | Neodymium | Nd | 60 | 144.24 |
| Antimony | Sb | 51 | 121.75 | Neon | Ne | 10 | 20.179 |
| Argon | Ar | 18 | 39.948 | Neptunium | Np | 93 | 237.0482 |
| Arsenic | As | 33 | 74.9216 | Nickel | Ni | 28 | 58.69 |
| Astatine | At | 85 | (210) | Nielsbohrium | Ns | 107 | (262) |
| Barium | Ba | 56 | 137.34 | Niobium | Nb | 41 | 92.9064 |
| Berkelium | Bk | 97 | (247) | Nitrogen | N | 7 | 14.0067 |
| Beryllium | Be | 4 | 9.01218 | Nobelium | No | 102 | (259) |
| Bismuth | Bî | 83 | 208.9804 | Osmium | Os | 76 | 190.2 |
| Boron | В | 5 | 10.81 | Oxygen | 0 | 8 | 15.9994 |
| Bromine | Br | 35 | 79.904 | Palladium | Pd | 46 | 106.42 |
| Cadmium | Cd | 48 | 112.41 | Phosphorus | P | 15 | 30.97376 |
| Calcium | Ca | 20 | 40.08 | Platinum | Pt | 78 | 195.08 |
| Californium | Cf | 98 | (251) | Plutonium | Pu | 94 | (244) |
| Carbon | C | 6 | 12.011 | Polonium | Po | 84 | (209) |
| Cerium | Ce | 58 | 140.12 | Potassium | Κ | 19 | 39.0983 |
| Cesium | Cs | 55 | 132.9054 | Praseodymium | Pr | 59 | 140.9077 |
| Chlorine | Cl | 17 | 35.453 | Promethium | Pm | 61 | (145) |
| Chromium | Cr | 24 | 51.996 | Protactinium | Pa | 91 | 231.0359 |
| Cobalt | Co | 27 | 58.9332 | Radium | Ra | 88 | 226.0254 |
| Copper | Cu | 29 | 63.546 | Radon | Rn | 86 | (222) |
| Curium | Cm | 96 | (247) | Rhenium | Re | 75 | 186.207 |
| Dysprosium | Dy | 66 | 162.50 | Rhodium | Rh | 45 | 102.9055 |
| Einsteinium | Es | 99 | (252) | Rubidium | Rb | 37 | 85.4678 |
| Erbium | Er | 68 | 167.26 | Rutherfordium | Rf | 104 | (261) |
| Europium | Eu | 63 | 151.96 | Ruthenium | Ru | 44 | 101.07 |
| Fermium | Fm | 100 | (257) | Samarium | Sm | 62 | 150.36 |
| Fluorine | F | 9 | 18.99840 | Scandium | Sc | 21 | 44.9559 |
| Francium | Fr | 87 | (223) | Seaborgium | Sg | 106 | (263) |
| Gadolinium | Gd | 64 | 157.25 | Selenium | Se | 34 | 78.96 |
| Gallium | Ga | 31 | 69.72 | Silicon | Si | 14 | 28.0855 |
| Germanium | Ge | 32 | 72.59 | Silver | Ag | 47 | 107.868 |
| Gold | Au | 79 | 196.9665 | Sodium | Na | 11 | 22.98977 |
| Hafnium | Hf | 72 | 178.49 | Strontium | Sr | 38 | 87.62 |
| Hahnium | Ha | 105 | (262) | Sulfur | S | 16 | 32.06 |
| Hassium | Hs | 108 | (265) | Tantalum | Ta | 73 | 180.9479 |
| Helium | He | 2 | 4.00260 | Technetium | Tc | 43 | 98.9072 |
| Holmium | Ho | 67 | 164.9304 | Tellurium | Te | 52 | 127.60 |
| Hydrogen | Н | 1 | 1.0079 | Terbium | Tb | 65 | 158.9254 |
| Indium | In | 49 | 114.82 | Thallium | TI | 81 | 204.383 |
| lodine | 1 | 53 | 126.9045 | Thorium | Th | 90 | 232.0381 |
| lridium | lr | 77 | 192.22 | Thulium | Tm | 69 | 168.9342 |
| lron | Fe | 26 | 55.847 | Tin | Sn | 50 | 118.69 |
| Krypton | Kr | 36 | 83.80 | Titanium | Ti | 22 | 47.88 |
| Lanthanum | La | 57 | 138.9055 | Tungsten | W | 74 | 183.85 |
| Lawrencium | Lr | 103 | (260) | Uranium | U | 92 | 238.029 |
| Lead | Pb | 82 | 207.2 | Vanadium | V | 23 | 50.9415 |
| Lithium | Li | 3 | 6.941 | Xenon | Xe | 54 | 131.29 |
| Lutetium | Lu | 71 | 174.967 | Ytterbium | Yb | 70 | 173.04 |
| Magnesium | Mg | 12 | 24.305 | Yttrium | Y | 39 | 88.9059 |
| Manganese | Mn | 25 | 54.9380 | Zinc | Zn | 30 | 65.38 |
| Meitnerium | Mt | 109 | (266) | Zirconium | Zr | 40 | 91.22 |
| Mendelevium | Md | 101 | (258) | l | | | |

Value in parentheses is the mass number of the most stable or best known isotope. Names of elements of atomic numbers 104 to 109 are as recommended by the American Chemical Society.

Noble Gases VIIIA 174.967 Ľ و ا (560) **VIIA** 173.04 ž 85 At (210) [∞] **2** (259)102 168.9342 ×۲ Tm 127,60 PΨ **2 0** 8 ع ع p orbitals (258) 74.9216 208.9804 Sp 121.75 167.26 33 As Fm ≸ ≋ **:⊡** (257) ᆲ 100 164,9304 Ge 8 118.69 H0 ₹ 28.0855 72.59 Sn Sn 82 Pb 207.2 % **ES** (252) z :2 26.98154 114.82 204.383 ¥ **₽** E g 162.50 10.81 69.72 **하 드** å Ç s 🚾 (251) £ % Ξ <mark>Ξ</mark> **Hg** 200.59 158.9254 112.41 f orbitals Periodic Table of the Elements $\sum_{n=1}^{\infty}$ 65.38 å S es Tb **B** 路 (247) Ag 107.868 Discovered December 196.9665 63.546 157.25 CH Çn 3 g g Au (247) 18 Discovered November 1994 106.42 58.69 195.08 151.96 Am ۳ å Pd En En (243) 28 Pt ← atomic number ← atomic weight 102.9055 58.9332 ပ္ 192.22 & 돈 s₂ 150.36 **=** ¥ (399) Pu (244) ۲ **۲** Z Z d orbitals 237.0482 55.847 101.07 Os 108 **HS** (265) Pm es Ru ²⁶ Fe 190.2 (145) 93 1.0079 98.9072 M 54.9380 238.029 VIIB 186.207 107 ZS (262) ²⁵ **Re** 144.24 Ž ئ ر - **I** 51.996 232.0381 231.0359 Mo 140.9077 95.94 183.85 VIB ڙ ۽ 58 263) چ م ¥ **≥** 92.9064 180.9479 50.9415 140.12 ₹ <mark>Ŝ</mark> ы **На** Ce VB (262) ت <mark>له</mark> * **1**8 47.88 91.22 178.49 $\frac{7}{4}$ **26**19 ≈ ;= å **Ž** 88.9059 138.9055 44.9559 226.0254 227.0278 Ac 2c Sc <u>B</u> La **68 57. £ > *Lanthanide series 9.01218 **Mg** 24.305 Metalloid Nonmetal 137.34 s orbitals Be 87.62 ¥ Ca [₽] 40.08 ₃₆ Ва å <u>ڇ</u> ج Metal 22.98977 85.4678 132,9054 Z 39.0983 37 **Rb** ပ ≤ 6.941 (223) =<u>د</u> پ ₽ 🔀 2 3 sboin99 4 5 9 7

TABLE OF FOUR-PLACE LOGARITHMS

| 10 | No. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|-----|------|------|------|------|------|------|------|------|------|------|
| 12 0792 0828 0864 0889 0934 0969 1004 1038 1072 1130 13 1139 1173 1206 1239 1271 1303 1335 1367 1399 1430 14 1461 1492 1523 1553 1584 1614 1644 1673 1703 1732 15 1761 1790 1818 1847 1875 1903 1931 1959 1987 2014 16 2041 2082 2095 2122 2148 2175 2201 2227 2253 2273 17 2304 2330 2355 2380 2405 2405 2485 2480 2504 2529 18 2553 2577 2601 2625 2648 2672 2695 2718 2742 2765 19 2788 2810 2833 2856 2878 2900 2923 2945 2967 | 10 | 0000 | 0043 | 0086 | 0128 | 0170 | 0212 | 0253 | 0294 | 0334 | 0374 |
| 13 1139 1173 1206 1239 1271 1303 1335 1367 1399 1430 14 1461 1492 1523 1553 1584 1614 1644 1673 1709 1818 1847 1875 1903 1931 1959 1987 2014 16 2041 2068 2095 2122 2148 2175 2201 2227 2253 2279 17 2304 2330 2355 2380 2405 2430 2455 2480 2504 2256 19 2788 2810 2833 2856 2878 2900 2923 2945 2967 2989 20 3010 3032 3054 3075 3096 3118 3139 3160 3181 3201 21 3222 3243 3263 3284 3304 3324 3345 3365 3383 3865 3874 3892 3909 3927 | | 0414 | | | | | | | | 0719 | |
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| 15 1761 1790 1818 1847 1875 1903 1931 1959 1987 2014 16 2041 2068 2095 2122 2148 2175 2201 2227 2253 2279 17 2304 2330 2355 2380 2405 2462 2455 2480 2529 18 2553 2577 2601 2625 2648 2672 2695 2718 2742 2765 19 2788 2810 2833 2856 2878 2900 2923 2945 2967 2989 20 3010 3032 3054 3075 3096 3118 3139 3160 3181 3201 21 3143 3461 3663 3655 3674 3892 3909 3927 3945 3962 23 3617 3636 3655 3674 3692 3711 3729 3747 3766 3784 | | | | | | | | | | | |
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| 21 3222 3243 3263 3284 3304 3324 3345 3365 3385 3404 22 3424 3446 34483 3502 3522 3541 3560 3579 3598 24 3802 3820 3838 3856 3874 3892 3909 3927 3945 3962 25 3979 3997 4014 4031 4048 4065 4082 4099 4116 4133 26 4150 4166 4183 4200 4216 4232 4249 4265 4281 4298 27 4314 4330 4346 4362 4378 4393 4409 4425 4440 4456 28 4472 4487 4502 4518 4533 4548 4564 4579 4594 4892 29 4624 4639 4654 4669 4883 4698 4713 4728 4757 | | | | | | | | | | | |
| 22 3424 3444 3464 3483 3502 3522 3541 3560 3579 3598 23 3617 3636 3655 3674 3692 3711 3729 3747 3766 3784 24 3802 3820 3838 3856 3874 3892 3909 3927 3945 3962 25 3979 3997 4014 4031 4048 4065 4082 4099 4116 4133 26 4150 4166 4183 4200 4216 4232 4249 4265 4281 4298 27 4314 4330 4346 4362 4378 4393 4409 4425 4440 4456 28 4472 4487 4502 4518 4533 4548 4564 4579 4594 4059 29 4624 4639 4654 4669 4683 4698 4713 4728 4757 | | | | | | | | | | | |
| 23 3617 3636 3655 3674 3692 3711 3729 3747 3766 3784 24 3802 3820 3838 3856 3874 3892 3909 3927 3945 3962 25 3979 3997 4014 4031 4048 4065 4082 4099 4116 4133 26 4150 4166 4183 4200 4216 4232 4249 4265 4281 4298 27 4314 4330 4346 4362 4378 4393 4409 4425 4440 4456 28 4472 4487 4502 4518 4533 4548 4564 4579 4594 4609 29 4624 4639 4654 4669 4683 4698 4713 4728 4742 4757 30 4771 4786 4800 4814 4829 4843 4857 4871 4886 | | | | | | | | | | | |
| 24 3802 3820 3838 3856 3874 3892 3909 3927 3945 3962 25 3979 3997 4014 4031 4048 4065 4082 4099 4116 4133 26 4150 4166 4183 4200 4216 4232 4249 4265 4281 4298 27 4314 4330 4346 4362 4378 4393 4409 4425 4440 4456 28 4472 4487 4502 4518 4533 4548 4564 4579 4594 4609 29 4624 4639 4654 4669 4683 4698 4713 4728 4742 4757 30 4771 4786 4800 4814 4829 4843 4857 4871 4886 4900 31 4914 4928 4942 4955 4969 4983 4997 5011 5021 | | | | | | | | | | | |
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| 55 | 7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 |
| 56 | 7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 |
| 57 | 7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 |
| 58 | 7634 | 7642 | 7649 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 |
| 59 | 7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 |
| 60 | 7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 |
| 61 | 7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 |
| 62 | 7924 7993 | 7931 | 7938 8007 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 |
| 63 64 | 8062 | 8000 8069 | 8075 | 8014 8082 | 8021 8089 | 8028 8096 | 8035 8102 | 8041 8109 | 8048 8116 | 8055 8122 |
| 65 | 8129 | 8136 | 8142 | 8149 | 8156 | 8162 | | 8176 | | |
| 66 | 8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8169 8235 | 8176 8241 | 8182 8248 | 8189 825 4 |
| 67 | 8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 |
| 68 | 8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 |
| 69 | 8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 |
| 70 | 8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 |
| 71 | 8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 |
| 72 | 8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 |
| 73 | 8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 |
| 74 | 8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 |
| 75 | 8751 | 8756 | 8762 | 8768 | 8774 | 8779 | 8785 | 8791 | 8797 | 8802 |
| 76 | 8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 |
| 77 | 8865 | 8871 | 8876 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 |
| 78 | 8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 |
| 79 | 8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 |
| 80 | 9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 |
| 81 | 9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 |
| 82 | 9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 |
| 83 84 | 9191 9243 | 9196 9248 | 9201 9253 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 |
| | | | | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 |
| 85 86 | 9294 9345 | 9299 9350 | 9304 9355 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 |
| 87 | 9345 | 9400 | 9405 | 9360 9410 | 9365 9415 | 9370 | 9375 | 9380 | 9385 | 9390 |
| 88 | 9445 | 9450 | 9455 | 9460 | 9415 | 9420 9469 | 9425 947 4 | 9430 9479 | 9435 9484 | 9440 9489 |
| 89 | 9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 |
| 90 | 9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 |
| 91 | 9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 |
| 92 | 9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 |
| 93 | 9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 |
| 94 | 9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 |
| 95 | 9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 |
| 96 | 9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 |
| 97 | 9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 |
| 98 | 9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 |
| 99 | 9956 | 9961 | 9965 | 9969 | 9974 | 9978 | 9983 | 9987 | 9991 | 9996 |
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