

# A Guide to Using This Text

*Essential Chemistry* seeks to present the core concepts of general chemistry directly and efficiently, through text and illustrations and with a selective array of features chosen to help the student to focus on the content and to practice problem-solving skills.

This illustrated guide walks you through each feature of the chapter, with an explanation of why it is included and how it can help you use the textbook to learn chemistry fully.

—Raymond Chang

## CHAPTER OPENER

The *Outline* provides a handy rundown of the numbered sections in the chapter and includes subheadings that indicate topics covered in the sections.

The new *Essential Concepts* feature is a succinct listing of the important concepts in the chapter. It can serve as a preview of the material you will be learning and as a review device to gauge your knowledge of the chapter content.

Chapter 3  
Stoichiometry

- 3.1 Atomic Mass 60  
Average Atomic Mass
- 3.2 Molar Mass of an Element and Avogadro's Number 61
- 3.3 Molecular Mass 64
- 3.4 The Mass Spectrometer 66
- 3.5 Percent Composition of Compounds 69
- 3.6 Experimental Determination of Empirical Formulas 70  
Determination of Molecular Formulas
- 3.7 Chemical Reactions and Chemical Equations 72  
Writing Chemical Equations • Balancing Chemical Equations
- 3.8 Amounts of Reactants and Products 77
- 3.9 Limiting Reagents and Yields of Reactions 81  
Yields of Reactions

**ESSENTIAL CONCEPTS**

- Atomic Mass and Molar Mass** The mass of an atom, which is extremely small, is based on the carbon-12 isotope scale. An atom of the carbon-12 isotope is assigned a mass of exactly 12 atomic mass units (amu). To work with the more convenient scale of grams, chemists use the molar mass. The molar mass of carbon-12 is exactly 12 g and contains an Avogadro's number ( $6.022 \times 10^{23}$ ) of atoms. The molar masses of other elements are also expressed in grams and contain the same number of atoms. The molar mass of a molecule is the sum of the molar masses of its constituent atoms.
- Writing Chemical Equations** An effective way to represent the outcome of a chemical reaction is to write a chemical equation, which uses chemical formulas to describe what happens. A chemical equation must be balanced so that we have the same number and type of atoms for the reactants, the starting materials, and the products, the substances formed at the end of the reaction.
- Mass Relationships of a Chemical Reaction** A chemical equation allows us to predict the amount of product formed, called the yield. Knowing how much reactant was (wasn't) used, this information is of great importance for reactions run on the laboratory or industrial scale. In practice, the actual yield is almost always less than the predicted from the equation because of various complications.
- Percent Composition of a Compound** The makeup of a compound is most conveniently expressed in terms of its percent composition, which is the percent by mass of each element the compound contains. A knowledge of its chemical formula allows us to calculate the percent composition. Experimental determination of percent composition and the molar mass of a compound enables us to determine its chemical formula.

58

The chapter-opening *Essays* are written to orient you to the content of the chapter, with a short vignette to demonstrate that chemistry is a human endeavor with a rich history and a connection to all parts of our lives.

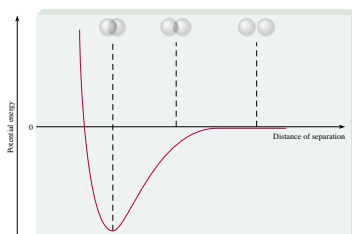
When wood, paper, and wax are burned, they appear to lose mass. The decrease in mass that results from these combustion reactions was once attributed to the release of "phlogiston" into the air. For most of the eighteenth century scientists accepted the phlogiston theory. Then, in August 1774, the English chemist and clergyman Joseph Priestley isolated oxygen—which he called "dephlogistonated air"—as a product of the decomposition of mercury(II) oxide,  $\text{HgO}$ . The French chemist Antoine Lavoisier had noticed that nonmetals like phosphorus actually gain mass when they burn in air. He concluded that these nonmetals must combine with something in the air. This substance turned out to be Priestley's dephlogistonated air. Lavoisier named the new element "oxygen" from the Greek word meaning "to form acid", because he knew that it is also a constituent of all acids.

Lavoisier ignited a mixture of hydrogen and oxygen gases.

Lavoisier determined the composition of water by igniting a mixture of hydrogen and oxygen gases with an electric spark. He also served on the commission that established the metric system on which SI is based. Unfortunately, his scientific career was cut short by the French Revolution. A member of the nobility, Lavoisier was also a tax collector. For these "crimes," he was sent to the guillotine in 1794.

Born in 1743, Lavoisier is generally regarded as the father of modern chemistry. He was noted for his carefully executed experiments and for the use of quantitative measurements. By carrying out chemical reactions, such as the decomposition of mercury(II) oxide in a closed container, he showed that the total mass of the products equals the total mass of the reactants. In other words, the quantity of matter is not changed by chemical reactions. This observation is the basis of the law of conservation of mass and the principle underlying stoichiometry.

10.3 Hybridization of Atomic Orbitals 311



**FIGURE 10.4** Change in potential energy of two H atoms with their distance of separation. At the point of minimum potential energy, the  $H_2$  molecule is in its most stable state and the bond length is 74 pm.

same and does not clearly explain why chemical bonds exist. For example, the Lewis theory describes the single bond between the H atoms in  $H_2$  and that between the F atoms in  $F_2$  in essentially the same way—as the pairing of two electrons. Yet these two molecules have quite different bond energies and bond lengths (436.4 kJ/mol and 74 pm for  $H_2$  and 150.6 kJ/mol and 142 pm for  $F_2$ ). These and many other facts cannot be satisfactorily explained by the Lewis theory. For a more complete explanation of chemical bond formation we must look to quantum mechanics. In fact, the quantum mechanical study of chemical bonding also provides a means for understanding molecular geometry.



In the 1930s *valence bond (VB) theory* was introduced to account for chemical bond formation. VB theory describes covalent bonding as the overlapping of atomic orbitals. This means that the orbitals share a common region in space. Thus the covalent bond in  $H_2$  is formed when the 1s orbitals on the two H atoms overlap (Figure 10.4). The region of overlap is a favorable one for electrons to reside in, for they are simultaneously attracted to the two positively charged nuclei.

Similarly, a stable  $F_2$  molecule forms when the 2p orbitals (containing the unpaired electrons) in the two F atoms overlap to form a covalent bond, and the formation of the HF molecule can be explained by the overlap of the 1s orbital in H with the 2p orbital in F. Because the orbitals involved are not the same kind in all cases, we can see why the bond energies and bond lengths in  $H_2$ ,  $F_2$ , and HF might be different.

The concept of atomic orbital overlap can also be applied to polyatomic molecules. However, a satisfactory bonding scheme must account for molecular geometry. We will discuss three examples of VB treatment of bonding in polyatomic molecules.

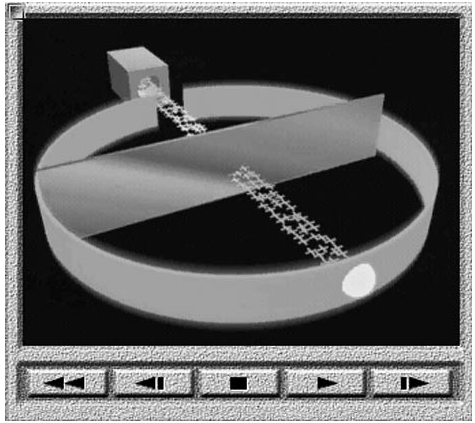
**sp Hybridization**

The  $BeCl_2$  (beryllium chloride) molecule is predicted to be linear by VSEPR. The orbital diagram for the valence electrons in Be is

## INTEGRATED MEDIA/ANIMATIONS

New to this edition is *Essential Animations*, a set of top-quality animations that vividly demonstrates the important concepts and processes. An icon in the margin points to material that is captured in an animation.



Animation: a-particle scattering

## ANIMATION TITLES :

- a-particle scattering
- Limiting reagent
- The hydration process
- Gas laws
- Emission spectra
- Atomic and ionic radius
- Hybridization
- Packing spheres
- Equilibrium vapor pressure
- Le Chatelier's principle
- Acid ionizations
- Buffer solutions
- Galvanic cells
- Activation energy
- Orientation of collision
- Radioactive decay

## THE PROBLEM-SOLVING APPROACH

The text is carefully designed to help you develop the skills to solve the many types of problems you will encounter in chemistry. The features shown here will help you apply an effective strategy for solving problems.

*Worked-Out Examples* appear throughout the text to demonstrate problem-solving methods for new material and concepts. Answers are thoroughly explained, and each example is followed by a sample problem for the student to solve. You can compare your work with solutions that appear at the end of the chapter.

*Essential Notes* accompany many of the Examples and provide helpful tips for working through problems.

14.1 The Rate of a Reaction 431

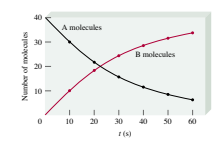


FIGURE 14.2 The rate of reaction A  $\rightarrow$  B, represented as the decrease of A molecules with time and as the increase of B molecules with time.

Two moles of A disappear for each mole of B that forms—that is, the rate of disappearance of A is twice as fast as the rate of appearance of B. We write the rate as either

$$\text{rate} = -\frac{1}{2} \frac{d[A]}{dt} \quad \text{or} \quad \text{rate} = \frac{d[B]}{dt}$$

For the reaction

$$aA + bB \rightarrow cC + dD$$

the rate is given by

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

**EXAMPLE 14.1**  
Writing Rate Expressions

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

(a)  $\text{I}^-(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{OI}^-(\text{aq})$   
 (b)  $4\text{NH}_3(\text{g}) + 5\text{SO}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

**Answer:** (a) Because each of the stoichiometric coefficients equals 1,

$$\text{rate} = -\frac{d[\text{I}^-]}{dt} = -\frac{d[\text{OCl}^-]}{dt} = \frac{d[\text{Cl}^-]}{dt} = \frac{d[\text{OI}^-]}{dt}$$

(b) In this reaction

$$\text{rate} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{SO}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

**PRACTICE EXERCISE**  
Write the rate expression for the following reaction:

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$$

**ESSENTIAL NOTE**  
What are the units for the rate of a reaction?

## REVIEW AND REINFORCEMENT

Chapters conclude with a *Summary* that restates the main concepts of the chapter.

Following the summary is a list of *Key Words* that includes the important terms discussed in the chapter. These terms are page referenced.

Key Words 323

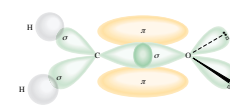


FIGURE 10.38 Bonding in the formaldehyde molecule. A sigma bond is formed by the overlap of the  $sp^2$  hybrid orbital of carbon and the  $sp^2$  hybrid orbital of oxygen; a pi bond is formed by the overlap of the  $2p$  orbitals of the carbon and oxygen atoms. The two lone pairs on oxygen are placed in the other two  $sp^2$  orbitals of oxygen.

**Summary**

The VSEPR model for predicting molecular geometry is based on the assumption that valence-shell electron pairs repel one another and tend to stay as far apart as possible. According to the VSEPR model, molecular geometry can be predicted from the number of bonding electron pairs and lone pairs. Lone pairs repel other pairs more strongly than bonding pairs do and thus distort bond angles from those of the ideal geometry.

The dipole moment is a measure of the charge separation in molecules containing atoms of different electronegativities. The dipole moment of a molecule is the resultant of whatever bond moments are present in a molecule. Information about molecular geometry can be obtained from dipole moment measurements.

In valence bond theory, hybridized atomic orbitals are formed by the combination and rearrangement of orbitals of the same atom. The hybridized orbitals are all of equal energy and electron density, and the number of hybridized orbitals is equal to the number of pure atomic orbitals that combine. Valence-shell expansion can be explained by assuming hybridization of  $s$ ,  $p$ , and  $d$  orbitals.

In  $sp$  hybridization, the two hybrid orbitals lie in a straight line; in  $sp^2$  hybridization, the three hybrid orbitals are directed toward the corners of a triangle; in  $sp^3$  hybridization, the four hybrid orbitals are directed toward the corners of a tetrahedron; in  $sp^3d$  hybridization, the five hybrid orbitals are directed toward the corners of a trigonal bipyramid; in  $sp^3d^2$  hybridization, the six hybrid orbitals are directed toward the corners of an octahedron.

In an  $sp^2$ -hybridized atom (for example, carbon), the one unhybridized  $p$  orbital can form a pi bond with another  $p$  orbital. A carbon-carbon double bond consists of a sigma bond and a pi bond. In an  $sp$ -hybridized carbon atom, the two unhybridized  $p$  orbitals can form two pi bonds with two  $p$  orbitals on another atom (or atoms). A carbon-carbon triple bond consists of one sigma bond and two pi bonds.

**Key Words**

Dipole moment (m), 308	Pi bond (p bond), 320	Valence-shell electron-pair repulsion (VSEPR) model, 298
Hybridization, 312	Polar molecule, 308	Sigma bond ( $\sigma$ bond), 320
Hybrid orbital, 312	Valence shell, 298	Valence-shell expansion, 319
Nonpolar molecule, 308		

124 CHAPTER 7B Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

### Questions and Problems

#### SIMPLE GEOMETRIC SHAPES

**Review Questions**

10.1 What is molecular geometry? Why is the study of molecular geometry important?

10.2 Sketch the shape of a linear triatomic molecule, a trigonal planar molecule containing four atoms, a tetrahedral molecule, a trigonal bipyramidal molecule, and an octahedral molecule. Give the bond angles in each case.

10.3 How many atoms are directly bonded to the central atom in a tetrahedral molecule, a trigonal bipyramidal molecule, and an octahedral molecule?

**VSEPR**

**Review Questions**

10.4 Discuss the basic features of the VSEPR model. Explain why the repulsion decreases in the following order: lone pair-lone pair, lone pair-bonding pair, bonding pair-bonding pair.

10.5 In the trigonal bipyramidal arrangement, why does a lone pair occupy an equatorial position rather than an axial position?

10.6 Another possible geometry for  $\text{CH}_4$  is square planar, with the four H atoms at the corners of a square and the C atom at the center of the square. Sketch this geometry and compare its stability with that of a tetrahedral  $\text{CH}_4$ .

**Problems**

10.7 Predict the geometries of the following species using the VSEPR method: (a)  $\text{PCl}_3$ , (b)  $\text{CHCl}_3$ , (c)  $\text{SiH}_4$ , (d)  $\text{TeCl}_4$ .

10.8 What are the geometries of the following species? (a)  $\text{AlCl}_3$ , (b)  $\text{ZnCl}_2$ , (c)  $\text{ZnCl}_2^{2-}$ .

10.9 Predict the geometry of the following molecules using the VSEPR method: (a)  $\text{HgBr}_2$ , (b)  $\text{N}_2\text{O}$  (arrangement of atoms is NNO), (c)  $\text{SCN}^2$  (arrangement of atoms is SCN).

10.10 What are the geometries of the following ions? (a)  $\text{NH}_2^-$ , (b)  $\text{NH}_4^+$ , (c)  $\text{CO}_3^{2-}$ , (d)  $\text{ICl}_3^-$ , (e)  $\text{ICl}_4^-$ , (f)  $\text{AlH}_4^-$ , (g)  $\text{SnCl}_5^-$ , (h)  $\text{H}_3\text{O}^+$ , (i)  $\text{BrF}_2^+$ .

10.11 Describe the geometry around each of the three central atoms in the  $\text{CH}_3\text{COOH}$  molecule.

10.12 Which of the following species are tetrahedral:  $\text{SiCl}_4$ ,  $\text{SeF}_6$ ,  $\text{XeF}_4$ ,  $\text{Cl}_4$ ,  $\text{CaCl}_2^{2+}$ ?

#### DIPOLE MOMENTS AND MOLECULAR GEOMETRY

**Review Questions**

10.13 Define dipole moment. What are the units and symbol for dipole moment?

10.14 What is the relationship between the dipole moment and bond moment? How is it possible for a molecule to have bond moments and yet be nonpolar?

10.15 Explain why an atom cannot have a permanent dipole moment.

10.16 The bonds in beryllium hydride ( $\text{BeH}_2$ ) molecules are polar, yet the dipole moment of the molecule is zero. Explain.

**Problems**


10.17 Arrange the following molecules in order of increasing dipole moment:  $\text{H}_2\text{O}$ ,  $\text{CBr}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{HF}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ . (See Table 10.3.)

10.18 The dipole moments of the hydrogen halides decrease from HF to HI (see Table 10.3). Explain this trend.


10.19 List the following molecules in order of increasing dipole moment:  $\text{H}_2\text{O}$ ,  $\text{CBr}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{HF}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ .

10.20 Does the molecule  $\text{OCS}$  have a higher or lower dipole moment than  $\text{CS}_2$ ?

10.21 Which of the following molecules has a higher dipole moment?




(a)




(b)

10.22 Arrange the following compounds in order of increasing dipole moments:



(a)



(b)

## END-OF-CHAPTER-PROBLEMS

The problems section at the end of the chapter provides a complete opportunity to practice your skills.

Grouped by chapter section, two types of problems are offered:

*Review Questions* test your knowledge of factual and conceptual content.

*Problems* pose quantitative situations to be solved. Solutions to even-numbered problems appear at the end of the book.

Answers to Practice Exercises

267

either side, carbon and oxygen, have substantial positive electron affinities.

8.100 Little is known of the chemistry of astatine, the last member of Group 7A. Describe the physical characteristics that you would expect this halogen to have. Predict the products of the reaction between sodium astatide ( $\text{NaAt}$ ) and sulfuric acid. (*Hint:* Sulfuric acid is an oxidizing agent.)

8.101 As discussed in the chapter, the atomic mass of argon is greater than that of potassium. This observation created a problem in the early development of the periodic table because it meant that argon should be placed after potassium. (a) How was this difficulty resolved? (b) From the following data, calculate the average atomic masses of argon and potassium: Ar-36 (37.9627 amu; 0.337 percent), Ar-40 (39.9624 amu; 99.660 percent); K-39 (38.9637 amu; 93.258 percent), K-40 (39.9640 amu; 0.0117 percent), K-41 (40.9618 amu; 6.730 percent).

8.102 Calculate the maximum wavelength of light (in nanometers) required to ionize a single sodium atom.

8.103 The first four ionization energies of an element are approximately 738 kJ/mol, 1450 kJ/mol,  $7.73 \times 10^4$  kJ/mol, and  $1.13 \times 10^6$  kJ/mol. To which periodic group does this element belong? Why?

8.104 Match each of the elements on the right with its description on the left:

(a) A greenish-yellow gas that reacts with water	Nitrogen ( $\text{N}_2$ )
(b) A soft metal that reacts with water to produce hydrogen	Boron (B)
(c) A metalloid that is hard and has a high melting point	Aluminum (Al)
(d) A colorless, odorless gas	Fluorine ( $\text{F}_2$ )
(e) A more reactive metal than iron, which does not corrode	Sodium (Na)

### SPECIAL PROBLEM

8.105 In the late 1800s the British physicist Lord Rayleigh accurately determined the atomic masses of a number of elements, but he obtained a puzzling result with nitrogen. One of his methods of preparing nitrogen was by the thermal decomposition of ammonia:

$$2\text{NH}_3(g) \rightarrow \text{N}_2(g) + 3\text{H}_2(g)$$

Another method was to start with air and remove oxygen, carbon dioxide, and water vapor from it. Invariably, the nitrogen from air was a little denser (by about 0.5 percent) than the nitrogen from ammonia.

Later the English chemist Sir William Ramsay carried out an experiment in which he passed nitrogen, which he had obtained from air by Rayleigh's procedure, over red-hot magnesium to convert it to magnesium nitride:

$$3\text{Mg}(s) + \text{N}_2(g) \rightarrow \text{Mg}_3\text{N}_2(s)$$

in air

**Answers to Practice Exercises**

8.1 (a)  $[\text{Ar}]4s^2$ ; (b) representative element; (c) diamagnetic. **8.2** Li - Be - C. **8.3** (a)  $\text{Li}^+$ ; (b)  $\text{Au}^{3+}$ ; (c)  $\text{N}^{3-}$ . **8.4** (a) N, (b) Mg. **8.5** No.

*Additional Problems*, which follow the section-grouped set, further test you with more challenging problems that may involve two or more concepts.

The chapters conclude with one or two *Special Problems*, which call on students to demonstrate their comprehension of multiple concepts and themes.