# Chemical Bonding— Explaining the Diversity of Matter

Winter in Alberta! While the snowboard, the clothing, and the energy all come from chemical reactions, the fun depends largely on the way water behaves when solid. This most common of substances has properties unlike any other; for example, water expands upon freezing, and ice liquefies momentarily under pressure. These properties help make skiing, snowboarding, skating, and sledding possible.

Describing, explaining, and predicting the nature and behaviour of substances is fundamental to chemistry. Inquiring scientists assumed there must be a reason why the complex structures of snowflakes always have hexagonal symmetries, and they applied scientific inquiry and techniques to find a plausible theory. When their initial theory also worked to describe many other properties of water, scientists considered the theory more valid. When scientists found the theory to be useful in predicting the properties of many other substances, it became generally accepted within the scientific community. All theories develop in this way: we constantly test them against what we know of the real world. When such testing eventually produces conflicting evidence, a theory is *restricted*, or *revised*, or perhaps even *replaced*, resulting in a newer theory that is better able to *describe*, *explain*, and *predict* what we observe. The knowledge-gathering process of science really has only two fundamental rules: theories must be based on reliable evidence, and theories must be tested for accuracy whenever possible.

Bonding theories assume that an understanding of how substances behave depends on understanding how the tiniest units of matter are held together. In addition, understanding chemical change always depends on the concept of breaking bonds and forming new ones. In this unit, you will study chemical bonding—the concept of forces that hold atoms, ions, and molecules together—and the relationship of these bonds to the properties and structure of matter.

#### As you progress through the unit, think about these focusing questions:

- · Why do some substances dissolve easily while others do not?
- · Why do different substances have widely different melting and boiling points?
- · How can models increase our understanding of invisible things such as bonds?

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# Unit 1

**Chemical Bonding**— **Explaining the Diversity of** Matter

## **Prerequisites**

#### **Concepts**

- · ionic and molecular compounds
- · atomic structure
- · formation of ions
- · nature and strength of electrostatic forces
- · relationship between laws and theories

#### **Skills**

· laboratory safety rules

You can review prerequisite concepts and skills in the **Chemistry Review unit and in** the Appendices.

A Unit Pre-Test is also available online.



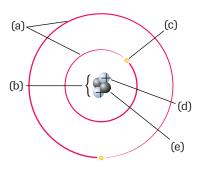


# **ARE YOU READY?**

These questions will help you find out what you already know, and what you need to review, before you continue with this unit.

## **Knowledge**

- 1. According to a chemistry classification system, each of the following statements applies only to elements or only to compounds:
  - cannot be decomposed into simpler substances by chemical means
  - composed of two or more kinds of atoms
  - iii. can be decomposed into simpler substances using heat or electricity
  - composed of only one kind of atom
  - (a) Which statements apply only to elements?
  - (b) Which statements apply only to compounds?
  - (c) Which statements are empirical?
  - (d) Which statements are theoretical?
- 2. Describe the atomic models presented by each of the following:
  - (a) J. J. Thomson
  - (b) Ernest Rutherford
  - (c) John Dalton
- 3. Provide the labels, (a) to (e), for **Figure 1** to describe an atom. In addition to the name, provide the international symbol for the three subatomic particles.



An atom model, as used to represent an atom (very simplistically) in the 1930s

4. Copy **Table 1**, and complete it using the periodic table and atomic theory.

Table 1 Components of Atoms and Ions

Entity	Number of protons	Number of electrons	Net charge
hydrogen atom			
sodium atom			
chlorine atom			
hydrogen ion			
sodium ion			
chloride ion			

- 5. Niels Bohr explained the periodic law and line spectra by creating the Bohr model of the atom. Draw energy-level diagrams to describe the following atoms:
  - (a) nitrogen, N
  - (b) calcium, Ca
  - (c) chlorine, Cl

6. Compounds can often be classified, based upon empirical definitions, as ionic or molecular. Copy and complete Table 2, indicating the properties of these compounds.

Table 2 Properties of Ionic and Molecular Compounds

	Classes of		Properties	
Class of compound	elements involved	Melting point (high/low)	State at SATP (s, l, g)	Electrolytes (yes/no)
ionic				
molecular				

- 7. Classify compounds according to the following empirical properties as ionic, molecular, or either:
  - (a) high solubility in water; aqueous solution conducts electricity
  - (b) solid at SATP; low solubility in water
  - (c) solid at SATP; low melting point; aqueous solution does not conduct electricity
- 8. According to atomic and bonding theories, atoms react by rearranging their electrons.
  - (a) Silicon tetrafluoride gas is used to produce ultra-pure silicon wafers (Figure 2). Draw an energy-level diagram for each atom or molecule in the following word equation for the formation of silicon tetrafluoride: silicon fluorine silicon tetrafluoride  $\rightarrow$
  - (b) Calcium fluoride occurs naturally as fluorite (pure compound) and as fluorspar (mineral, Figure 3). Calcium fluoride is the principal source of the element fluorine, and is also used in a wide variety of applications such as metal smelting, certain cements, and paint pigments. Draw an energylevel diagram for each atom or ion in the following word equation for the formation of calcium fluoride:
    - calcium fluorine calcium fluoride
  - (c) What is the difference in the electron rearrangement in (a) compared with (b)?
- 9. What is the difference between a scientific law and a scientific theory?
- 10. In the progress of chemistry, what generally comes first, laws or theories?

#### Skills

- 11. What document provides information about safe handling and safe disposal of a chemical?
- 12. If a corrosive chemical comes in contact with your skin, what is the normal procedure to follow?
- 13. List two items common to school labs that should routinely be worn for personal protection against chemical hazards.
- 14. List three types of general safety equipment common to school chemistry labs.
- 15. When evaluating a scientific theory or concept, what three basic criteria are used?

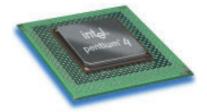


Figure 2 In 1972, Intel's 8008 computer processor had 3500 transistors. By 2000, the Pentium 4 processor had 42 million transistors on a silicon chip.

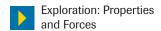


Figure 3 Fluorspar is a mineral that can be found in many countries. It takes a variety of colours and has different properties, depending on contaminants.



# **Understanding Chemical Compounds**

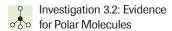
## In this chapter

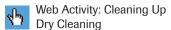


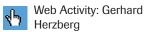


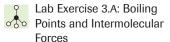












Investigation 3.3:

Molecular Compound
Melting Points

Web Activity: Cloud Seeding

Investigation 3.4:
Hydrogen Bonding

Case Study: Current
Research in
Intermolecular Forces

Mini Investigation: Floating Pins

Web Activity: Modelling Molecules

Mini Investigation:
Building an Ionic Crystal
Model

Web Activity: Jillian Buriak

Investigation 3.5:
Classifying Unknown
Solids

When enough atoms or molecules bond to each other, they must eventually form a quantity of substance that is big enough for a human to detect and measure. The compound shown crystallizing from solution in **Figure 1** illustrates this process.

As you study this chapter, you will follow much the same sequence of ideas as chemists did in the early 1900s. As some chemists refined atomic theory, others developed ideas about how atoms bond to each other. Initial bonding theories were restricted to simple ionic and molecular compounds, but expanded over time through constant questioning and testing. All theories are considered to be only as good as their ability to accurately describe, explain, and predict phenomena. Eventually, bonding theory became highly sophisticated, allowing structural descriptions of very complex substances. Bonding theory development is a good example of the cyclical nature of science. Curiosity about initial observations leads to creation of theory, which is then used to describe, explain, and predict new observations. The new observations in turn may require better theories for a more complete explanation. The net result of this cycle is a constant accumulation of knowledge.

Chemists use ideas about bonding to explain physical properties such as hardness and melting point, as well as chemical properties such as reactivity and acidity. Chemical engineers study bonding and molecular structure to synthesize useful new substances such as semiconductors and detergents. Ultimately, chemistry is about reactions. When a reaction is thought of as the breaking of bonds holding the original substances together, followed by the formation of different bonds to form new substances, it becomes obvious why a study of bonding is essential to any study of theoretical chemistry.

## STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

- 1. When atoms collide, what rearrangement of their structures can take place?
- 2. What properties of a substance are affected by the shape of its molecules?
- **3.** How can the behaviour and properties of a pure substance or a composite material be explained by theories of bonding between its basic entities?
- **4.** How can differences in physical properties of molecular liquid substances, such as  $C_2H_5OH(1)$  and  $CH_3OCH_3(1)$ , and of solid substances, such as  $SiO_2(s)$  and  $CO_2(s)$ , be predicted by understanding current bonding theories?



Career Connections: Biochemist; Geologist/Gemmologist



# Exploration

## **Properties and Forces**

Every property of a substance should be predictable once we have a complete understanding of the interactions between atoms and molecules. To obtain this understanding, we need to observe carefully and develop explanations. Record your observations for the following activity, and see what explanations flow from them.

Materials: 2 small, flat-bottom drinking glasses or beakers; 2 small ceramic bread plates (china, stoneware, or glass); some dishwashing liquid; some canola oil

- Place the drinking glass on the bread plate, and press down firmly while trying to move the glass in a small horizontal
- (a) Both the glass and the plate are very smooth. Does this mean they slide over each other easily?
- Add dishwashing liquid to the plate until it is about 2 mm deep, and try the first step again with a clean glass.
- (b) Dishwashing liquid makes your fingers feel slippery. Does dishwashing liquid actually make the contact surface between the glass and plate slippery?

- Add canola oil to the second plate until it is about 2 mm deep, and try the first step again with a clean glass.
- (c) The canola oil makes your fingers feel slippery. Does oil actually make the contact surface between the glass and plate slippery?
- Lift the glass on both plates vertically, and note the tendency of the plate to stick.
- (d) Which liquid seems to be a more effective adhesive?
- In one small glass (or beaker) add about 1 cm of detergent to 2 cm of water, and stir. In the other glass, add about 1 cm of canola oil to 2 cm of water, and stir. Let each container sit undisturbed for approximately one minute.
- (e) What evidence do you have for these liquids about the strengths of the attractive forces between their molecules (cohesion), and between their molecules and the water molecules (adhesion)?
- Dispose of the liquids down the sink with lots of water.



Wash your hands thoroughly after completing this activity.

# **3.1** Bonding Theory and Lewis Formulas







#### Figure 1

Structural formulas (also called line formulas and structural diagrams) for water, ammonia, and methane. Structural formulas are more descriptive than molecular formulas, since they show which atoms are bonded to each other.



Figure 2

Light is polarized by passing through polarized lenses like those in sunglasses. When the polarized light passes through most transparent substances, we notice nothing unusual. However, certain substances dramatically change the light to produce some beautiful effects. This effect can be explained only by 3-D versions of structural formulas.

Bonding is one of the most theoretical concepts in chemistry. While we can now detect single atoms (just barely) with the most advanced microscopes, we have no direct visible evidence for bonds between atoms. Our concepts of bonding must be created from, and based on, indirect experimental evidence and logic.

The development of bonding theory starts before the Mendeleyev periodic table with Edward Frankland (1852) stating that each element has a fixed bonding capacity. Friedrich Kekulé (1858) extended the idea to illustrating a bond as a dash between bonding atoms, that is, what we now call a **structural formula** (**Figure 1**).

Sixteen years after Kekulé created these diagrams, Jacobus van't Hoff and Joseph Le Bel independently extended them to three dimensions (3-D). They revised existing theory in order to explain the ability of certain substances to change light as it passes through a sample of the substance (optical activity, **Figure 2**). Note that all of this work was done by working only with the Dalton atom, before any concept of a nucleus or bonding electrons. As yet, there was no explanation for the bonds that were being represented in the diagrams.

That explanation started with Richard Abegg, a German chemist, in 1904. Abegg was the first to suggest that bonding capacity must somehow be associated with an atom's electron structure. Almost immediately, Rutherford's evidence for the nuclear atom made Abegg's theory seem probable, since it became obvious that any interaction between atoms had to involve their surrounding electrons. Abegg suggested that the stability of the "inert" (noble) gases was due to the number of electrons in the atom. He looked at the periodic table and noted that a chlorine atom had one less electron than the stable electron structure of argon. He theorized that, in a reaction with another atom, a chlorine atom was likely to gain one electron to form a stable, unreactive chloride ion. Likewise, he suggested that a sodium atom had one more electron than needed for stability. A reacting sodium atom should, according to his theory, lose one electron to form a stable sodium ion. Such a transfer of electrons, between a sodium and a chlorine atom, is indicated below. The newly formed ions would, in turn, be held together by electrostatic forces. In a reaction between sodium metal and chlorine gas, enormous numbers of cations and anions can form and bond this way to form visible crystals of table salt. The attraction force holding the ions together is called ionic bonding.

Na + Cl 
$$\rightarrow$$
 Na<sup>+</sup> + Cl<sup>-</sup>  $\rightarrow$  NaCl  
sodium + chlorine  $\rightarrow$  sodium chloride

In 1916, Gilbert Lewis, an American chemist, combined the evidence of many known chemical formulas, the concept of valence, and the concept of stable electron numbers for atoms. He proposed that atoms could achieve stable electron arrangements by sharing electrons as well as by transferring them. This would only work if the atoms stayed close together, which would have to result in an attraction force. This force became known as the covalent bond. The electrons involved were called **valence electrons**. These are the electrons in the highest energy level of the atom. Immediately, many molecular compounds became more understandable. An ionic bond, then, is explained as the simultaneous attraction between positive and negative ions resulting from the transfer of one or more valence electrons. A covalent bond is explained as the simultaneous attraction of the nuclei of two atoms for valence electrons that they share between them. These types of bonding are formally defined and discussed in more detail later in this section.

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The culmination of all this work was the brilliant synthesis of all these concepts with the complex ideas of quantum mechanics. Quantum mechanics, which developed from Einstein's revolutionary theories of matter, energy, space, and time, is a mathematical model. In it, electrons are described in terms of their energy content and by the probability of being in certain regions of space around a nucleus. In 1939, Dr. Linus Pauling published a book called *The Nature of the Chemical Bond*, which he dedicated to Gilbert Lewis. Pauling's work explained, for the first time, why certain electron arrangements are stable; it also showed that electron sharing must cover a complete range from equal attraction to total transfer. The theory was so complete and explained both known and unknown situations so well, that in 1954 it won Dr. Pauling his first Nobel Prize. Just like all other scientific theories, Pauling's theory was valued for how well it was able to describe, explain, and predict.

## DID YOU KNOW F

#### **Simplicity**

Scientists generally agree that simplicity is a characteristic of an acceptable theory. Einstein never fully accepted the theory of quantum mechanics, partly because of its complexity. In spite of his suspicions, he admired the ability of quantum mechanics to describe, explain, and predict observations.

## **EXPLORE** an issue

## Funding Research and **Development**

Science, technology, and society are interdependent: Society depends on science to provide explanations for natural phenomena and on technology to provide beneficial materials and processes. Science and technology both depend on society for funding their research. The goal of research and development (R&D) is to gain and use knowledge. Research and development can be classified into three broad categories:

- · pure research: to advance knowledge for its own sake, such as researching the empirical properties of semimetals (e.g., silicon) to develop theoretical explanations for their crystal structure and semiconductivity
- applied research: to advance technology, for example, researching how the semiconductivity of semi-metals can be enhanced to make even smaller integrated circuits in electronic devices
- development: to transform technological knowledge into concrete operational hardware, such as a microscopic electronic circuit to be used in a medical diagnostic device. The end product is judged by the criteria of cost, efficiency, reliability, and simplicity of use.

A simple view of R&D is that applied research uses the ideas generated by pure research in making inventions, which, in turn, are made commercially viable through development. In reality, science and technology are mutually dependent, and developments in one field prompt developments in the other. Technology provides the tools for scientific research, while science provides the theoretical background that guides research in technology.

Society supports R&D through grants from both federal and provincial governments. The Natural Sciences and Engineering Research Council of Canada (NSERC) is the primary federal agency investing in university research and training in the natural sciences and engineering. NSERC supports R&D by supporting more than 20 000 university students and postdoctoral fellows in their advanced studies and funding more than 10 000 university professors every year. NSERC also promotes innovation by encouraging Canadian companies to

#### **Issue Checklist**

- O Issue Resolution
- Design
- Analysis
- Evidence
- Evaluation

invest in university research. In 2004-2005, NSERC invested \$850 million in university-based research and training in all the natural sciences and engineering.

Provincial governments also provide funding for R&D. For example, the Alberta Science and Research Authority (ASRA) provides strategic direction to research funding priorities for the provincial government, which centre on agriculture, energy, forestry, and information/communication technology. In addition, the Alberta Research Council receives government funds to conduct applied R&D focusing on energy, life sciences, engineered products and services, and integrated resource management.

While many Canadians believe that federal and provincial governments should increase funding for R&D, there are many others who question why any public money should be used for scientific research. The second group maintains that taxpayer dollars would be better spent on improving health care and social services than on improving theories of solid-state physics. In their view, the research required to develop new technologies should be paid for by the private industries that benefit from selling the new products. The issue for Canadian society is to find the best long-term strategy for using public money to improve the quality of life for all its citizens.

What is the most effective use of government funding for research in science and technology?

#### Resolution

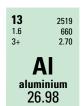
The provincial and federal governments should direct all their research funding to applied research.

#### Design

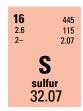
Within small groups, research the pros and cons of using public money to fund each of the three categories of research. Gather information from a wide variety of perspectives.

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$$\frac{3 e^{-} \rightarrow 1 e^{-} 1 e^{-} 1 e^{-} 0 e^{-}}{8 e^{-} 2 e^{-} 13 p^{+}}$$
Al
aluminium atom



$$\frac{6 e^{-} \rightarrow 2 e^{-} 2 e^{-}}{8 e^{-}}$$

$$\frac{2 e^{-}}{16 p^{+}}$$
S

#### Figure 3

sulfur atom

To explain bonding, the valence (highest) energy level is considered to have four orbitals. Each orbital may be unoccupied, or it may contain one or two electrons. In these diagrams for aluminium and sulfur, the distribution of the valence electrons in the four valence orbitals is shown to the right of the arrow. Aluminium has three half-filled valence orbitals and one vacant valence orbital. Sulfur has two full valence orbitals and two half-filled valence orbitals.

## **Bonding Theory: Valence Electrons and Orbitals**

Based upon evidence and logic, chemists believe that bonding changes for main group atoms in chemical reactions involve only the valence electrons occupying the highest energy level. Atomic theory says that electrons in lower energy levels are held so strongly by their (positively charged) nucleus that, during a reaction, they remain essentially unchanged.

To describe where electrons exist in the atom, chemists created the concept of an orbital. According to quantum mechanics, an **orbital** is a specific volume of space in which an electron of certain energy is likely to be found. Each orbital may contain two, one, or no electrons. The word "orbital" was an unfortunate choice because it tends to make you think of little particles in an orbit, and we now know that electrons are nothing like that. An orbital may be thought of as a sort of 3-D space that defines where an electron may be. For bonding study, we are only concerned with an atom's **valence orbitals**, the volumes of space that can be occupied by electrons in an atom's highest energy level.

According to this theory, valence electrons are classified in terms of orbital occupancy. An atom with a valence orbital that is occupied by a single electron can theoretically share that electron with another atom. Such an electron is, therefore, called a **bonding electron**. A full valence orbital, occupied by two electrons, has a repelling effect on electrons in any nearby orbitals. Two electrons occupying the same orbital are called a **lone pair**.

According to quantum mechanics, the number and occupancy of valence orbitals in the atoms of the main group elements are determined by the following theoretical rules plus the descriptions in **Table 1**, and the energy-level diagrams in **Figure 3**:

- The first energy level has room for only one orbital with a maximum of two electrons. Hydrogen, the smallest reactive atom with the simplest structure, has only one energy level. This gives hydrogen unique properties; it is an exception to most rules and generalizations that apply to other atoms.
- Energy levels above the first contain four orbitals, that is, eight electrons maximum. The noble gases have this valence electronic structure; their lack of reactivity indicates that a structure with eight electrons filling a valence level is very stable. This is known as the **octet rule** and is usually obeyed by main group atoms. However, only C, N, O, and F atoms *always* obey the octet rule when bonding.
- An orbital may be unoccupied, or it may contain one or two electrons. This means that two (but never more than two) electrons may share the same region of space at the same time. (This is called the Pauli exclusion principle, first stated in 1925 by Austrian scientist Wolfgang Pauli.)
- Electrons "spread out" to occupy any empty valence orbitals before forming electron pairs.

Table 1 Theoretical Definitions of Orbitals

Orbital	Number of electrons in the orbital	Description of electrons	Type of electrons
empty	0	_	_
half-filled	1	unpaired	bonding
filled	2	lone pair	nonbonding

## **Atomic Models: Lewis Symbols**

Gilbert Lewis also created a simple model of the arrangement of electrons in atoms that explains and predicts empirical formulas. He used the symbol for the element to represent the nucleus plus all the electrons *except* the valence electrons. He reasoned that in reactions, this collection of subatomic particles, with its net positive charge, did not change. The valence electrons, which do change, are shown as dots around the central symbol, with the entire diagram showing (for an atom) a net charge of zero. This is called a **Lewis symbol** and is an extremely useful model to help describe how atoms bond. Figure 4 shows the relationship of a Lewis symbol to an energy-level diagram for the oxygen atom. In Figure 4(b), the symbol O represents the oxygen nucleus and the two electrons in the first energy level, with a net charge of 6+. The oxygen atom is thought to have two lone pairs and two bonding electrons in its four valence orbitals.

To draw Lewis symbols for main group atoms:

- Write the element symbol to represent the nucleus and any filled energy levels of the atom.
- Add a dot to represent each valence electron.
- Start by placing valence electrons singly into each of four valence orbitals (represented by the four sides of the element symbol).
- If additional locations are required for electrons once each orbital is half-filled, start filling each of the four orbitals with a second electron until up to eight valence electrons have been represented by dots.

The Lewis symbols for atoms of the Period 2 elements show the dot arrangement for main group atoms.

It is important to understand that Lewis symbols do not mean that electrons are dots or that they are stationary. The four sides of the atomic symbol just represent the four valence level space regions (orbitals) that may be occupied by electrons. The dots simply keep count of how many electrons are in each orbital (or not); that's all the information that Lewis symbols provide. They are simplistic 2-D diagrams of complex 3-D structures that help us visualize and account for each electron.

## Electronegativity

On theoretical grounds, chemists believe that atoms have different abilities to attract valence electrons. For example, the farther away from the nucleus that electrons are, the weaker their attraction to the nucleus. In addition, inner electrons (those closer to the nucleus) shield the valence electrons from the attraction of the positive nucleus. Finally, the greater the number of protons in the nucleus, the greater the attraction for electrons must be. Combining these three points, it is possible to assign a value to any atom, describing how well it attracts electrons shared in a covalent bond with another atom.

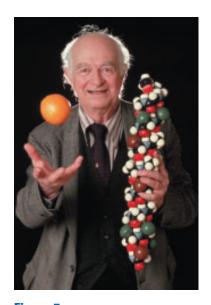
Chemists use the term **electronegativity** to describe the relative ability of an atom to attract a pair of bonding electrons in its valence level. Electronegativity is usually assigned on a scale developed by Linus Pauling (Figure 5). Empirically, Pauling based his scale on energy changes in chemical reactions. According to his scale, fluorine has the highest electronegativity, 4.0. Of the nonradioactive metal atoms, cesium has the lowest electronegativity, 0.8. Note that these are the most reactive nonmetal and metal, respectively. Metals tend to have low electronegativities, and nonmetals tend to have high electronegativities. See the inside front cover of this book for data on electronegativities of atoms.

<u>6 e⁻</u>	
<u>2 e</u> -	0.
8 p <sup>+</sup>	
0	
oxygen atom	

- (a) Electron energy-level diagram of oxygen atom
- (b) Lewis symbol for oxygen atom

#### Figure 4

An energy-level diagram and a Lewis symbol are two (of many) models that can be used to represent the structure of an atom.



Linus Pauling (1901-1994) was a dual winner of the Nobel Prize. In 1954, he won the prize in chemistry for his work on molecular structure, and in 1962, he received the Nobel Peace Prize for campaigning against the nuclear bomb.

## DID YOU KNOW ?

#### Crystallography

Louis Pasteur (1848) studied crystals (as well as germs) under a microscope; Friedrich Kekulé (1858) established a method of communicating the bonding within crystals; Jacobus van't Hoff (1874) described crystal structures with different abilities to polarize light in terms of orientations of atoms (Figure 6); and Linus Pauling used X-ray diffraction of crystals to further his understanding of chemical bonding. Crystallography forced the theory of chemical bonding to greater and greater refinements.



**Figure 6**A photomicrograph of a solid's crystal structure—taken with polarized light.

#### Figure 7

In the molecular substance acetone (a), each molecule is described as containing three carbon atoms, six hydrogen atoms, and one oxygen atom; theory suggests that all 10 atoms are held together by 9 covalent bonds (b). The bond between the carbon and oxygen atoms can only be explained if it involves four electrons, which is called a double bond, a type discussed in more detail in Section 3.2. This is a type of stereochemical formula, which is a formula that shows the molecule in three dimensions.

#### Practice

- 1. Place the following chemistry concepts in the order in which they were created:
  - (a) Lewis symbols

- (d) Kekulé structures
- (b) empirical formulas
- (e) quantum mechanics

- (c) Dalton atom
- 2. Write the Lewis formula, the electron energy-level diagram, and the electronegativitiy value for each of the following atoms:
  - (a) aluminium

(c) calcium

(b) chlorine

- (d) argon
- **3.** (a) Draw the Lewis symbol for a calcium atom, but omit the two dots for valence electrons. Show that the remaining structure has a double positive charge by enclosing the Lewis structure in large square brackets and writing the overall charge to the upper right side, outside the brackets.
  - (b) What structure is represented by your symbol? What is it called?
- 4. In a Lewis symbol of a potassium atom, describe what entities are assumed to be included in its element symbol.
- **5.** List the requirements (criteria) for a new scientific concept, such as the Lewis theory, before it becomes accepted by the scientific community.

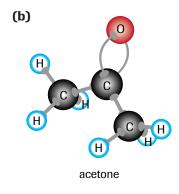
## **Bonding**

Imagine that two atoms, each with an orbital containing one bonding electron, collide in such a way that these half-filled orbitals overlap. As the two atoms collide, the nucleus of each atom attracts and attempts to "capture" the bonding electron of the other atom. A "tug-of-war" over the bonding electrons occurs. Which atom wins? Comparing the electronegativities of the two atoms can predict the result of the contest.

## **Covalent Bonding**

If the electronegativities of both atoms are relatively high, neither atom will "win," and the pair of bonding electrons will be shared between the two atoms. The simultaneous attraction of two nuclei for a shared pair of bonding electrons is known as a **covalent bond**. This kind of bond normally forms between two nonmetal atoms. When this kind of bond forms during chemical reactions, often the products are molecular substances (**Figure 7**). The electron sharing may be equal (between two carbon atoms) or unequal (between a carbon atom and an oxygen atom or between a carbon atom and a hydrogen atom).





### **Ionic Bonding**

If the electronegativities of two colliding atoms are quite different, the atom with the stronger attraction for electrons may succeed in removing the bonding electron from the other atom. An *electron transfer* then occurs, and positive and negative ions are formed. The term **ionic bond** refers generally only to the attraction between any specific cation and any specific anion. However, the bonding in ionic compounds necessarily involves enormous numbers of both kinds of ions, and is not nearly as simple as an ionic formula makes it seem. After electron transfer, the ions arrange themselves in positions where the maximum total attraction between positive and negative charges occurs. This determines the numerical ratio of ions in a compound, for example, 1:2 for the compound calcium chloride, CaCl<sub>2</sub>(s). This happens because ions are always attracted such that the total net charge becomes zero. If there were to be any extra negative charge, more positive ions would be attracted and vice versa. Ions in an ionic compound always "pack together" to arrange themselves in some regular, repeating 3-D pattern. This 3-D arrangement is called the crystal lattice because, when enough ions assemble to form a visible amount of the compound, we see that the structure is always crystalline in form, with a particular predictable crystal shape for each compound (Figure 8). Ordinary table salt, for example, always forms crystals in a cubic pattern. Within such a crystal, we use the term ionic bonding to describe the overall force holding it together. (Crystals are discussed in more detail in Section 3.5.)

### Metallic Bonding

If both types of colliding atoms have relatively low electronegativities, the atoms can share valence electrons, but no actual chemical reaction takes place between the substances. Mixing melted lead and tin, for example, followed by cooling the mixture until it solidifies, produces a solid, called solder, that is shiny, flexible, and conducts well. The bonding in such substances is called a metallic bond. In metallic bonding, the valence electrons are not held very strongly by their atoms, and the atoms have vacant valence orbitals. The result is that the valence electrons are free to move about between the atoms. Wherever the electrons move, they are acting to hold atoms together because positive nuclei on either side will both be attracting the electrons between them. The bonding in metallic substances has been described as a great number of positive ions surrounded by a "sea" of mobile electrons (Figure 9). The valence electrons act like a glue that holds the whole structure together.

Due to this mobility of valence electrons, the attractive force around a metal atom acts in every direction, somewhat like the attraction force around any ion in an ionic compound. But the attractive force is very unlike the strong attractions between covalently bonded atoms, which act only in one location and, therefore, in only one specific direction. In addition, unlike the ions in ionic solids, metal atoms do not have to be in any particular arrangement to attract each other, which results in the most useful property observed in metals. The atoms in solid metals may be moved around each other without moving them farther apart from each other, so the bonds between them are not weakened or broken by changing the shape of the solid. This allows the physical formation of metals into any convenient shape, creating the properties we call flexibility, malleability, and ductility. Making objects from metal has defined the progress of human technology since the Bronze Age, when metal alloys first came into use to make edged weapons and armour that did not break upon impact.



The regular geometric shape of ionic crystals is evidence for an orderly array of positive and negative ions.

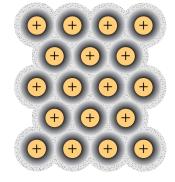


Figure 9 In this model of metallic bonding, each circled positive charge represents the nucleus and inner electrons of a metal atom, surrounded by a mobile "sea" or "cloud" of valence electrons (occupying the grey area).

# SUMMARY

## **Bonding Theory**

- The formation of a chemical bond involves competition for bonding electrons occupying valence orbitals.
- If the competing atoms have equal electronegativities, the bonding electrons are shared equally.
- Electron sharing between atoms with high electronegativity results in covalent bonding.
- Electron sharing between atoms with low electronegativity often results in metallic bonding.
- If the competing atoms have unequal electronegativities, the result may be unequal covalent bonding; if unequal enough that electrons transfer, the result will be ionic bonding.
- Bonding theory was created by chemists to describe, explain, and predict natural events and observed properties.

## Section 3.1 Questions

- **1.** Use bonding theory to describe the following in terms of electrons and orbitals: bonding electron, lone pair.
- 2. Write a theoretical definition of electronegativity, covalent bond, and ionic bond, and describe the bonds in terms of a difference in electron rearrangement.
- 3. Copy **Table 2** using computer software, if available, and fill it in for each of the main group elements of Period 3.
- **4.** How do Lewis symbols that represent metal atoms differ from those of nonmetals?
- Using the electronegativity data in the periodic table, describe the variation in electronegativities within a group and a period.
- **6.** Which element is an exception to almost every rule or generalization about elements? What is unique about this element compared with all other elements in the periodic table?
- 7. What category of substances would have perfectly equal sharing of valence electrons?
- **8.** What characteristic of valence electrons makes most metals very good conductors of electricity?

**9.** Potassium and calcium both have valence electrons in the fourth energy level, presumably about the same distance from their nuclei, yet calcium has higher electronegativity (**Figure 10**). Why?

<b>(a)</b> <u>1 e⁻</u>	<b>(b)</b> <u>2 e</u> -
<u>8 e</u> -	<u>8 e</u> -
<u>8 e</u> -	<u>8 e</u> -
<u>2 e</u> -	<u>2 e</u> -
19 p <sup>+</sup>	20 p <sup>+</sup>
K	Ca
potasium atom	calcium atom

#### Figure 10

Energy-level diagrams for (a) potassium and (b) calcium

- 10. Electronegativities are an indication of how strongly atoms attract electron pairs shared in bonds. Why are no electronegativities listed for the two smallest Group 18 atoms?
- 11. Briefly outline how bonding theory has developed and has been improved through successive contributions by scientists from 1904 to the present day.
- **12.** Dr. Linus Pauling's bonding theory gained rapid acceptance by the scientific community. What characteristics must any scientific theory have in order to be successful?

Table 2 Theoretical Descriptions of Main Group Elements of Period 3

Element symbol	Electronegativity	Group number	Number of valence electrons	Lewis symbol	Number of bonding electrons	Number of lone pairs of electrons	

# **Explaining Molecular Formulas**

The theory of chemical bonding developed in Section 3.1 paves the way for a more complete understanding of molecular elements and compounds. In this section, molecular substances are discussed in terms of their chemical bonding.

## **Molecular Elements**

Using evidence that gases react in simple ratios of whole numbers and Avogadro's theory that equal volumes of gases contain equal numbers of molecules, early scientists were able to determine that the most common forms of hydrogen, oxygen, nitrogen, and the halogens are diatomic molecules. Modern evidence shows that phosphorus and sulfur commonly occur as P<sub>4</sub>(s) and S<sub>8</sub>(s). An acceptable theory of molecular elements must provide an explanation for evidence such as these empirical formulas. Recall that, according to atomic theory, an atom such as chlorine, with seven valence electrons, requires one electron to complete the stable octet. This electron may be obtained from a metal by electron transfer or by sharing a valence electron with another atom. Two chlorine atoms could each obtain a stable octet of electrons if they shared a pair of electrons with each other. Bonding theory suggests that a covalent bond between the atoms results from the simultaneous attraction of two nuclei for a shared pair of electrons, explaining why chlorine molecules are diatomic (Figure 1). Lewis formulas are particularly useful for communicating electron sharing and octet formation:

$$:Cl \cdot + .Cl : \rightarrow :Cl :Cl :$$

According to atomic theory, oxygen atoms have six valence electrons, and evidence shows that the element is diatomic. Sharing a pair of bonding electrons would leave both oxygen atoms with less than a stable octet. Initially, molecular theory could not explain the diatomic character of oxygen. Instead of replacing the theory, scientists revised it by introducing the idea of a double bond. If two oxygen atoms can share a pair of electrons, chemists hypothesized that perhaps they can share two pairs of electrons at once to form a double covalent bond:

$$\vdots \overset{\cdot}{O} \cdot + \overset{\cdot}{O} \vdots \rightarrow \vdots \overset{\cdot}{O} \vdots \overset{\cdot}{O} \vdots$$

This arrangement is consistent with accepted theory, since stable octets of electrons result. This idea explains many empirically known molecular formulas, in addition to  $O_2(g)$ , in a simple way, without the necessity of changing most of the previous assumptions. Chemists created the concept of a triple bond to explain the empirically determined chemical formulas for nitrogen (N<sub>2</sub>) and hydrogen cyanide (HCN). This triple bond results from two atoms sharing three pairs of electrons.

Lewis formulas are a form of electron "bookkeeping" to account for valence electrons. They do not show what orbitals look like or where electrons may actually be at any instant—they simply keep track of which electrons are involved in bonds. Once this is understood, the simple and efficient structural formula can be used to represent bonding in molecules (Figure 2). In structural formulas, lone pairs of electrons are not indicated, and each shared pair of bonding electrons is represented by a line. Although we indicate a double bond with two lines, and a triple bond with three lines, each type is only one bond. The lines just tell us how many electrons are shared by the bonded atoms.

#### Learning Tip

Many molecular elements are diatomic, and some are polyatomic. It is very useful to memorize the formulas of the nine molecular elements:

mino molocalai	010111
hydrogen	$H_2(g)$
nitrogen	$N_2(g)$
oxygen	$O_{2}(g)$
fluorine	$F_2(g)$
chlorine	$Cl_2(g)$
iodine	l <sub>2</sub> (s)
bromine	$Br_2(I)$
phosphorus	$P_4(s)$
sulfur	$S_8(s)$

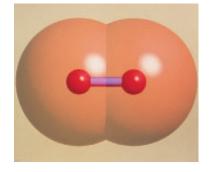


Figure 1

The chlorine, Cl<sub>2</sub>, molecule is represented here by a computergenerated combination of spacefilling and ball-and-stick models.

$$CI-CI$$
  $O=0$ 

#### Figure 2

To help visualize bonding, chemists use structural formulas. A single line represents a single covalent bond (as shown in the chlorine molecule), and a double line represents a double covalent bond (as shown in the oxygen molecule).

#### Practice

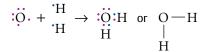
- **1.** Use bonding theory to draw Lewis formulas for the elements in the halogen family. How are these diagrams consistent with the concept of a chemical family?
- **2.** The Lewis formula of a hydrogen molecule is automatically an exception to the octet rule. Considering the positions of hydrogen and helium in the periodic table, how is the Lewis formula for hydrogen a good explanation of its empirical formula?
- 3. Use a Lewis formula to explain the molecular formula for nitrogen,  $N_2(g)$ . Recall that N atoms always obey the octet rule.
- **4.** According to atomic theory, a sulfur atom has six valence electrons, including two bonding electrons. Therefore, any molecule containing only sulfur would have either two single covalent bonds or one double covalent bond from each sulfur atom.
  - (a) Use a Lewis formula to predict the simplest chemical formula for sulfur.
  - (b) Assuming two single covalent bonds from each sulfur atom, draw a structural formula that might explain the molecular formula for sulfur,  $S_8(s)$ .



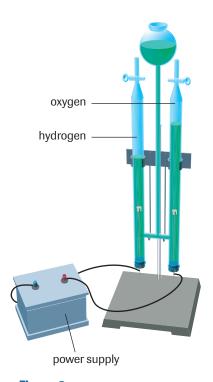
Molecular compounds cannot usually be represented by a simplest ratio formula in the way that ionic compounds can. Simplest ratio formulas indicate only the relative numbers of atoms or ions in a compound; they provide no evidence for the actual number or arrangement. For example, the simplest ratio formula CH represents a compound composed of molecules containing equal numbers of carbon and hydrogen atoms. Empirical work indicates that several very different common compounds, for example, acetylene,  $C_2H_2(g)$ , and benzene,  $C_6H_6(l)$ , can be described by means of the simplest ratio formula CH. To distinguish between these compounds, it is necessary to represent them with molecular formulas. Molecular formulas also accurately represent the actual composition of the smallest units of molecular compounds, which is very different from ionic compound structure, where the entire crystal lattice is really all one continuously bonded unit.

Explanations of molecular formulas are based on the same concepts used to explain molecular elements. The rules of the atomic theory, the idea of overlapping half-filled orbitals, and a consideration of differences in electronegativity all work together to produce a logical, consistent, simple explanation of experimentally determined molecular formulas.

A covalent bond in molecular compounds, just as in molecular elements, is a strong, directional force within a complete structural unit: the molecule. The theoretical interpretation of the empirical formula for water,  $H_2O(l)$ , is that a single molecule contains two hydrogen atoms and one oxygen atom held together by covalent bonds (**Figures 3** and **4**). The purposes of explaining a molecular formula are to show the arrangement of the atoms that are bonded together and to test the explanatory power of the bonding theory. As shown below, an oxygen atom requires two electrons to complete a stable octet. These two electrons are thought to be supplied by the bonding electrons of two hydrogen atoms. In this way, oxygen achieves a stable octet, and all atoms complete their unfilled energy levels.



The concept of a double covalent bond explains empirically known molecular formulas such as  $O_2(g)$  and  $C_2H_4(g)$ . The atoms involved must share more than one bonding electron. A double bond involves the sharing of two pairs of electrons between two atoms.



**Figure 3**When water is decomposed by electricity, the volume of hydrogen gas produced is twice the volume of oxygen gas produced. This evidence led to the acceptance of H<sub>2</sub>O as the

empirical formula for water.

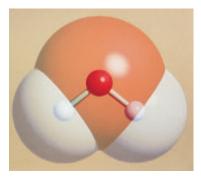


Figure 4
The empirical formula for water is described theoretically by this computer-generated model.

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Similarly, a triple covalent bond involves two atoms sharing three pairs of electrons. In common molecular compounds, there is no empirical evidence for the formation of a bond involving more than three pairs of electrons. According to accepted rules and models, there are many atoms that can form more than one kind of covalent bond. For example, carbon, nitrogen, and oxygen, which are three of the most important elements in molecules in living organisms, can all form more than one kind of covalent bond. The maximum number of single covalent bonds that an atom can form is known as its **bonding capacity**, which is determined by its number of bonding electrons (Table 1). For example, nitrogen, with a covalent bonding capacity of three, can form three single bonds, one single bond and one double bond, or one triple bond. The theory suggests that carbon, with a bonding capacity of four, can form four single bonds, two double bonds, one single and one triple, or one double and two single bonds.

**Table 1** Bonding Capacities of Some Common Atoms

Atom	Number of valence electrons	Number of bonding electrons	Bonding capacity
carbon	4	4	4
nitrogen	5	3	3
oxygen	6	2	2
halogens	7	1	1
hydrogen	1	1	1

Evidence for the reaction of ammonia with boron trihydride required a revision to bonding theory. A covalent bond in which one of the atoms donates both electrons is called a coordinate covalent bond. This concept is useful in explaining the structure of many molecules and polyatomic ions. The following equation shows the formation of a coordinate covalent bond, where a nitrogen atom overlaps a full valence orbital (its lone pair) with the empty (unoccupied) valence orbital of a boron atom:

The properties of coordinate covalent bonds do not differ from those of a normal covalent bond because all electrons are alike, regardless of their source. For purposes of writing Lewis formulas, it is irrelevant which atom the electrons "come from."

In the discussion presented in this textbook, the sharing of electrons has been restricted to valence electrons. This restricted theory also requires that all valence electrons in molecules be paired. Of course, no theory in science is absolute, and there are exceptions to both parts of this theory. Some molecules, such as nitrogen monoxide, appear to have unpaired electrons. Other molecules, like the boron trihydride shown above, appear not to follow the octet rule. Rather than developing a more detailed theory, this textbook specifically notes such cases as exceptions.

## **Types of Formulas**

Over time, different groups of consumers, technologists, and scientists have developed different terms for the same thing. For accuracy in communication, it is necessary that terms be mutually understood, so a convention is normally established. Some conventions, like those for symbols for elements and SI units, are international and universal. Others are more regional or specialized, for example, the "barrel" volume unit (151 L) used only by the oil industry.

## DID YOU KNOW F

#### **Creativity in Science**

Many people consider science to be very structured, with no room for human creativity. Nothing could be further from the truth. Forming new concepts and thinking up new areas to explore require scientists to act like artists. Consider the following quote from Dr. John Polanyi (Figure 5), a Canadian Nobel Prize winner for chemistry:

"To obtain an answer of note, one must ask a question of note; a question that is exquisitely phrased. It must be one that matters, on a topic that is new, to which an answer can be found. So. yes, we do 'turn over stones', but the art is to pick the right stone."



Figure 5 John Polanyi (1929- )

## Learning Tip

The word "empirical" has two common meanings, both of which are used in this unit. To this point, "empirical" has been used to mean "as obtained by direct observation, such as in a laboratory." Thus, any formula determined from evidence in a laboratory can be said to be empirically determined.

When a formula is called an empirical formula, however, the meaning is quite different. In this case, the term means that the formula shows the simplest whole-number ratio of atoms or ions present in a compound.





# Computer-Generated Models

Scientists have been collecting empirical evidence of the shapes of molecules for decades. Recently, as computing power and speed increase, software engineers have converted scientific findings into interactive models that appear to be three dimensional. There are many Web sites where you can explore these models.

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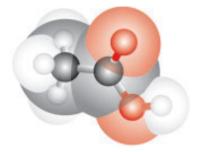


Figure 6
A computer-generated image, combining two models (ball-and-stick and space-filling) for an acetic acid molecule

## **Ionic Compound Formulas**

All ionic compounds have empirical formulas, representing the crystal lattice with a formula unit that shows only the simplest number ratio of cations to anions. The ion charges are omitted, so the formula must be memorized or referenced. The molar mass of an ionic compound is the mass of a mole of formula units.

### **Molecular Compound Formulas**

**Table 2** defines and gives examples of the terminology used in this book to refer to the various kinds of molecular compound formulas. Acetic acid is used as a comparative example.

Table 2 Names of Types of Formulas for Molecular Compounds

Empirical formula	CH O	An ampirical formula above the
Empirical formula	CH₂O	An empirical formula shows the simplest whole-number ratio of atoms in the compound. Empirical formulas are rarely useful for molecular compounds.
Molecular formula	$\mathrm{C_2H_4O_2}$	A molecular formula shows the actual number of atoms that are covalently bonded to make up each molecule.
	CH₃COOH	A molecular formula often has the atom symbols written in a sequence that helps you determine which atoms are bonded to which.
Lewis formula	н н:с:с:о:н н <u>;</u> о:	*A Lewis formula is also commonly called a Lewis diagram, or an electrondot diagram. It uses Lewis symbols to show electron sharing in covalent bonds, and the formation of stable valence octets of electrons in molecules and ions.
Structural formula	H O   H - C - C - O - H   H	*A structural formula is also commonly called a structural diagram. As well as showing which atoms are bonded, the type of covalent bond is represented by the number of lines drawn between atomic symbols.
Stereochemical formula	$\begin{array}{c} H \\ C - C \\ H \end{array}$	A stereochemical formula is a structural formula drawn to try to represent the three-dimensional molecular shape. For much larger molecules, this style of representation often becomes too complex to be practical.

<sup>\*</sup> It is strongly recommended that you memorize this terminology information.

Several kinds of physical models (or visual depictions of such models) can also help us understand the shape, relative size, and structure of molecules. Pictures and diagrams of various kinds of models are used throughout this textbook (**Figure 6**).

## **Determining Lewis Formulas**

Chemists make use of bonding theory to predict valence electron distribution for molecules and polyatomic ions. A Lewis formula allows further predictions of entity structure, polarity, and shape. In this textbook, Lewis formula predictions are limited to entities with only one central atom, unless extra information is included with the question. The **central atom** is the atom to which all the other atoms—**peripheral atoms**—are bonded. Simple Lewis formulas can be predicted with a series of five steps.

## SAMPLE problem 3.1

Determine the Lewis formula and the structural formula for sulfur trioxide, SO<sub>3</sub>(g).

1. Count the total valence electrons in the entity by adding the valence electrons of each atom. If the entity is a polyatomic ion, add (usually) or subtract valence electrons to account for the net charge, one for each unit of charge.

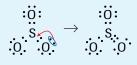
3 oxygen atoms and 1 sulfur atom and no net charge  $3(6e^{-}) + 1(6e^{-}) + 0e^{-} = 24e^{-}$ 

It is usually obvious from relative numbers which atom is central; if not, the central atom will usually be the one with the highest bonding capacity. In this molecule, the single S atom must be central.

- 2. Arrange the peripheral atom symbols around the central atom symbol, and place one pair of valence electrons between each peripheral atom and the central atom (bond pairs).
- 3. Place more pairs of valence electrons (lone pairs) on all the peripheral atoms, to complete their octets. Recall that a hydrogen atom's energy level is completed with only two valence electrons.
- 4. Place any remaining valence electrons on the central atom as lone pairs. For this example, all 24 valence electrons have already been assigned.
- 5. If the central atom's octet is not complete, move a lone pair from a peripheral atom to a new position between that peripheral atom and the central atom. Repeat until the central atom has a complete octet. For a molecule, this completes the Lewis formula.

If the entity is a polyatomic ion, place square brackets around the entire Lewis formula, and then write the net charge outside the bracket on the upper right.

Sulfur atom has an incomplete octet.





To show the structural formula, omit all lone pairs and replace every bond pair with a line.

## **Practice**

- 5. Use both Lewis formulas and structural formulas to represent molecules of the following compounds:
  - (a) CS<sub>2</sub>(l), carbon disulfide
- (d) H<sub>2</sub>Se(g) hydrogen selenide
- (b) PH<sub>3</sub>(g), phosphine
- (e) CH<sub>3</sub>SH(g), methanethiol
- (c) H<sub>2</sub>S(g), hydrogen sulfide
- (f) SF<sub>6</sub>(g), sulfur hexafluoride\*

\*This molecule's central atom does not follow the octet rule.

- **6.** Use both Lewis formulas and structural formulas to represent the following ions:
  - (a) hydrogen ion

(d) nitrate ion

(b) hydroxide ion

- (e) carbonate ion
- (c) hydrogen sulfide ion
- (f) hydrogen carbonate ion\*
- \*Hint: A hydrogen ion (proton) bonds to any lone pair from answer (e).

#### Learning Tip

You will find that structural formulas can be written directly for most molecules (even large ones) that have central C atoms, just by using atom bonding capacity. This works because C, N, O, and F atoms always obey the octet rule, and so do other nonmetals when they are peripheral atoms.

## **EXTENSION**



#### Resonance

What if empirical evidence does not support the theoretical Lewis structure? Or if more than one Lewis structure can be drawn? Find out about resonance, the apparent existence of multiple structures at the same time.

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#### Learning Tip

When molecules have more than one possible arrangement of atoms, the molecular formula may be written differently to indicate groups of atoms that are bonded together. For example, the molecular formula for ethanol, C<sub>2</sub>H<sub>5</sub>OH, clearly shows that one hydrogen atom is bonded to the oxygen atom. Dimethyl ether, which has exactly the same number and kind of atoms but very different properties, is written as  $CH_3OCH_3$  or  $(CH_3)_2O$  to distinguish it from ethanol. Structural formulas make the difference much easier to see.



#### **INVESTIGATION 3.1 Introduction**

#### Molecular Models

Chemists use molecular models to explain and predict molecular structure, relating structure to the properties and reactions of substances.

#### **Purpose**

The scientific purpose of this investigation is to test the ability of bonding theory to explain some known chemical reactions by using molecular models.

#### **Problem**

How can theory, represented by molecular models, explain certain chemical reactions?

#### Design

Chemical reactions are simulated with model kits (Figure 7) to test the ability of bonding theory to explain reaction evidence.

To perform this investigation, turn to page 131. 🚴

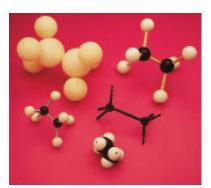
Section 3.2 Questions

#### **Report Checklist**

- Purpose Design O Problem
- O Materials Hypothesis O Procedure
- Prediction Evidence
- Analysis Evaluation



You can use molecular model kits to test the explanatory power of bonding theories.



- 1. Why is it incorrect to write the structural formula of the H<sub>2</sub>S molecule as H-H-S?
- 2. Why is the molecular formula for the methanol molecule usually written as CH<sub>3</sub>OH instead of CH<sub>4</sub>O?
- 3. For each of the following molecular compounds, name the compound, and explain the empirically determined formula by drawing a Lewis formula and a structural formula:
  - (a) HCI
  - (b) NH<sub>3</sub>
  - (c)  $H_2S$
  - (d)  $CO_2$
- 4. Use the bonding capacities listed in Table 1 (page 87) to draw a structural formula of each of the following entities. In each case (for these particular molecules), every C must connect to 4 lines, every N to 3 lines, every O to 2 lines, and every H to one line because C, N, and O atoms always obey the octet rule. Hint: Use the sequence of atoms in some of these molecular formulas to guide you.
  - (a)  $H_2O_2$
  - (b)  $C_2H_4$
  - (c) HCN
  - (d)  $C_2H_5OH$
  - (e) CH<sub>3</sub>OCH<sub>3</sub>
  - (f) CH<sub>2</sub>NH<sub>2</sub>

- 5. Using Lewis symbols, predict the simplest binary molecular compound and write the chemical name for a product of each of the following reactions. Include a structural formula for a molecule of the product.
  - (a)  $I_2(s) + Br_2(l) \rightarrow$
  - (b)  $P_4(s) + Cl_2(g) \rightarrow$
  - (c)  $O_2(g) + Cl_2(g) \rightarrow$
  - (d) C(s) +  $S_8(s) \rightarrow$
  - (e)  $S_8(s) + O_2(g) \rightarrow$
- 6. Draw Lewis formulas for the following common polyatomic anions:
  - (a) hypochlorite ion, OCI
  - (b) bromite ion, BrO<sub>2</sub>
  - (c) iodate ion IO<sub>3</sub>
  - (d) perchlorate ion, ClO<sub>4</sub>
  - (e) ammonium ion, NH<sub>4</sub>

#### Extension

7. Compare your predictions from question 5 with empirical evidence from a reference such as The CRC Handbook of Chemistry and Physics.

# Molecular Shapes and Dipoles

The shape of molecules has long been investigated through crystallography, using microscopes and polarimeters in the late 1800s, and X-ray and other spectrographic techniques since the early 1900s. One of the most important applications of molecular shape research is the study of enzymes. Enzymes are large proteins that, because of their shape, will react only with specific molecules, much like a key's shape will fit only one specific lock. There are about three thousand enzymes in an average living cell, and each one carries out (catalyzes) a specific reaction. There is no room for error without affecting the normal functioning of the cell; different molecular shapes help to ensure that all processes occur properly. Despite extensive knowledge of existing enzymes, the structure of these proteins is so complex that it is still effectively impossible to predict the shape an enzyme will take, even though the sequence of its constituent amino acids is known. The study of molecular shapes, particularly of complex biological molecules, is still a dynamic field.

## **VSEPR Theory**

The valence bond theory created and popularized by Linus Pauling in the late 1930s successfully explained many of the atomic orientations in molecules and ions. Pauling's main empirical work was with the X-ray analysis of crystals. The valence bond theory of bonding was created to explain what he observed in the laboratory. Pauling extended the work of his friend and colleague, Gilbert Lewis, who, as you saw earlier, is famous for creating Lewis symbols (also called electron-dot diagrams).

However, it was not until 1957 that Ronald Nyholm from Australia and Ron Gillespie (Figure 1) from England created a much simpler theory for describing, explaining, and predicting the stereochemistry of chemical elements and compounds. **Stereochemistry** is the study of the 3-D spatial configuration of molecules and how this affects their reactions. The theory that Nyholm and Gillespie created is highly effective for predicting the shape of molecules.

The name of the Nyholm-Gillespie theory is the valence-shell-electron-pairrepulsion theory, or **VSEPR** (pronounced "vesper") **theory**. The theory is based on the electrical repulsion of bonded and unbonded electron pairs in a molecule: pairs of electrons in the valence shell of an atom stay as far apart as possible because of the repulsion of their negative charges. The number of electron pairs can be counted by adding the number of bonded atoms plus the number of lone pairs of electrons (Figure 2). Once the counting is done, the 3-D distribution about the central atom can be predicted by arranging all pairs of electrons as far apart as possible. The type, number, and direction of bonds to the central atom determine the shape of the resulting molecule or polyatomic ion.

According to VSEPR theory:

- Only the valence electrons of the central atom(s) are important for molecular shape.
- Valence electrons are paired in a molecule or polyatomic ion.
- Bonded pairs of electrons and lone pairs of electrons are treated approximately
- Valence electron pairs repel each other electrostatically.
- The molecular shape is determined by the positions of the electron pairs when they are a maximum distance apart.

#### **CAREER CONNECTION**



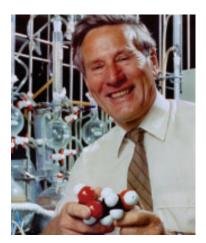
#### **Biochemist**

Biochemists study the chemistry of living matter, including enzymes and proteins. They conduct research in a variety of areas such as medicine, agriculture, and environmental science.

Find a university that offers a program in biochemistry, and find out what other disciplines are part of the program.

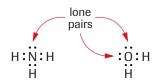
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#### Figure 1

Dr. Ronald Gillespie co-created VSEPR theory in 1957. He moved from England to McMaster University in Hamilton, Ontario, the following year. His work in molecular geometry and in chemistry education is renowned.



Both the ammonia molecule and the water molecule have four pairs of electrons surrounding the central atom. Some of these are bonding pairs, and some are lone pairs.

## mini Investigation

## **Electrostatic Repulsion Model**

The electrostatic repulsion of electron pairs around a central atom in a molecule can be modelled using balloons.

**Materials**: eye protection; four balloons; string; one wooden dowel, 1 cm in diameter and 50 cm long, with a small "eye" screw (metal loop) in one end.

- Inflate the balloons and tie them off, leaving long (50 cm) pieces of string attached to each.
- Thread the strings of two balloons through the metal ring on the end of the dowel, and pull the strings tight, to pull the balloons as close to each other as possible.
- (a) What is the orientation (e.g., angle of a line through the centres) of the two balloons?
- Repeat with three and then four balloons.
- (b) What is the orientation of the three balloons?
- (c) What is the orientation of the four balloons?
- · Reuse or recycle the balloons as directed.
- (d) What are the pros and cons of using balloons for a physical model of the repulsion of electron pairs about a central atom in a molecule?

## **Using VSEPR Theory to Predict Molecular Shape**

Chemists use VSEPR theory to predict molecular shape. What is the shape of the hydrogen compounds of Period 2:  $BeH_2(s)$ ,  $BH_3(g)$ ,  $CH_4(g)$ ,  $NH_3(g)$ ,  $H_2O(l)$ , and HF(g)?

First, we draw Lewis formulas of each of the molecules and then consider the arrangement of all pairs of valence electrons. The key concept is that all pairs of valence electrons repel each other and try to get as far from each other as possible.

## Beryllium Dihydride

Table 1 Geometry of Beryllium Dihydride

Lewis formula	Bond pairs	Lone pairs	Total pairs	General formula	Electron pair arrangement	Stereochemical formula
H∶Be∶H	2	0	2	AX <sub>2</sub>	linear	Н — Ве — Н
						linear

The Lewis formula indicates that  $BeH_2$  has two bonds and no lone pairs of electrons. The number of bond pairs of electrons around the central atom (Be) is two. This is represented by  $X_2$  in the general formula; the A represents the central atom. VSEPR theory suggests that these electron pairs repel each other. According to VSEPR theory, the farthest the electron pairs can get away from each other is to move to opposite sides of the Be atom. This gives the molecule a linear orientation, with the two bonds at an angle of  $180^\circ$ .

## **Boron Trihydride**

Table 2 Geometry of Boron Trihydride

Lewis formula	Bond pairs	Lone pairs	Total pairs	General formula	Electron pair arrangement	Stereochemical formula
Н Н:В:Н	3	0	3	AX <sub>3</sub>	trigonal planar	H B H H trigonal planar

As indicated in **Table 2**, BH $_3$  has three bonds and three pairs of electrons around the central atom, B. The three pairs of electrons repel one another to form a plane of bonds at 120° to each other. According to VSEPR theory, this arrangement or geometry is called trigonal planar.

### Learning Tip

Tetrahedral, trigonal planar, and linear orientations of atoms are common in molecules. To represent 3-D shapes on paper, we use the following conventions: a solid line - is a bond in the plane of the page; a dashed line --- is a bond to an atom behind the plane of the page (away from the viewer); and a wedged line 

✓ is a bond to an atom ahead of the plane of the page (toward the viewer). See the stereochemical formula for acetic acid in Table 2, page 88, for a typical example.



A

tetrahedral



— A linear

#### Methane

Table 3 Geometry of Methane

Lewis	Bond	Lone	Total	General	Electron pair	Stereochemical formula
formula	pairs	pairs	pairs	formula	arrangement	
H:C:H H:C:H	4	0	4	AX <sub>4</sub>	tetrahedral	H C H H tetrahedral

Lewis theory indicates that CH<sub>4</sub> has four bonds or four pairs of electrons repelling each other around the central atom, C. Experimental work and VSEPR theory both agree that a tetrahedral arrangement minimizes the repulsion. Tetrahedral bonds, if identical, orient in three dimensions so that every bond makes an angle of 109.5° with each of the others (Figure 3).



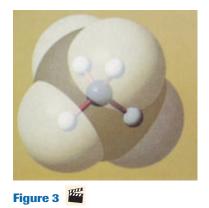
Table 4 Geometry of Ammonia

Lewis formula	Bond pairs	Lone pairs	Total pairs	General formula	Electron pair arrangement	Stereochemical formula
H:N:H H	3	1	4	AX₃E	tetrahedral	H H
						trigonal pyramidal

The Lewis formula shows that NH<sub>3</sub> has three bonding pairs and one lone pair (reppresented by E in the general formula) of electrons. VSEPR theory indicates that the four groups of electrons should repel each other to form a tetrahedral arrangement of the electron pairs just like methane, CH<sub>4</sub>. The molecular geometry is always based on the atoms present; therefore, if we ignore the lone pair, the shape of the ammonia molecule is like a three-sided (triangular) pyramid (called trigonal pyramidal). We would expect the angle between the atoms H-N-H to be 109.5°, which is the angle for an ideal tetrahedral arrangement of electron pairs. However, in ammonia, the atoms form a trigonal pyramidal arrangement with an angle of 107.3° (Figure 4). Chemists hypothesize that this occurs because there is slightly stronger repulsion between the lone pair of electrons and the bonding pairs than between the bonding pairs. According to VSEPR theory, this causes the bonding pairs to be pushed closer together.



Figure 4 Evidence indicates that the shape of the ammonia molecule, NH3, is trigonal pyramidal.



This image shows the ball-and-stick model of methane superimposed on its space-filling model. This model most accurately represents scientists' empirical and theoretical knowledge of the CH4 molecule. The methane molecule has a classic tetrahedral shape.

## DID YOU KNOW T

#### **Ronald Gillespie**

Professor Gillespie is best known for developing a theory of molecular shapes and angles known as VSEPR theory. Gillespie has also done ground-breaking work on acids, including superacids, and has identified previously unknown polyatomic nonmetal cations.

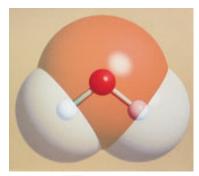


Figure 5

Empirical evidence shows that in water molecules, the two hydrogens bond to the central oxygen at an angle. Such molecules are said to be angular, bent, or V-shaped. The most appropriate and correctly descriptive term is probably Dr. Gillespie's original word, "angular."

#### Water

Table 5 Geometry of Water

Lewis formula	Bond pairs	Lone pairs	Total pairs	General formula	Electron pair arrangement	Stereochemical formula
:0:H H	2	2	4	$AX_2E_2$	tetrahedral	H H angular (V-shaped)

According to the Lewis formula, the water molecule has two bonding pairs and two lone pairs of electrons. Based upon VSEPR theory, the four pairs of electrons repel each other to produce a tetrahedral orientation. The geometry of the water molecule is called angular with an angle of 104.5° (Figure 5). Notice that this angle is again less than the ideal angle of 109.5° for a tetrahedral arrangement of electron pairs. Again, the slightly stronger repulsion exerted by lone pairs is thought to force the bonding electron pairs a bit closer together.

## Hydrogen Fluoride

Table 6 Geometry of Hydrogen Fluoride

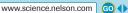
Lewis formula	Bond pairs	Lone pairs	Total pairs	General formula	Electron pair arrangement	Stereochemical formula
H:F:	1	3	4	AXE <sub>3</sub>	tetrahedral	Н — F
••						linear

Based upon the Lewis theory of bonding, the hydrogen fluoride molecule has one bonding pair and three lone pairs of electrons. VSEPR theory indicates that the four electron pairs repel to create a tetrahedral arrangement for the electrons. Since there are only two atoms with one covalent bond holding them together, by definition, the shape of HF is linear, as is the shape of every other diatomic molecule.

#### Learning Tip



Although beryllium is classified as a metal, this very small atom forms some molecular compounds when reacted with nonmetals. Such a molecule obviously cannot obey the octet rule, because beryllium has only two bonding electrons. Similarly, boron (classified as a semi-metal, or metalloid) forms several molecular compounds. With only three bonding electrons, boron cannot form an octet in a simple molecule where one boron is the central atom.





# **SUMMARY**

## Shapes of Molecules

VSEPR theory describes, explains, and predicts the geometry of molecules by counting pairs of electrons that repel each other to minimize repulsion. The process for predicting the shape of a molecule is summarized below:

- Step 1: Draw the Lewis formula for the molecule, including the electron pairs around the central atom.
- Step 2: Count the total number of bonding pairs (bonded atoms) and lone pairs of electrons around the central atom.
- Step 3: Refer to Table 7, and use the number of pairs of electrons to predict the shape of the molecule.

 Table 7
 Using VSEPR Theory to Predict Molecular Shape

				Molecula		
General	Bond	Lone	Total	0	Stereochemical	F
formula*	pairs	pairs	pairs	Geometry**	formula	Examples
$AX_2$	2	0	2	linear (linear)	X — A — X	CO <sub>2</sub> , CS <sub>2</sub>
$AX_3$	3	0	3	trigonal planar (trigonal planar)	X   X   X   X   X   X   X   X   X   X	CH <sub>2</sub> O, BH <sub>3</sub>
AX <sub>4</sub>	4	0	4	tetrahedral (tetrahedral)	X	CH <sub>4</sub> , SiH <sub>4</sub>
AX <sub>3</sub> E	3	1	4	trigonal pyramidal (tetrahedral)	x X X	NH <sub>3</sub> , PCl <sub>3</sub>
AX <sub>2</sub> E <sub>2</sub>	2	2	4	angular (V-shaped)	x ^ A _ x	H <sub>2</sub> O, OCl <sub>2</sub>
AXE <sub>3</sub>	1	3	4	linear (tetrahedral)	A X	HCl, BrF

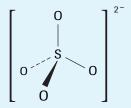
<sup>\*</sup>A is the central atom; X is another atom; E is a lone pair of electrons.

## SAMPLE problem 3.2

Use the Lewis formula and VSEPR theory to predict the shape of a sulfate ion,  $SO_4^{2-}$ .

Determining the shape of a polyatomic ion is no different than determining the shape of a molecule. Again, you first draw the Lewis formula of the ion. For the sulfate ion, the central sulfur atom is surrounded by four oxygen atoms. Add (or subtract) valence electrons to get the net ion charge. In this case, add 2 electrons for a total of 32e. See question 6, page 89, for a hint about predicting this Lewis formula.

Notice that you have four pairs of electrons around the central sulfur atom. This corresponds to the VSEPR theory AX, category in **Table 7**; therefore, the ion has a tetrahedral shape.



## DID YOU KNOW 7

#### **Confusing Mosquitoes**

Research has shown that molecules with a round shape are better in mosquito repellents than long, thin molecules. It seems round molecules are better able to block the sensory nerves in the mosquito's antennae. This makes it difficult for mosquitoes to detect carbon dioxide, moisture, and heat from humans and animals.



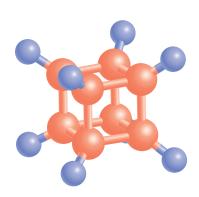
Figure 6 Mosquitoes can be dangerous when they transmit diseases such as malaria and West Nile fever.

<sup>\*\*</sup>The electron pair arrangement is in parentheses.

## DID YOU KNOW 🔂

#### **Predictive Power**

Concepts are tested by their power to explain and to predict. In this section, VSEPR theory is used to predict the shape of molecules with one central atom. Of course, these predictions must be tested in the laboratory. Some of the evidence is provided herein, but more is needed. If a concept, such as VSEPR theory, predicts accurately in a reliable fashion, then the concept is said to have predictive power.



**Figure 7** Cubane

## Learning Tip

It is important to always remember that a double bond or a triple bond is one bond, and to treat it as such, when using VSEPR theory to predict shapes of molecules containing these bonds.

## COMMUNICATION example 1

Draw Lewis and stereochemical formulas for a chlorate ion, ClO<sub>3</sub><sup>-</sup>, and predict the shape.

#### **Solution**

$$\begin{bmatrix} : \ddot{0} : \ddot{0} : \ddot{0} : \ddot{0} \\ \vdots \ddot{0} : \ddot{0} : \ddot{0} : \ddot{0} \end{bmatrix} \quad \begin{bmatrix} 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

According to VSEPR theory, the chlorate ion has a trigonal pyramidal shape.

## Practice

- **1.** Explain how the words that the VSEPR acronym represents communicate the main ideas of this theory.
- 2. Use VSEPR theory to predict the geometry of a molecule of each of the following substances. Draw a stereochemical formula for each molecule, and state whether the central atom obeys the octet rule.

(a)  $Cl_2O(g)$ 

(c)  $H_2S(g)$ 

(e) SiBr<sub>4</sub>(l)

(b)  $PF_3(g)$ 

(d)  $BBr_3(l)$ 

(f) HCl(g)

**3.** Use VSEPR theory to predict the shape of each of the following polyatomic ions:

(a) PO<sub>4</sub><sup>3-</sup>

(b)  $BrO_3^-$ 

(c) NH<sub>4</sub><sup>+</sup>

- 4. Cubane is a hydrocarbon with the formula C<sub>8</sub>H<sub>8</sub>(s). It has a cubic shape, as its name implies, with a carbon atom at each corner of the cube (Figure 7). This molecule is very unstable, and some researchers have been seriously injured when crystals of the compound exploded while being scooped out of a bottle. Not surprisingly, cubane has been the subject of some research as an explosive.
  - (a) According to VSEPR theory, what should be the shape around each carbon atom? Why?
  - (b) If we assume an ideal cubic shape, what are the actual bond angles around each carbon?
  - (c) Explain how your answers to (a) and (b) suggest why this molecule is so unstable.
- 5. Where did the evidence come from that led to the creation of VSEPR theory?

## The Multiple Bond in VSEPR Models

By observing the rate at which hydrocarbon substances react with bromine, a highly reactive reagent, chemists have determined that molecules can contain a double covalent bond or a triple covalent bond. Hydrocarbons with molecules that contain a multiple bond react rapidly, quickly removing the orange-brown colour of the reagent. Hydrocarbon molecules with only single bonds react extremely slowly. Further evidence indicates that a double bond or a triple bond is always shorter and stronger than a single bond between the same kind of atoms. Evidence from crystallography (such as the X-ray analysis of crystals) indicates that any multiple bond is treated just like any single bond for describing, explaining, or predicting the shape of a molecule. This has implications for using VSEPR theory for molecules containing a multiple bond. Let's look at some examples.

## SAMPLE problem 3.3

Ethene (ethylene, C<sub>2</sub>H<sub>4</sub>(g)) is the most common hydrocarbon with a multiple covalent bond. Crystallography indicates that the orientation around the central carbon atoms is trigonal planar. Is VSEPR theory able to explain the empirically determined shape of this molecule?

The first step in testing the ability of VSEPR theory to explain the shape of ethene is to draw a Lewis formula for the molecule.

The second step is to count the number of "pairs" of electrons around the central atoms (the carbon atoms). If a multiple bond is present, there are more than two shared electrons involved in that bond. For VSEPR theory to explain the trigonal planar shape around each carbon, it must assume that any "group" of electrons shared in a bond behaves in much the same way, regardless of how

$$C = C$$

many electrons (2, 4, or 6) are being shared. In other words, you count the numbers of lone pairs and bonded atoms around a central atom to determine the shape. This is a typical revision of a theory, one that increases its power to explain. Each carbon is seen to have three bonds (two single and one double) and no lone pairs. This is an AX<sub>3</sub> configuration, and it explains a trigonal planar shape around each carbon atom, which agrees with the evidence from crystallography.

VSEPR theory passes the test by being able to explain the trigonal planar shape of ethene. Now let's see if VSEPR theory can pass another test by predicting the stereochemistry of the ethyne molecule. Ethyne is the IUPAC name for the substance commonly called acetylene (Figure 8). Acetylene is widely used in high-temperature torches for cutting and welding metals.

# **COMMUNICATION** example 2



Draw a stereochemical formula of ethyne,  $C_2H_2(g)$ , to predict the shape of the molecule.

#### **Solution**

$$H - C \equiv C - H$$

According to VSEPR theory, the shape of the ethyne molecule is linear.

## **COMMUNICATION** example 3

Draw a stereochemical formula for a nitrite ion, NO<sub>2</sub><sup>-</sup>, to predict the shape of the ion.

#### **Solution**

$$\begin{bmatrix} \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ 0 & N & \vdots \end{bmatrix}^{-} \quad \begin{bmatrix} 0 & N & 0 \end{bmatrix}^{-}$$

The central N atom has one lone pair and forms two bonds. Therefore, according to VSEPR theory, a nitrite ion has an angular shape.



Figure 8

Ethyne (acetylene), when mixed with oxygen, burns with a very hightemperature flame. Operating at up to 2500 °C, an oxy-acetylene torch will melt most metals easily.

## DID YOU KNOW ?

#### **Prediction Accuracy**

To show octets for all atoms, bonding theory suggests that ethene has one double bond and ethyne has one triple bond. This can be tested empirically, using the evidence that a multiple covalent bond is shorter than a single bond. For both molecules, X-ray evidence agrees that shapes and bond types are both predicted accurately.

The nitrite ion, however, is predicted to have one single and one double bond. In this case, the evidence does not agree; it indicates that both bonds are identical in length and strength. The shape prediction works very well, but the bond type prediction does not.

As previously stated, electrons are not really small particles, and bonding theory that treats them as such is necessarily limited, a typical case of restriction of a scientific theory.

## DID YOU KNOW 🔐

#### **Theories**

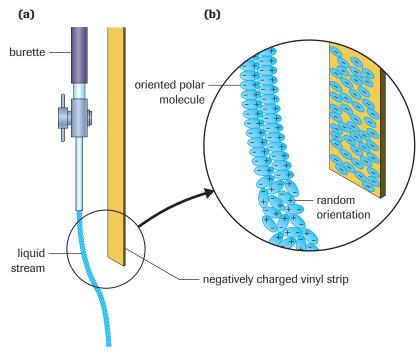
Just as scientists have special definitions for words that apply in the context of science (e.g., the definition of "work" in physics), philosophers who study the nature of chemistry have special definitions for terms such as "theory." To them, a theory is not a hypothesis. To philosophers of chemistry a theory uses the unobservable (such as electrons and bonds) to explain observables (such as chemical and physical properties).

#### Practice

- **6.** In order to make the rules of VSEPR theory work, how must a multiple (double or triple) bond be treated?
- **7.** Use Lewis formulas and VSEPR theory to predict the shapes around each central atom of the following molecules:
  - (a) CO<sub>2</sub>(g), carbon dioxide (in "carbonated" beverages)
  - (b) HCN(g), hydrogen cyanide (odour of bitter almonds, extremely toxic)
  - (c) CH<sub>2</sub>CHCH<sub>3</sub>(g), propene (monomer for polypropylene)
  - (d) CHCCH<sub>3</sub>, propyne (in specialty fuels, such as MAPP gas, for welding)
  - (e) H<sub>2</sub>CO(g), methanal (formaldehyde)
  - (f) CO(g), carbon monoxide (highly toxic gas)
- **8.** Is VSEPR a successful scientific theory? Defend your answer.

## **Molecular Polarity: Dipole Theory**

Chemists believe that molecules are made up of charged particles (electrons and nuclei). A **polar molecule** is one in which the negative (electron) charge is not distributed symmetrically among the atoms making up the molecule. Thus, it will have partial positive and negative charges on opposite sides of the molecule. A molecule with symmetrical electron distribution is a **nonpolar molecule**. The existence of polar molecules can be demonstrated by running a stream of water past a charged object (**Figure 9**). When repeated with a large number of pure liquids, this experiment produces a set of empirical rules for predicting whether a molecule is polar (**Table 8**).



#### Figure 9

- (a) Testing a liquid with a charged object, in this case a vinyl strip, provides evidence for the existence of polar molecules in a substance.
- **(b)** In a liquid, molecules are able to rotate freely. Polar molecules in a liquid will rotate so that their positive sides are closer to a negatively charged material. Near a positively charged material they become oriented in the opposite direction. Logically, then, we can hypothesize that polar molecules will be attracted by either kind of charge.

 Table 8
 Empirical Rules for Polar and Nonpolar Molecules

	Туре	Description of molecule	Examples
Polar	AB	diatomic with different atoms	HCI(g), CO(g)
	N <sub>x</sub> A <sub>y</sub>	containing nitrogen and other atoms	NH <sub>3</sub> (g), NF <sub>3</sub> (g)
	$O_x A_y$	containing oxygen and other atoms	H <sub>2</sub> O(l), OCl <sub>2</sub> (g)
	$C_x A_y B_z$	containing carbon and two other kinds of atoms	CHCl <sub>3</sub> (I), C <sub>2</sub> H <sub>5</sub> OH(I)
Nonpolar	A <sub>x</sub>	all elements	Cl <sub>2</sub> (g), N <sub>2</sub> (g)
	$C_xA_y$	containing carbon and only one other kind of atom	CO <sub>2</sub> (g), CH <sub>4</sub> (g)

investigation 3.2 Introduction	Report Checklist			
Evidence for Polar Molecules	O Purpose	<ul><li>Design</li><li>Metarials</li></ul>	• Analysis	
Use the empirical rules ( <b>Table 8</b> ) to predict the molecular polarity of the liquids provided.	<ul><li>Problem</li><li>Hypothesis</li><li>Prediction</li></ul>	<ul><li> Materials</li><li> Procedure</li><li> Evidence</li></ul>	• Evaluation (1, 2, 3)	
<b>Purpose</b> The purpose of this investigation is to test the empirical rules for predicting molecular polarity.	Problem Which of the liquids provided have polar molecules?			

To perform this investigation, turn to page 131.

## **Electronegativity and Bond Polarity**

Linus Pauling saw the need for a theory to explain and predict the observed polarity of some molecular substances. He combined valence bond theory and bond energy theory, as well as several empirical measures, to create the concept of an atomic property that he called electronegativity (Section 3.1). Electronegativity is found to be a periodic property of atoms, increasing as an atom's position on the periodic table is located farther to the right in a row or higher up in a column (Figure 10).

Pauling explained the polarity of a covalent bond as the difference in electronegativity of the bonded atoms. If the bonded atoms have the same electronegativity, they will attract any shared electrons equally and form a **nonpolar covalent bond**. If the atoms have different electronegativities, they will form a **polar covalent bond**. The greater the electronegativity difference, the more polar the bond will be. For a very large electronegativity difference (combined with other factors), the difference in attraction may transfer one or more electrons from one atom to the other, forming cations and anions. The resulting ions will group to form an ionic compound, held together by ionic bonding.

Pauling explained that polar covalent bonds form when two different atoms share electrons. Because the attraction for those electrons is unequal, the electrons spend more of their time closer to one atomic nucleus than the other. The side of the bond where electrons spend more time is labelled as being partially negative  $(\delta -)$ ; we use the Greek lowercase delta to represent partial charge. The side of the bond that is partially positive is labelled  $\delta$  + (**Figure 11**).

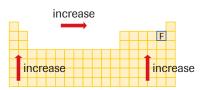


Figure 10 Electronegativity of the elements increases as you move up the periodic table and to the right.

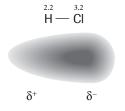


Figure 11 Unequal attraction of the shared electrons gives one side of the covalent bond a partial negative charge  $(\delta -)$  and the other side a partial positive charge  $(\delta +)$ .

Pauling liked to think of chemical bonds as being different in degree rather than different in kind. According to him, all chemical bonds involve a sharing of electrons, with ionic bonds and nonpolar covalent bonds being just the two extreme cases (**Figure 12**). The bonding in substances therefore ranges anywhere along a continuum from nonpolar covalent to polar covalent to ionic. For polar covalent bonds, the greater the electronegativity difference of the atoms, the more polar the bond.

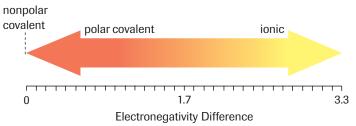


Figure 12

This model of the bonding type continuum shows the relationship of bonded atom electronegativity to bond polarity.

#### Learning Tip

The gradual variation in bond character is shown in beryllium compounds. BeF<sub>2</sub>(s) behaves more like an ionic substance, while BeCl<sub>2</sub>(s) behaves more like a molecular substance. Empirical behaviour is also partly due to size of atoms and shape of molecules, so predicting bond type from electronegativity only is not very reliable, except at the far ends of the scale shown.

## DID YOU KNOW H

#### **Evidence for Polar Bonds**

The energy required to break a bond can be determined experimentally. The energy required to break the H-F bond is considerably greater than the energy required to break either H-H or F-F bonds. Pauling realized that an unequal sharing of the electron pair produced a polar bond that enhanced the bonding between the atoms.

## SAMPLE problem 3.4

Consider the bond that forms between the entities in the following pairs. Label each entity and bond with its electronegativity and bond polarity, and classify the bond:

- (a) H and H
- (b) Pand Cl
- (c) Na and Br

From the periodic table, assign each atom an electronegativity.

- (a) H H
  - 2.2 2.2

The electronegativity difference is 0.0, indicating a nonpolar covalent bond.

- (b) Chlorine is more electronegative, so it is assigned the  $\delta$  charge.
  - $\delta + \delta -$
  - P CI
  - 2.2 3.2

The electronegativity difference is 1.0, indicating a polar covalent bond.

- (c) +
  - Na Br
  - 0.9 3.0

The electronegativity difference is 2.1. These atoms are a metal and a nonmetal, and the electronegativity difference is large. In such a case we assume that an electron transfers completely, forming a cation and an anion. The electrostatic attraction between the newly formed ions is called an ionic bond.

#### Practice

- 9. Draw the following bonds, label the electronegativities, and label the charges (if any) on the ends of the bond. Classify the bond as ionic, polar covalent, or nonpolar covalent:
  - (a) H and Cl
- (d) I and Br
- (b) C and H
- (e) Mg and S
- (c) N and O
- (f) Pand H
- 10. Using electronegativity as a guide, classify the following bonds as ionic, polar covalent, or nonpolar covalent:
  - (a) the bond in HBr(g)
  - (b) the bond in LiF(s)
  - (c) a C-C bond in propane, C<sub>3</sub>H<sub>8</sub>(g)

**100** Chapter 3

- 11. List and order the bonds in the following substances according to increasing bond polarity. Provide your reasoning.
  - (a) H<sub>2</sub>O(l), H<sub>2</sub>(g), CH<sub>4</sub>(g), HF(g), NH<sub>3</sub>(g), LiH(s), BeH<sub>2</sub>(s)
  - (b) PCl<sub>3</sub>(l), Lil(s), l<sub>2</sub>(s), ICl(s), RbF(s), AlCl<sub>3</sub>(s)
  - (c) CH<sub>2</sub>OH(l)
  - (d) CHFCl<sub>2</sub>(g)

## **Bond Polarity and Molecular Polarity**

Chemists have found that, logically and experimentally, the existence of polar bonds in a molecule does not necessarily mean that you have a polar molecule. For example, carbon dioxide is found to be a nonpolar molecule, although each of the C=O bonds is a polar bond. To resolve this apparent contradiction, we need to look at this molecule more closely. Based on the Lewis formula and the rules of VSEPR, carbon dioxide is a linear molecule (Figure 13(a)). Using electronegativities, we can predict the polarity of each of the bonds. It is customary to show the bond polarity as an arrow, pointing from the positive  $(\delta +)$  to the negative  $(\delta -)$  side of the bond (**Figure 13(b**)). This arrow represents the **bond dipole**. The bond dipole is the charge separation that occurs when the electronegativity difference of two bonded atoms shifts the shared electrons, making one end of the bond partially positive and the other partially negative. The arrow representing a bond dipole points from lower to higher electronegativity.

These arrows are vectors and when added together, produce a zero total. In other words, the equal and opposite bond dipoles balance each other, and the result is that the molecule is nonpolar. A nonpolar molecule is one where the bond dipoles balance each other, producing a molecular dipole (vector sum) of zero.

Let's try this procedure again with another small molecule. As you know from Investigation 3.2, water is a polar substance and the O-H bonds in water are polar bonds. The Lewis formula and VSEPR rules predict an angular molecule, shown in **Figure 14** together with its bond dipoles.

In this case, logic indicates that the bond dipoles do not balance. Instead, they add together to produce a nonzero molecular dipole (shown in red). Whenever bond dipoles add to produce an overall dipole for the molecule, the result is a polar molecule. Notice that the water molecule has a partial positive charge on the side by the oxygen and a partial negative charge on the side by the two hydrogens. This explains why a stream of water is attracted to a positively charged strip or rod. This example shows how we can use theory to explain our empirical observations.

From the two examples, carbon dioxide and water, you can see that the shape of the molecule is as important as the bond polarity.

Evidence indicates that methane is a nonpolar substance, although its C-H bonds are polar. Does the same explanation we used for carbon dioxide apply to methane? The stereochemical formula with bond dipoles (Figure 15) shows four equal bond dipoles at tetrahedral (3-D) angles. The bond dipoles balance, the vector sum is zero, and the molecule has no overall dipole. This is true because the CH<sub>4</sub> molecule is symmetrical. In fact, all symmetrical molecules with one central atom, such as CCl<sub>4</sub> and BF<sub>3</sub>, are nonpolar for the same reason.

The theory created by combining the concepts of covalent bonds, electronegativity, bond polarity, and VSEPR logically and consistently explains the polar or nonpolar nature of molecules. We are now ready to put this combination of concepts to a further test—to predict the polarity of a molecule.

**(b)** 
$$0 = 0 = 0$$
 $0 = 0$ 
 $0 = 0$ 
 $0 = 0$ 
 $0 = 0$ 
 $0 = 0$ 

#### Figure 13

(a) The central carbon atom has no lone pairs and two groups of electrons (remember that a double bond counts as one group of electrons). According to VSEPR theory, the least repulsion of two groups of electrons is a linear arrangement. (b) Bond polarity for carbon dioxide

$$\begin{array}{c}
\delta^{+} \\
\delta^{-} \\
H \\
22
\end{array}$$

#### Figure 14

In water, the two bond dipoles are at an angle and do not balance. This creates a resultant molecular dipole (in red) equal to the sum of the bond dipoles.



#### Figure 15

Notice how all the bond dipoles point into the central carbon atom. There are no positive and negative areas on the outer part of the methane molecule. A tetrahedral molecule is symmetrical in three dimensions, and four equal tetrahedral bond dipoles always sum to zero.

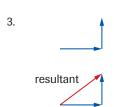
## Learning Tip

A vector quantity is a quantity that has a size and a direction and is often represented by a vector, which is an arrow pointing in a particular direction. When we want to add vector quantities, we usually add the vectors (arrows) "head to tail" to obtain the final (resultant) vector. Bond dipoles are vector quantities because they have a size (difference in electronegativities) and a direction, defined as pointing toward the negative end of the bond.

 head-to-tail addition (resultant vectors in red)



2. resultant: none



Adding vectors in three dimensions follows the same rules but it is mathematically more difficult. For symmetrical molecules, like  $\mathrm{CH}_4$ , it is much easier to use the symmetry of the molecule to reach the conclusion that the molecule is nonpolar.

## SAMPLE problem 3.5

Predict the polarity of the ammonia, NH<sub>3</sub>, molecule. Include your reasoning.

First, draw the Lewis formula.

Based on VSEPR theory, draw the stereochemical formula.



Add the electronegativities of the atoms, from the periodic table, and assign  $\delta+$  and  $\delta-$  to the bonds.

Draw in the bond dipoles.



The ammonia molecule is polar because it has bond dipoles that do not balance (cancel). Each of the bond dipoles shown is angled upward as well as sideways. The molecule is symmetrical sideways (viewed from above), but not vertically (viewed from the side), so there is a resulting molecular dipole, oriented vertically. An ammonia molecule is polar, slightly positive on the side with the hydrogens, and slightly negative on the opposite side.

# SUMMARY

## Theoretical Prediction of Molecular Polarity

To use molecular shape and bond polarity to predict the polarity of a molecule, complete these steps:

- Step 1: Draw a Lewis formula for the molecule.
- Step 2: Use the number of electron pairs and VSEPR rules to determine the shape around each central atom.
- Step 3: Use electronegativities to determine the polarity of each bond.
- Step 4: Add the bond dipole vectors to determine whether the final result is zero (nonpolar molecule) or nonzero (polar molecule).

## Practice

- **12.** Predict the shape of the following molecules. Provide Lewis formulas and stereochemical formulas.
  - (a) silicon tetrabromide, SiBr<sub>4</sub>(l)
- (c) boron trifluoride, BF<sub>2</sub>(q)
- (b) nitrogen trichloride, NCl<sub>3</sub>(l)
- (d) sulfur dichloride, SCl<sub>2</sub>(l)
- **13**. Predict the bond polarity for the following bonds. Use a diagram that includes the partial negative and positive charges and direction of the bond dipole:
  - (a) C≡N in hydrogen cyanide
- (c) P-S in  $P(SCN)_3(s)$
- (b) N=0 in nitrogen dioxide
- (d) C-C in  $C_8H_{18}(I)$

- 14. Predict the polarity of the following molecules. Include a stereochemical formula, bond dipoles, and the final resultant dipole (if nonzero) of the molecule.
  - (a) boron trifluoride, BF<sub>3</sub>(g)
- (c) carbon disulfide, CS<sub>2</sub>(l)
- (b) oxygen difluoride, OF<sub>2</sub>(g)
- (d) phosphorus trichloride, PCl<sub>3</sub>(l)
- 15. Use the empirical rules from **Table 8**, page 99, to predict the polarity of an octane, C<sub>8</sub>H<sub>18</sub>(I), molecule. Explain your answer without drawing the molecule.
- **16.** Use bonding theory to predict the polarity of hydrogen sulfide, H<sub>2</sub>S(q), a toxic gas with a rotten-egg odour. Design an experiment to test your prediction.

#### **Polar Substances**

Whether or not a substance has polar molecules will necessarily affect how it interacts with other substances. For example, solubility evidence consistently shows that "like dissolves like." We find experimentally that polar compounds are soluble in polar solvents, and nonpolar compounds are soluble in nonpolar solvents. Research indicates that greases and oils are nonpolar substances, and water is an extremely polar liquid. Therefore, water is not very good at dissolving oil or grease. This can be a difficult problem when trying to remove



Figure 16 Polar water is useless for removing a nonpolar oil stain.

an oily stain from clothing (Figure 16). On the other hand, we often use greases and oils as protective coatings because they repel water and therefore keep metal parts from rusting. Aboriginal peoples knew that waterproofing leather clothing was easily done by rubbing animal fat into the surface. Modern silicone water repellent sprays use synthetic molecules to accomplish the same end.

Cleaning clothing is a matter of concern to everyone. Soap has been made (from lye and animal fats) and used for all of recorded history, because it helps make oily dirt dissolve in wash water. It does not work well in cold or hard water, though. By learning the molecular structure of soap, scientists were able to create new molecules that would do this job better. Detergents are artificially created molecules with structures that are very long chains of atoms. Most of the length of a detergent molecule is nonpolar and will mix easily with the oil in a stain. At one end of a detergent molecule, however, are many highly polar bonds; that end is attracted strongly by water. The net result is a process that pulls the oil away from the fabric and suspends it in the wash water as tiny droplets (Figure 17), another science research and development success story.

In the other cleaning process, called dry cleaning, clothing is washed with a nonpolar liquid solvent that dissolves the oil directly. (Dry cleaning is not really dry; it just doesn't use water.) This is necessarily a commercial process because it involves toxic solvents and specialized equipment.

Mixing nonpolar and polar liquids results in them forming layers, with the least dense liquid on top. This occurs because the polar molecules attract each other more strongly; thus they stay close together, excluding the nonpolar molecules (**Figure 18**).

#### Learning Tip

Parallel empirical and theoretical ways of knowing are common in chemistry. For example, the polarity of the simplest molecules can be predicted from either empirical or theoretical rules.

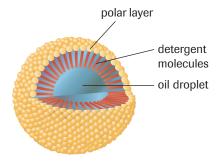


Figure 17

Long, nonpolar sections of detergent molecules are attracted to (dissolve in) a tiny oil droplet. The polar end of each of these detergent molecules helps form a polar "layer" around the droplet, which attracts polar water molecules. This allows them to pull the oil droplet away from a stained area of fabric and hold it suspended in the wash water.



Figure 18

Two clear liquids formed layers in this tube: nonpolar hexane,  $C_6H_{14}(I)$ , on top, and polar water,  $H_2O(I)$ , below. Nonpolar dark orange liquid bromine, Br<sub>2</sub>(I), was then added. The bromine dissolves much more readily in the nonpolar hexane.



### Web Quest-Cleaning Up Dry Cleaning

An organic solvent called perchloroethylene, or PERC, is widely used by the dry-cleaning industry because both PERC and most stains are nonpolar. Like so many other organic solvents, however, PERC can be harmful to both the environment and human health. This Web Quest requires you to look into the chemistry, health, and legislation of the dry-cleaning industry.

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#### Section 3.3 Questions

You can predict the structural formula for any molecule that has more than one central atom by assuming that all atoms (except hydrogen) follow the octet rule and by using the bonding capacity of those atoms.

- Use Lewis formulas and VSEPR theory to predict the molecular shape of the following molecules. Include a stereochemical formula for each molecule.
  - (a) H<sub>2</sub>S(g), hydrogen sulfide (poisonous gas)
  - (b) BBr<sub>3</sub>(l), boron tribromide (density of 2.7 g/mL)
  - (c) PCl<sub>3</sub>(l), phosphorus trichloride
  - (d) SiBr<sub>4</sub>(l), silicon tetrabromide
  - (e) Bel<sub>2</sub>(s), beryllium iodide (soluble in CS<sub>2</sub>(l))
- 2. Use Lewis formulas and VSEPR theory to predict the molecular shape around the central atom(s) of each of the following molecules. Provide stereochemical formulas.
  - (a) CS<sub>2</sub>(l), carbon disulfide (solvent)
  - (b) HCOOH(g), formic acid (lacquer finishes)
  - (c) N<sub>2</sub>H<sub>4</sub>(l), hydrazine (toxic; explosive)
  - (d) H<sub>2</sub>O<sub>2</sub>(l), hydrogen peroxide (disinfectant)
  - (e) CH<sub>3</sub>CCCH<sub>3</sub>(l), 2-butyne (reacts rapidly with bromine)
- 3. Draw the Lewis formula and describe the shape of each of the following ions:
  - (a)  $10_{h}^{-}$
- (b)  $SO_3^{2-}$
- (c)  $CIO_2^-$
- 4. Scientific concepts are tested by their ability to explain current observations and predict future observations. To this end, explain why the following molecules are polar or nonpolar, as indicated by the results of diagnostic tests:
  - (a) beryllium bromide, BeBr<sub>2</sub>(s); nonpolar
  - (b) nitrogen trifluoride, NF<sub>3</sub>(g); polar
  - (c) methanol, CH<sub>3</sub>OH(l); polar
  - (d) hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>(l); polar
  - (e) ethylene glycol, C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>(l); polar
- 5. Predict the polarity of the following molecules:
  - (a) dichlorofluoromethane, CHFCl<sub>2</sub>(g)
  - (b) ethene, C<sub>2</sub>H<sub>4</sub>(g)
  - (c) chloroethane, C<sub>2</sub>H<sub>5</sub>Cl(g)
  - (d) methylamine, CH<sub>3</sub>NH<sub>2</sub>(g)
  - (e) ethanol, C<sub>2</sub>H<sub>5</sub>OH(l)

- **6.** Polar substances may be used in a capacitor, a device for storing electrical energy. For example, a capacitor may store enough electrical energy to allow you to change the battery in your calculator without losing data in the memory. Based upon polarity alone, is water or pentane, C<sub>5</sub>H<sub>12</sub>(I), better for use in a capacitor? Provide your reasoning.
- 7. Search the Internet for information on the current workplace and position of Dr. Ronald Gillespie, the co-creator of VSEPR theory. What degrees does he hold? What are some of the awards that he has won? What is his major topic of research?

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8. Some scientists argue that taste has developed as a protective mechanism. Many poisonous molecules taste bitter, and ones that are useful to us have a more pleasant, often sweet, taste. On the Internet, research the relationship between taste and molecular structure, and write a brief summary.

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- 9. Various consumer products and books exist to help people remove greasy stains from clothing, carpets, etc. Discuss how a knowledge of polar and nonpolar substances is related to the removal of these kinds of stains.
- **10.** For each of the following pairs of atoms, label the electronegativity and bond polarity. In addition, classify the bond as nonpolar covalent, polar covalent, or ionic.
  - (a) Cl and Cl
- (d) O and H
- (b) K and I
- (e) Mg and O
- (c) P and CI
- (f) Xe and F

#### **Extension**

- Astronomers have detected an amazing variety of molecules in interstellar space.
  - (a) One interesting molecule is cyanodiacetylene,  ${\rm HC_5N}$ . Draw a structural formula and predict its shape.
  - (b) How do astronomers detect molecules in space?

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12. Values for the Pauling electronegativities have changed over time. Why would these values change? Are the new values the "true" values?

There are many physical properties that demonstrate the existence of **intermolecular forces**, the forces of attraction and repulsion between molecules. (This term is not to be confused with intramolecular, meaning within a molecule, a term that is sometimes used to refer to the covalent bonds that hold a molecule together.) For example, chemists suggest that a simple property like "wetting" depends to a large extent on intermolecular forces. Consider cotton: The molecules that make up cotton can form many intermolecular attractions with water molecules. Therefore, cotton is very good at absorbing water and easily gets wet. You would not want a raincoat made from cotton. On the other hand, rubber and plastic materials do not absorb water because there is little intermolecular attraction between water molecules and the molecules of the rubber or plastic (**Figure 1**). Rubber and plastics may not be comfortable materials to wear. Alternatively, you can use cotton if it is treated with a water repellent, a coating that has little attraction to water molecules. As you can see, the development of water repellents requires a good knowledge of intermolecular forces.





Cotton (left) will absorb a lot more water than polyester, because the molecules in cotton are better able to attract and hold water molecules.

Another property that demonstrates the existence of an intermolecular force is capillary action. Capillary action allows trees to move water from the ground to the leaves (Figure 2). We will look at this and other properties in terms of intermolecular forces.

## **Van der Waals Forces**

In 1873, Johannes van der Waals suggested that there must be a reason that all gases will condense if cooled. Although molecules in gases act as if they do not affect each other, when the molecular motion is slowed enough, the molecules collect together and form a liquid. Van der Waals assumed that the molecules of a gas must have a small but definite volume, and the molecules must exert weak attractive forces on each other. These forces are often simply referred to as van der Waals forces. It is now believed that in many substances, van der Waals forces are actually a combination of many types of intermolecular forces. In general, intermolecular forces vary over a much wider range and are always considerably weaker than the covalent bonds inside a molecule.

The evidence for this comparison comes primarily from experiments that measure bond energies. For example, it takes much less energy to boil water (overcoming intermolecular forces) than it does to decompose water (breaking covalent bonds), even though the intermolecular forces in water are some of the strongest known.

$$\begin{split} &H_2O(l) \, \rightarrow \, H_2O(g) &\qquad 41 \text{ kJ/mol} \\ &H_2O(l) \, \rightarrow \, H_2(g) \, + \, \frac{1}{2} \, O_2(g) &\quad 286 \text{ kJ/mol} \end{split}$$



Research shows that water is transported in thin, hollow tubes in the trunk and branches of a tree. This is accomplished by several processes, including capillary action. Intermolecular bonding theory suggests that it is necessary that water molecules attract each other to maintain a continuous column of water. They must also attract the molecules in the walls of the tiny tubes in the wood.

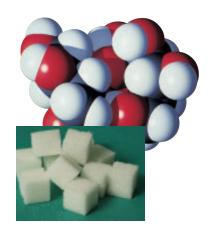
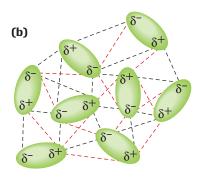


Figure 3 Sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s)

(a)





attraction -----repulsion -----

#### Figure 4

- (a) Oppositely charged sides of polar molecules attract.
- (b) In a liquid, polar molecules can move and rotate to maximize attractions and minimize repulsions. The net effect is greater overall attraction.

Chemists theorize that intermolecular forces are responsible for what we physically observe about molecular substances. For example, to have a sample of sucrose (table sugar) (**Figure 3**) that is big enough to see, there must be trillions of trillions of molecules present, all attracting each other to hold the sample together. These trillions of forces are strong enough to create a crystalline solid structure from the molecules.

Intermolecular forces also appear to control the physical behaviour of molecular substances. In the case of sugar, water dissolves it extremely well but alcohol does not. How do we explain this? We can heat sugar to try to break the bonds between its molecules, but that doesn't work. When heated to a temperature of about 170 °C, long before the molecules start to separate completely from each other (called vaporization, or boiling), the covalent bonds in the molecules start to break, and we don't have sugar any more. However, there is a change—a chemical reaction (decomposition)—that creates totally new substances.

Now we continue the study of intermolecular forces and their effect on several other physical properties of substances, such as boiling point, rate of evaporation, and surface tension. We will interpret these properties using intermolecular forces, but there are other factors that also affect these properties. To minimize this problem, we will try to compare simple, similar substances and do only qualitative comparisons. Before we try to tackle this problem, we need to look at various kinds of intermolecular forces.

### **Dipole-Dipole Force**

In Investigation 3.2, you learned how to test a stream of liquid to see whether the molecules of the liquid are polar. You also learned, in Section 3.3, how to predict whether a molecule was polar or nonpolar. (Recall that polar molecules have dipoles—oppositely charged sides.) Attraction between dipoles is called the **dipole**—**dipole force** and is thought to be due to a simultaneous attraction between any dipole and surrounding dipoles (**Figure 4**). Dipole—dipole forces are among the weakest intermolecular forces; nonetheless, they can still control important properties. For instance, they have a pronounced effect on the ability of solvents to dissolve some solutes and not others.

#### **London Force**

After repeated failures to find any pattern in physical properties like the boiling points of polar substances, Fritz London (**Figure 5**) suggested that the van der Waals force was actually two forces: the dipole–dipole force and what we now call the **London force** (or dispersion force). The evidence for this was that substances with nonpolar molecules would still liquefy upon cooling; something other than dipole–dipole attraction had to be pulling such molecules together. London knew that any forces must be due to the electrostatic forces acting between positive nuclei and negative electrons. He reasoned that, although electron distribution in a molecule might *average* to a zero dipole, any electron movement *within* the molecule could still produce a *momentary dipole*, one that would last for just the instant that the electrons were not distributed perfectly evenly. London also showed that momentary dipoles occurring in adjacent molecules would result in an overall attraction.

A full treatment of London's theory is too involved for the scope of this book. The key point is that the more electrons a molecule has, the more easily momentary dipoles will form, and the greater the effect of the London force will be. Note that London force is necessarily present between *all* molecules, whether or not any other types of attractions are present. Because weak momentary dipoles cause effective attraction only over very short distances, the shape of larger molecules also has an effect on London force.

**106** Chapter 3

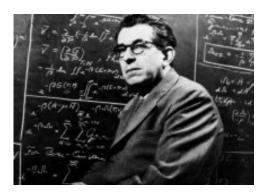


Figure 5

German-American physicist Fritz London (1900-1954). Linus Pauling indicated that London made "the greatest single contribution to the chemists conception of valence" since Lewis created the concept of the shared pair of electrons. Pauling was referring to the use of quantum mechanics by London to describe the covalent bond in the hydrogen molecule.

# **SUMMARY**

## **Dipole-Dipole and London Forces**

- The dipole–dipole force is due to the simultaneous attraction between any one dipole and all surrounding dipoles.
- The strength of the dipole–dipole force is dependent on the overall polarity of the molecule.
- The London force is due to the simultaneous attraction between a momentary dipole in a molecule and the momentary dipoles in the surrounding molecules.
- The strength of the London force is directly related to the number of electrons in the molecule, and inversely related to the distance between the molecules.

## **Using Dipole-Dipole and London Forces** to Predict Boiling Points

Let's take a look at the boiling points of Group 14 hydrogen compounds (**Table 1**). Based on VSEPR and molecular polarity theories, we would expect these molecules to be nonpolar, based on their four equivalent bonds and their tetrahedral shape.

Table 1 Boiling Points of Group 14 Hydrogen Compounds

Compound (at SATP)	Electrons	Boiling point (°C)	
CH <sub>4</sub> (g)	10	-164	
SiH <sub>4</sub> (g)	18	-112	
GeH <sub>4</sub> (g)	36	-89	
SnH <sub>4</sub> (g)	54	-52	

In **Table 1**, you can see that as the number of electrons (and protons) in the molecule increases (from 10 to 54), the boiling point increases (from -164 °C to -52 °C). Since boiling point measures how difficult it is to separate the molecules completely from each other, we assume it is a good relative measure of intermolecular force. The evidence presented in Table 1 supports London's theory, and provides a generalization for describing, explaining, and predicting the relative strength of London forces between molecules. For simplicity, we just count the electrons in a molecule as an indicator of relative London force strength.

## DID YOU KNOW ?

#### A Synthesis

Scientists are always seeking a synthesis of different explanations. For example, all bonding can be explained by referring to simultaneous electrostatic attractions. The covalent bond involves a simultaneous attraction of a pair of negative electrons by two positive nuclei. An ionic bond is the simultaneous attraction of any two oppositely charged ions. Note, also, the theoretical definitions of dipole-dipole force and London force in the Summary.

**Table 2** Boiling Points of Hydrocarbons

Alkane	Boiling point (°C)
methane	-162
ethane	-89
propane	-42
butane	-0.5

Table 3 Isoelectronic Substances

Substance	Electrons	Boiling point (°C)
Br <sub>2</sub> (I)	70	59
ICI(I)	70	97

## SAMPLE problem 3.6

Use London force theory to predict which of these hydrocarbons has the highest boiling point: methane  $(CH_4)$ , ethane  $(C_2H_6)$ , propane  $(C_3H_8)$ , or butane  $(C_4H_{10})$ .

According to intermolecular force theory, butane should have the highest boiling point. The reasoning behind this prediction is that, according to empirical rules, all of these molecules are nonpolar, but butane has the most attractive London force, because it has the greatest number of electrons in its molecules. This prediction is verified by the evidence shown in **Table 2**.

**Isoelectronic molecules**, that is, molecules with the same number of electrons, are predicted to have the same or nearly the same strengths for the London force of intermolecular attraction, provided the shapes of the molecules are similar. Isoelectronic molecules help us study intermolecular forces. For example, if one of two isoelectronic substances is polar and the other is nonpolar, then the polar molecule should have a higher boiling point, as shown in Sample Problem 3.7.

## SAMPLE problem 3.7

Consider two isoelectronic molecules, bromine ( $\mathrm{Br_2}$ ) and iodine monochloride (ICl). Based upon your knowledge of intermolecular forces, explain the difference in the boiling points of the two substances: bromine, 59 °C, and iodine monochloride, 97 °C.

Both bromine and iodine monochloride have 70 electrons per molecule (**Table 3**). Therefore, the strength of the London forces between molecules of each should be about the same. Bromine is nonpolar and, therefore, has only London forces between its molecules. Iodine monochloride is polar, which means it also has dipole–dipole forces between its molecules, in addition to London forces. This extra attraction between ICl molecules produces a higher boiling point. Both molecules are diatomic, with similar shape; so shape should not be a factor affecting London force. All atoms in each molecule have complete octets.

# SUMMARY

# Predicting with Dipole-Dipole and London Forces

- Isoelectronic molecules of similar shape have approximately the same strength of London force between them.
- If all other factors are equal, then
  - the more polar the molecule, the stronger the dipole—dipole force and, therefore, the higher the boiling point
  - the greater the number of electrons per molecule, the stronger the London force and, therefore, the higher the boiling point
- You can explain and predict the relative boiling points of two substances if
  - the London force is the same, but the dipole–dipole force is different
  - the dipole—dipole force is the same, but the London force is different
  - both the London force and the dipole–dipole force are greater for one substance
- You cannot explain and predict the relative boiling points of two substances if
  - one of the substances has a stronger dipole dipole force, and the other substance has a stronger London force
  - the molecules of the two substances differ significantly in shape
  - the central atom of either molecule has an incomplete octet

# WWW WEB Activity

## Canadian Achievers—Gerhard Herzberg

In 1971, Gerhard Herzberg (Figure 6) became the first Canadian to win the Nobel Prize in Chemistry. In announcing the prize, the Swedish Academy stated that Herzberg's ideas and discoveries stimulated "the whole modern development of chemistry from chemical kinetics to cosmochemistry."

- What technological device was central to Herzberg's research?
- 2. What is a free radical?
- Herzberg was a physicist; why was he awarded the Nobel Prize in Chemistry?

Figure 6 Gerhard Herzberg (1904-1999)

## DID YOU KNOW F

## **Canadian Nobel Laureates** in Chemistry

Gerhard Herzberg (1971) Henry Taube (1983) John Polanyi (1986) Sidney Altman (1989) Rudolph Marcus (1992) Michael Smith (1993)

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## **Practice**

- 1. Using London forces and dipole—dipole forces, state the kind of intermolecular force(s) present between molecules of the following substances in their liquid or solid state:
  - (a) water (solvent)
  - (b) carbon dioxide (dry ice)
  - (c) methane (in natural gas)
  - (d) ethanol (beverage alcohol)
  - (e) ammonia (cleaning agent)
  - (f) iodine (disinfectant)
- 2. Which compound in each of the following pairs has stronger dipole dipole forces than the other in their liquid or solid state? Provide your reasoning.
  - (a) hydrogen chloride or hydrogen fluoride
  - (b) chloromethane, CH<sub>3</sub>Cl(g), or iodomethane, CH<sub>3</sub>I(I)
  - (c) nitrogen tribromide or ammonia
  - (d) water or hydrogen sulfide
- 3. Based upon London force theory, which of the following pure substances has the stronger London forces in their liquid or solid state? Provide your reasoning.
  - (a) methane, CH<sub>4</sub>, or ethane, C<sub>2</sub>H<sub>6</sub>
  - (b) oxygen or nitrogen
  - (c) sulfur dioxide or nitrogen dioxide
  - (d) methane or ammonia
- 4. Based upon dipole—dipole and London forces, predict, where possible, which molecular substance in the following pairs has the higher boiling point. Provide your reasoning.
  - (a) boron trifluoride or nitrogen trifluoride
  - (b) chloromethane or ethane
- **5.** Why is it difficult to predict whether NF<sub>3</sub> or Cl<sub>2</sub>O has the higher boiling point?
- 6. Using a chemical reference, look up the boiling points for the substances in questions 4 and 5. Evaluate your predictions for question 4.

## Learning Tip

In the liquid state, molecules are held close together by intermolecular forces. Boiling (or vaporizing) a liquid means adding enough energy to overcome these forces and to separate the molecules to positions far from each other in the gas state. The temperature at which a liquid boils reflects the strength of the intermolecular forces present among the molecules. A higher boiling point temperature means more energy has to be added, and thus the intermolecular forces must be stronger.



## LAB EXERCISE 3.A

# **Boiling Points and Intermolecular Forces**

In this investigation, you will state a hypothesis about the trend in boiling points of compounds containing elements within and between Groups 14 to 17. Your Hypothesis should refer to dipole–dipole and London forces as part of the general reasoning. It could include a general sketch of a predicted graph of boiling point versus number of electrons per molecule. For Analysis of the Evidence, plot the data for each group as a graph of boiling point versus number of electrons per molecule, using the same axes for all four groups. Evaluate your hypothesis as well as the concept of intermolecular forces used to make the hypothesis. Note, and suggest a revised hypothesis to explain, any anomalies (unexpected results).

### **Purpose**

The scientific purpose of this lab exercise is to test a new hypothesis based on the theory and rules for London and dipole—dipole forces.

### **Problem**

What is the trend in boiling points of the hydrogen compounds of the elements of each of the periodic table Groups 14 to 17 (**Table 4**)?

### **Evidence**

See Table 4.

## **Report Checklist**

- O PurposeO ProblemO DesignO Materials
- HypothesisProcedurePredictionEvidence
- Analysis
- Evaluation (2, 3)

**Table 4** Boiling Points of the Hydrogen Compounds of Elements in Groups 14–17

Group	Hydrogen compound	Boiling point (°C)
14	CH <sub>4</sub> (g)	-162
	SiH <sub>4</sub> (g)	-112
	GeH <sub>4</sub> (g)	-89
	SnH <sub>4</sub> (g)	-52
15	NH <sub>3</sub> (g)	-33
	PH <sub>3</sub> (g)	-87
	AsH <sub>3</sub> (g)	<b>-55</b>
	SbH <sub>3</sub> (g)	<del>-</del> 17
16	H <sub>2</sub> O(I)	100
	H <sub>2</sub> S(g)	-61
	H <sub>2</sub> Se(g)	-42
	H <sub>2</sub> Te(g)	-2
17	HF(g)	20
	HCl(g)	-85
	HBr(g)	<del>-67</del>
	HI(g)	-36

## **INVESTIGATION 3.3 Introduction**

## **Molecular Compound Melting Points**

In this investigation, you will accurately measure the melting point of a molecular compound. You will then combine your laboratory evidence with that of other research groups to see if a hypothesized relationship between melting point and molecular size is supported.

## **Purpose**

The purpose of this investigation is to test the hypothesis of a relationship between melting point and molecular size.

### **Hypothesis**

The melting point of similar molecular compounds increases with increased molecular size, as described by the total number of electrons in the molecule.

### **Report Checklist**

- O PurposeO ProblemO DesignO Materials
- Hypothesis○ Procedure○ Prediction○ Evidence
- Evaluation (1, 2, 3)

Analysis

### **Problem**

What is the relationship between molecular size and melting point?

### Design

Hot and cold water baths are used to melt a solid compound and then to freeze and remelt it, with the temperature measured at regular intervals. The phase change (freezing point/melting point) temperature is found from superimposed temperature-versus-time graphs of this evidence. This is combined with evidence from other research groups for a second similar compound and with information from other references to test the Hypothesis.

To perform this investigation, turn to page 132. 🧄



## **Hydrogen Bonding**

The graph you drew for Lab Exercise 3.A makes it very evident that ammonia, water, and hydrogen fluoride have anomalously high boiling points, far higher than would be predicted from their size or polarity. Some significant attraction effect other than dipole-dipole and London forces (and stronger than either) must be acting between the molecules of these compounds.

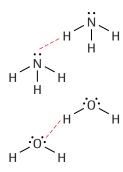
In 1920, Maurice Huggins (a graduate student of Lewis), Wendell Latimer, and Worth Rodebush devised the concept of a **hydrogen bond**, where a hydrogen nucleus (a proton) could be shared between pairs of electrons on adjacent molecules. A hydrogen bond can be thought of as a very special type of polarity that results in an unusually strong intermolecular force. For hydrogen bonding to occur, two things must be simultaneously true about a molecular structure.

- First, a hydrogen atom must be covalently bonded to another very electronegative atom, one that can pull the hydrogen's electron strongly away from the proton that is its nucleus. The proton is then said to be "unshielded," meaning that another molecule's lone pair can approach this proton much more closely than before, on the side opposite its covalent bond.
- Second, there must also be at least one lone pair of electrons on the atom bonded to the hydrogen. This sets up a condition where the lone pair on one molecule can attract the unshielded proton on the next molecule (Figure 7). The proton has a pair of electrons on one side shared in a covalent bond, and a more distant pair on the other side shared in the much weaker (intermolecular) hydrogen bond.

In practice, only three possible structures show hydrogen bonding, and one case is trivial because it only includes one possible compound: HF(g). The other two cases are extremely important, however. Any molecule with an -OH bond or an -NH bond in any part of its structure will show hydrogen bonding. That includes most of the millions of different molecules found in living things. It is important to note that hydrogen bonding is not a "bond" in the sense that a covalent bond is. For substances in liquid state, hydrogen bonds are momentary attractive forces between passing mobile molecules. Hydrogen bonds only act as continuous bonds between molecules in solids, where the molecules are moving slowly enough to be locked into position. Hydrogen force would have been a better name for this intermolecular force.

For a common example of some effects of hydrogen bonding, consider table sugar again (**Figure 8**). The formula is often written  $C_{12}H_{22}O_{11}(s)$  for brevity, but that doesn't give any hint about the structure. Suppose we now write the formula in a less condensed form, as  $C_{12}H_{14}O_3(OH)_8(s)$ , to show that this molecule has no fewer than eight –OH groups in its structure. Now the question of what causes the strong intermolecular attractions (that make this substance a crystalline solid) is easily explained: Every sucrose molecule has multiple hydrogen bonds holding it firmly to the surrounding sucrose molecules. In addition, the extreme solubility of sugar in water is explained as being due to the formation of many new hydrogen bonds to water molecules.

Additional evidence for hydrogen bonding can be obtained by looking at energy changes associated with the formation of hydrogen bonds. Chemists theorize that endothermic and exothermic reactions are explained by the difference between the energy absorbed to break bonds in the reactants and the energy released when new bonds in the products are formed. For example, in the exothermic formation of water from its elements, more energy is released in forming the new O-H bonds than was required to break the old H-H and O=O bonds. (See equations on page 105.) In a sample of glycerol, you would expect some hydrogen bonding between glycerol molecules. However, these molecules are rather bulky, and their shape limits the number of



## Figure 7

A hydrogen bond (----) occurs when a hydrogen atom bonded to a strongly electronegative atom is attracted to a lone pair of electrons in an adjacent molecule. Another way of thinking of this is that a hydrogen nucleus (proton) is simultaneously attracted to two pairs of electrons: one closer (in the same molecule) and one further away (on the next molecule).



## Figure 8

Every white-to-red part of this sucrose model represents an -OH group. Theory suggests that each of these is a site where as many as three hydrogen bonds to this molecule could form.

## Learning Tip

Don't be confused about the difference between intermolecular and intramolecular (covalent) bonds. Intermolecular bonds act between molecules, and are weaker than the covalent bonds that act within molecules (or polyatomic ions). The hydrogen nucleus in any hydrogen bond has an intramolecular (covalent) bond on one side and an intermolecular (hydrogen) bond on the other.

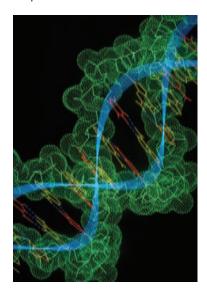


water

glycerol

### Figure 9

Water and glycerol molecules. Glycerol is commonly called glycerine; it is an ingredient in many soaps and cosmetics.



### Figure 10

According to Francis Crick, co-discoverer with James D. Watson of the DNA structure, "If you want to understand function, study structure." Hydrogen bonding (blue dashes) explains the shape and function of the DNA molecule. The interior of the double helix is cross-linked by hydrogen bonds.



## EXTENSION



## Water Transportation in Plants

Why are intermolecular forces so important to plants? Without the forces that result in water's physical properties, plants as we know them could not exist. Find out more about plants and intermolecular forces.

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possible hydrogen bonds that can form. If water is mixed with glycerol (**Figure 9**), theory suggests that additional hydrogen bonds should be possible. The small size of water molecules should allow water to form many new hydrogen bonds to each glycerol molecule. Experimentally, you find that mixing water with each glycerol is an exothermic process, indicating the formation of new bonds. The temperature increase upon mixing is evidence that verifies the prediction from theory.

The theory of hydrogen bonding is necessary to explain the functions of biologically important molecules. Proteins are chains of amino acids, and amino acids have  $-\mathrm{NH}_2$  and  $-\mathrm{COOH}$  structural groups, both of which fulfill the conditions for hydrogen bonding. Similarly, the double helix of the DNA molecule owes its unique structure largely to hydrogen bonding. The central bonds that hold the double helix together are hydrogen bonds (**Figure 10**). If the helix were held together by covalent bonds, the DNA molecule would not be able to unravel and replicate because the bonds would be too strong to break and reform (react) at body temperature.

Unlike nearly all other substances on Earth, water expands rather than contracts when it freezes. This means that the solid form (ice) is less dense than the liquid and will float. Thus, a body of water freezes from the surface down, rather than from the bottom up. When an ice layer forms on the surface, it insulates the liquid beneath, so that "frozen" lakes, rivers, and oceans remain mostly liquid—a very good thing for everything living in them! The reason ice is less dense than water has to do both with hydrogen bonding and the angular shape of water molecules (**Figure 11**). The hydrogen bonds hold water molecules in a hexagonal lattice with open space in the centre, explaining the low density. This also explains why individual snowflakes are hexagonal in structure: the hexagonal lattice repeats throughout each one.

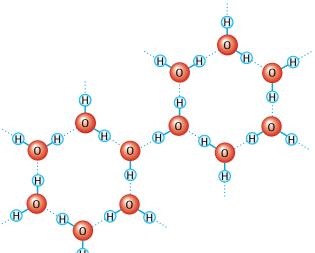




Figure 11

In ice, hydrogen bonds between the molecules result in a regular hexagonal crystal structure. The ···H— represents a hydrogen (proton) being shared unequally between two pairs of electrons.



## WWW WEB Activity

## Web Quest-Cloud Seeding

Attempting to control natural forces is a goal for many researchers because the possible benefits are tremendous. Seeding clouds, for example, uses properties of chemical bonding to change how much, where, and when precipitation will fall. Unfortunately, changing a natural system may have unforeseen consequences. This Web Quest will lead you to explore cloud seeding and its results, both expected and unexpected!

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### **INVESTIGATION 3.4 Introduction**

## Hydrogen Bonding

Breaking bonds absorbs energy, and forming bonds releases energy. Forming new bonds within a liquid should produce a temperature effect. For this investigation, write a Prediction that includes a bonding concept. Add to the design by identifying the manipulated and responding variables as well as the major controlled variable.

### **Purpose**

The purpose of this investigation is to test the concept of hydrogen bonding.

### **Report Checklist** Purpose O Design Analysis Problem Materials Evaluation (1, 2, 3) Hypothesis Procedure Prediction Evidence

### **Problem**

How does the temperature change upon mixing ethanol, C<sub>2</sub>H<sub>5</sub>OH(I), with water compare with the temperature change upon mixing glycerol (glycerin), C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>(I), with water?

### Design

Equal volumes of ethanol and water, and then of glycerol and water, are mixed. The change in temperature is recorded in each case.

To perform this investigation, turn to page 134.



## **Physical Properties of Liquids**

Liquids have a variety of physical properties that can be explained by intermolecular forces. As you have seen, comparing boiling points provides a relatively simple comparison of intermolecular forces in liquids, if we assume that the gases produced have essentially no intermolecular forces between their molecules. What about some other properties of liquids, such as surface tension, shape of a meniscus, volatility, and capillary action? Surface tension is pretty important for water insects (Figure 12). The surface tension on a liquid seems to act like an elastic skin. Molecules within a liquid are attracted by other molecules in all directions equally, but molecules right at the surface are only attracted downward and sideways (Figure 13). This means that the surface tends to stay intact. Consistent with this theory, substances containing molecules with stronger intermolecular forces have higher surface tensions. Water is a good example—it has one of the highest surface tensions of all liquids.

The shape of the meniscus of a liquid and capillary action in a narrow tube are both thought to be due to intermolecular forces. In both cases, two intermolecular attractions need to be considered—attraction between like molecules (called cohesion) and attraction between unlike molecules (called adhesion). Both cohesion and adhesion are intermolecular attractions. For example, compare water and mercury, two very different liquids: water rises in a narrow tube, but mercury does not (Figure 14). The adhesion between the water and the glass is thought to be greater than the cohesion between the water molecules. In a sense, the water is pulled up the tube by the intermolecular forces between the water molecules and the glass.

Another property connected to intermolecular forces is the volatility of a liquid, that is, how rapidly it tends to evaporate. Gasoline is a mix of nonpolar hydrocarbon liquids that evaporate very readily because their intermolecular attractions are not very strong. For gasoline, high volatility is a necessary property; it has to vaporize almost instantly when injected into the cylinder of a car engine. Liquids that are both volatile and flammable are always dangerous because the mix of their vapour with air can be explosive.



Figure 12

The weight of the water strider is not enough to overcome the intermolecular forces between the water molecules. This would be like you walking on a trampoline. The fabric of the trampoline is strong enough to support your weight.

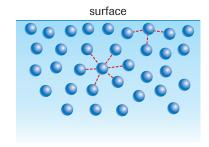


Figure 13

The model suggests that the intermolecular forces on a molecule inside a liquid are relatively balanced. The forces on a molecule right at the surface are not balanced; the net pull is downward, creating surface tension.

### Figure 14

Capillary action is the movement of a liquid up a narrow tube. For water, capillary action is very noticeable; for mercury, it is insignificant. (The water is coloured red with dye to make it more visible.)

## **BIOLOGY CONNECTION**

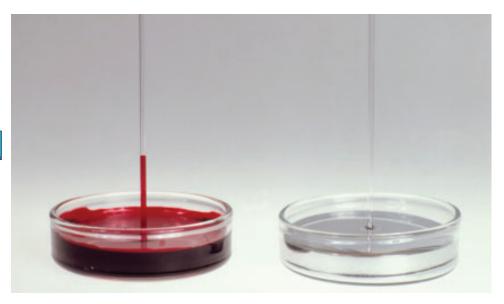


## **Water-Dependent Processes**

Water plays a vital role in many biological and geological cycles. If you are studying biology, you will find out about many processes that depend on the chemical and physical properties of water.

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## Case Study

# Current Research in Intermolecular Forces

In almost any area of science today, experimental work runs parallel to the theoretical work, and there is constant interplay between the two areas. In Canada, there are several theorists whose research teams examine the forces between atoms and molecules, to increase our understanding of the properties of substances. One such individual is Dr. Robert J. Le Roy (**Figure 15**), currently working in theoretical chemical physics at the University of Waterloo, in Ontario.



### Figure 15

Dr. Robert J. Le Roy and his research team study intermolecular forces and the behaviour of small molecules and molecular clusters; develop methods to simulate and analyze the decomposition of small molecules; and create computer models to simulate and predict molecular properties.

Dr. Le Roy's field of interest is intermolecular forces. He uses quantum mechanics and computer modelling to define and analyze the basic forces between atoms and molecules. Early in his career, Dr. Le Roy developed a criterion for defining a radius for a small molecule, now known as the Le Roy radius. This defines a theoretical boundary around the molecule. For atomic separations inside this boundary, chemical bonding and electron exchange between atoms are most important;

outside this boundary, the classical "physical" interactions between charge distributions predominate. In his work, the study of atomic and molecular spectra (called spectroscopy) plays a crucial role. Measurements from spectroscopy help theoreticians develop better models and theories for explaining molecular structure. Computer programs that Dr. Le Roy developed for converting experimental data information on intermolecular forces, shape, and structure (and vice versa) are freely available on his Web site, and are widely used in laboratories around the world.

It is important not to assume that theories of molecular forces and structures are well established. Our knowledge of bonding and structure becomes scantier and more unreliable for larger molecular structures. A huge amount of research remains to be done if we are ever to be able to describe bonding and structure very accurately for complex substances. As Dr. Le Roy states on his Web site, "... except for the simplest systems, our knowledge of (interactions between molecules) is fairly primitive." The classic example is our poor understanding of the forms and activity of proteins—the stuff of life. Proteins are extremely large molecules with highly complex shapes. We know the atomic composition of many proteins quite precisely, but protein reactions depend largely on how bonding has folded and shaped the protein's structure. How a protein behaves depends on its precise bonding, structure, and shape, which is something scientists describe with the common scientific phrase "not well understood."

Living things build proteins in multi-step chemical reactions that bond together long chains of small molecules called amino acids. There are about 25 different amino acids that make up human proteins, of which only about half are synthesized in the body. One fascinating thing about bonding between amino acids is that almost all of them are chiral. This means they can exist in two different structures that are identical, except that the two forms are mirror images of each

other, like your hands. In fact, such molecules are often called left- or right-handed to identify which form is being discussed. Understanding how this difference in form can affect intermolecular forces is critical, because in living things only one form of such a molecule will "work" in a given chemical reaction. For example, all the amino acids in the human body are "left-handed," and all the simple sugars (such as glucose) are "right-handed" (Figure 16). Only left-handed amino acids can bond together to build proteins, and only right-handed sugars can be digested for energy. The two forms of any chiral substance will rotate beams of polarized light in opposite directions, so polarized light microscopes can be useful for determining molecular and crystal structures (see Figure 2 in Section 3.1, page 78).

Current research in this area is being done by Dr. Yunjie Xu, working in the Chemistry Department of the University of Alberta (Figure 17). She is studying the precise mechanisms, at a molecular level, that enable one molecule to accept or reject bonding to another molecule, based on its specific chiral structure. This requires learning exactly where on the molecules various intermolecular forces come into play and how a molecule's orientation in space plays a part in this process. Dr. Xu uses very sophisticated equipment and techniques to work at the molecular level.

### **Case Study Questions**

- 1. Explain briefly what the Le Roy radius of a molecule represents, and discuss how it might be useful to someone studying interactions between small molecules.
- 2. The simplest (smallest) amino acid in your body is glycine, H<sub>2</sub>NCH<sub>2</sub>COOH. Draw a structural formula for this molecule. Discuss the probable solubility of glycine in terms of intermolecular bonding.

### **Extension**

3. The smallest chiral amino acid is alanine, H<sub>2</sub>NCHCH<sub>3</sub>COOH. It may be thought of as a glycine where one of the hydrogens attached to the central carbon has been replaced by a carbon (which also has three hydrogens attached to it; a -CH<sub>3</sub> group). Draw its structural formula, and note that the central carbon has



## Figure 16

This computer-generated model of a glucose molecule is shown in its "right-handed" form, as produced by living plants. An old name for this simple sugar was dextrose, from the Latin word for right. A left-handed form of glucose can be produced in a laboratory but is not found naturally in life on Earth.



Figure 17

Dr. Xu and her research team study intermolecular forces between different forms (isomers) of molecules to better understand how only specific molecules are selected for reaction by living things, and to develop systems to better identify such molecules in chemical samples.

four different things attached to it. Any such molecule is chiral, including all the other amino acids. To examine this feature, you can use any molecular model kit that shows 3-D (tetrahedral) bonding to carbon. Make two exact copies of a model by attaching four spheres (all of different colours) to a central sphere representing carbon. Then, on one model, switch any two of the coloured spheres attached to the central carbon. You now have models representing a chiral substance. All the covalent bonds are identical and the molecular formulas are exactly the same, but the orientation in space is different. Draw stereochemical formulas for your models to show more clearly what this difference is. To better appreciate why this might be important to the way molecules fit together, just try to put your left glove on your right hand.

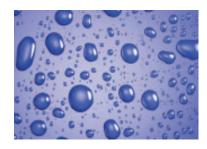
## mini *Investigation*

## **Floating Pins**

Materials: beaker or glass, water, several other different liquids, dishwashing detergent, straight pin, tweezers, toothpick

- Make sure the straight pin is clean and dry.
- Using clean tweezers, carefully place the pin in a horizontal position on the surface of each liquid, one at a time. Wash and dry the pin between tests.
- (a) What happens for each liquid? Why?

- Using tweezers, carefully place the pin vertically into the surface of the water. Try both ends of the pin.
- What happens this time? Why do you think the result is different than before?
- Place the pin horizontally onto the surface of water. Using a toothpick, add a small quantity of dish detergent to the water surface away from the pin.
- (c) Describe and explain what happens.



### Figure 18

Modern spray "protectants" have molecules that join together (polymerize) as the liquid dries to form a super thin layer that bonds very strongly to the surface. The "beading" you see is explained by differences in the attraction of water molecules for each other and the attraction of water molecules of the surface protectant layer.



**Figure 19** A lava lamp



Figure 20 Setup for question 13

## Practice

- **7.** For each of the following compounds, evidence indicates that hydrogen bonds contribute to the attraction between molecules. Draw a Lewis formula using a dashed line to represent any hydrogen bond between two molecules of the substance.
  - (a) hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>(I) (disinfectant)
  - (b) hydrogen fluoride, HF(l) (aqueous solution etches glass)
  - (c) methanol, CH<sub>3</sub>OH(l) (wood alcohol)
  - (d) ammonia, NH<sub>3</sub>(l) (anhydrous ammonia for fertilizer)
- 8. (a) Refer to or construct a graph of the evidence from Lab Exercise 3.A. Extrapolate the Group 15 and 16 lines to estimate the boiling points of water and ammonia if they followed the trend of the rest of their family members.
  - (b) Approximately how many degrees higher are the actual boiling points for water and ammonia compared to your estimate in (a)?
  - (c) Explain why the actual boiling points are significantly higher for both water and ammonia.
  - (d) Propose an explanation why the difference from (b) is much greater for water than for ammonia.
- Water beads on the surface of a freshly waxed car hood. Use your knowledge of intermolecular forces to explain "beading" (Figure 18).
- **10.** A lava lamp is a mixture of two liquids with a light bulb at the bottom to provide heat and light (**Figure 19**). What interpretations can you make about the liquids, intermolecular forces, and the operation of the lamp?
- **11.** To gather evidence for the existence of hydrogen bonding in a series of chemicals, what variables must be controlled?
- **12.** (a) Design an experiment to determine the volatility (rate of evaporation) of several liquids. Be sure to include a list of variables.
  - (b) Suggest some liquids to be used in this experiment. Predict the results. Provide your reasoning.
  - (c) What safety precautions should be taken with volatile liquids?
- 13. Theories are valued by their ability to describe, explain, and predict. Intermolecular bond theory may be tested by investigating the solubility of substances in the laboratory. Complete the Prediction, Analysis, and Evaluation of this investigation report. Evaluate the Prediction as well as the reasoning used to make the Prediction.

### **Purpose**

The purpose of this investigation is to test the ability of intermolecular bond theory to predict.

### **Problem**

Does ammonia gas have high or low solubility in water?

### Design

A Florence flask full of ammonia is inverted above a beaker of coloured water. The ammonia flask has a medicine dropper of water inserted through one hole of its rubber stopper. A glass tube through the other hole in the stopper connects the flask to coloured water in the beaker below. The medicine dropper is squeezed to add a small amount of water to the ammonia gas in the flask.

### **Evidence**

The coloured water in the beaker is drawn up the tube and sprays into the flask like a fountain (**Figure 20**); this flow continues until the beaker is completely emptied.

14. Natural substances were used for their adhesive and cohesive properties long before scientific knowledge allowed us to synthesize glues and sealants. Aboriginal peoples of North America used spruce and pine tree secretions for a wide variety of purposes, including the "leakproofing" of birchbark canoes. Does this application illustrate adhesion, cohesion, or both? Explain your answer in terms of intermolecular forces.

# **SUMMARY**

## Intermolecular Forces

- Intermolecular forces, like all forces involving atoms, are electrostatic—they involve the attraction of positive and negative charges.
- All molecules attract each other through the London force, the simultaneous attraction of momentary dipoles in adjacent molecules.
- Dipole—dipole force exists between polar molecules, the simultaneous attraction of permanent dipoles in adjacent molecules.
- Hydrogen bonding exists when hydrogen atoms are bonded to the highly electronegative atoms N, O, and F—the proton is simultaneously attracted to a lone pair of electrons on the N, O, or F atom of an adjacent molecule.
- Intermolecular forces affect many physical properties, for example, the melting point, boiling point, capillary action, surface tension, volatility, and solubility of substances.





## Simulation—Modelling Molecules

Many computer programs that model a wide variety of molecular shapes (and other features) are available on the Internet. Examine the programs on the links provided to see how well the models correspond to the kinds of predictions you have been making in this chapter. You can explore VSEPR and Lewis theory and examine molecular structures and shapes that are not predictable within the scope of this chapter.

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## Section 3.4 Questions

- 1. All molecular compounds may have London, dipole-dipole, and hydrogen-bonding intermolecular forces affecting their physical and chemical properties. Using the rules and definitions for intermolecular forces and Table 8 (page 99), indicate which intermolecular forces contribute to the attraction between molecules in each of the following classes of organic compounds (many of which are described in detail in Chapter 10). It should not be necessary to draw Lewis formulas. Look carefully at the sequence of atoms in the molecular formula.
  - (a) hydrocarbon; e.g., pentane,  $C_5H_{12}(I)$  (in gasoline)
  - (b) alcohol; e.g., propan-2-ol, CH<sub>3</sub>CHOHCH<sub>3</sub>(l) (rubbing alcohol)
  - (c) ether; e.g., dimethylether, CH<sub>3</sub>OCH<sub>3</sub>(g) (polymerization catalyst)
  - (d) carboxylic acid; e.g., acetic acid, CH<sub>3</sub>COOH(l) (in
  - (e) ester; e.g., ethylbenzoate, C<sub>6</sub>H<sub>5</sub>COOC<sub>2</sub>H<sub>5</sub>(I) (cherry flavour)
  - (f) amine; e.g., dimethylamine, CH<sub>3</sub>NHCH<sub>3</sub>(g) (depilatory agent)
  - (g) amide; e.g., ethanamide, CH<sub>2</sub>CONH<sub>2</sub>(s) (lacquers)
  - (h) aldehyde; e.g., methanal, HCHO(g) (corrosion inhibitor)
  - (i) ketone; e.g., acetone, (CH<sub>3</sub>)<sub>2</sub>CO(l) (varnish solvent)

- 2. Use structural formulas and hydrogen bonding theory to explain the very high solubility of methanol, CH<sub>3</sub>OH(I), in
- 3. Predict the solubility of the following organic compounds in water as low (negligible), medium, or high. Provide your reasoning.
  - (a) 2-chloropropane, C<sub>2</sub>H<sub>7</sub>Cl(l) (solvent)
  - (b) propan-1-ol, C<sub>2</sub>H<sub>7</sub>OH(l) (brake fluids)
  - (c) propanone, (CH<sub>3</sub>)<sub>2</sub>CO(l) (cleaning precision equipment)
  - (d) propane, C<sub>3</sub>H<sub>8</sub>(g) (gas barbecue fuel)
- 4. For each of the following pairs of chemicals, which one is predicted to have the stronger intermolecular attraction? Provide your reasoning.
  - (a) chlorine or bromine
  - (b) fluorine or hydrogen chloride
  - (c) methane or ammonia
  - (d) water or hydrogen sulfide
  - (e) silicon tetrahydride or methane
  - (f) chloromethane, CH<sub>3</sub>Cl(g), or ethanol
- **5.** Which liquid, propane  $(C_3H_8)$  or ethanol  $(C_2H_5OH)$ , would have the greater surface tension? Justify your answer.

- 6. In cold climates, outside water pipes, such as those used in underground sprinkler systems, need to have the water removed before it freezes. What might happen if water freezes in the pipes? Explain your answer.
- 7. A glass can be filled slightly above the brim with water without the water running down the outside. Explain why the water does not overflow even though some of it is above the glass rim.
- **8.** Design an experiment to determine whether hydrogen bonding has an effect on the surface tension of a liquid. Clearly indicate the variables in this experiment.
- 9. Critique the following experimental design: The relative strength of intermolecular forces in a variety of liquids is determined by measuring the height to which the liquids rise in a variety of capillary tubes.
- 10. A student is intent upon finding a way to reduce the effect of "hot" spices in spicy food. The student finds that water does not help alleviate the effect of spices but sour cream does. Use your knowledge of chemistry to explain this finding.
- 11. Volatile organic compounds (VOCs) are compounds that vaporize and are distributed in Earth's atmosphere. VOCs can increase smog formation in the lower atmosphere and promote global warming in the upper atmosphere. Predict the order of the following compounds in terms of decreasing volatility. Provide your reasoning.
  - · hexane, C<sub>6</sub>H<sub>14</sub>
  - hexan-1-ol C<sub>6</sub>H<sub>13</sub>OH
  - 1-chlorohexane, C<sub>6</sub>H<sub>13</sub>Cl

[Note: The "1" in the names tells you that the OH and the Cl are bonded to the end of a carbon chain.]

- **12.** (a) Draw a bar graph with temperature on the vertical axis and the three isoelectronic compounds listed below on the horizontal axis. Mark the temperature scale from absolute zero, -273 °C (the lowest temperature possible) to +100 °C. For each compound, draw a vertical bar from absolute zero to its boiling point: propane,  $CH_3CH_2CH_3(g)$  (-42 °C); fluoroethane,  $CH_3CH_2F(g)$  (-38 °C); and ethanol,  $CH_3CH_2OH(l)$  (78 °C).
  - (b) Divide each of the three bar graphs into the approximate component for the intermolecular force involved. (Assume that the London force is the same for each chemical and that the dipole—dipole force is the same for the two polar molecules.)
  - (c) Based upon the proportional components for the three possible intermolecular forces, infer the relative strength of these forces.
- 13. In the far North, groundwater is permanently in the solid state (called permafrost), because the ground does not warm enough in the short, cool summers for this water to thaw. In some areas of Siberia, the permafrost layer is over a kilometre deep! In northern Canadian communities, warm

structures such as heated buildings, sewer systems, and oil pipelines must be built over the permafrost. The unique intermolecular bonding of water creates a huge problem if the permafrost melts under a building. State which physical property of water (other than its physical state) changes significantly when it thaws, and explain how this change causes the problem depicted in **Figure 21**.



### Figure 21

These two buildings, in Dawson City, Yukon, have been nick-named the "kissing buildings"; they date back to the Gold Rush era.

### Extension

- **14.** Some vitamins are water soluble (e.g., B series and C), while others are fat soluble (e.g., vitamins A, D, E, and K).
  - (a) What can you infer about the polarity of these chemicals?
  - (b) Find and draw the structure of at least one of the water-soluble and one of the fat-soluble vitamins.
  - (c) When taking vitamins naturally or as supplements, what dietary requirements are necessary to make sure that the vitamins are used by the body?
  - (d) More of a vitamin is not necessarily better. Explain why you can take a fairly large quantity of vitamin C with no harm (other than the cost), but an excess of vitamin E can be dangerous.

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15. Plastic cling wrap is widely used in North America. Why does it cling well to smooth glass and ceramics but not to metals? Describe the controversial social issue associated with the use of this plastic wrap. How are intermolecular forces involved in starting the process that leads to this controversy?

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## Structures and Physical **Properties of Solids**

All solids, including elements and compounds, have a definite shape and volume, are virtually incompressible, and do not flow readily. However, research shows that there are many specific properties, such as hardness, melting point, mechanical characteristics, and conductivity, that vary considerably between different solids. For example, if you hit a piece of copper with a hammer, you can easily change its shape. If you do the same thing to a lump of sulfur, you crush it. A block of paraffin wax when hit with a hammer will deform and may break (Figure 1). Why do these solids behave differently?

The way solids break is called fracture, a term familiar to anyone who has ever broken a bone. Glass is a special case, because it has a special kind of bonding (discussed in detail later in this section). Glass has conchoidal fracture; this means it breaks along a curve. Wherever two fracture curves meet, the edge is extremely sharp. The natural minerals obsidian (volcanic glass), flint, and chert all have a bonding structure like that of glass; that is, they break with conchoidal fracture. Aboriginal cultures depended on this property for thousands of years. A piece of flint can be chipped carefully to produce a stone knife (or spearhead or arrowhead) that is much superior to any point or edge that can be made on a wooden object. An entire historic period based on this technique is called the Stone Age. Archaeologists believe Aboriginal peoples moved into North America as the last Ice Age retreated. Much of the evidence for this belief comes from the spread throughout the continent of what are called Clovis points (Figure 2). A testimony to the efficiency of hunters using such spearheads may be the extinction of large mammals like the mammoth and the short-faced bear at about this time. Later techniques allowed small sharp points to be made that could be used to tip small throwing spears and arrows, creating even more formidable weapons.

By observing properties of chemical substances, we were able to classify them empirically (Table 1). To now explain the properties of each category, we use our knowledge of chemical bonding. In both elements and compounds, the structure and properties of the solid are related to the forces between the particles. Although all forces are electrostatic in nature, they vary in strength.

Table 1 Classifying Solids

Class of substance	Elements combined	Examples
ionic	metal + nonmetal	NaCl(s), CaCO <sub>3</sub> (s)
metallic	metal(s)	Cu(s), CuZn <sub>3</sub> (s)
molecular	nonmetal(s)	I <sub>2</sub> (s), H <sub>2</sub> O(s), CO <sub>2</sub> (s)
covalent network	semi-metals/nonmetals	C(s), SiC(s), SiO <sub>2</sub> (s)

## **Ionic Crystals**

Ionic compounds are abundant in nature. Soluble ionic compounds are present in both fresh water and salt water. Ionic compounds with low solubility make up most rocks and minerals. Relatively pure deposits of sodium chloride (table salt) occur in Alberta, and Saskatchewan has the world's largest deposits of potassium chloride (potash fertilizer) and sodium sulfate (used for manufacturing paper).

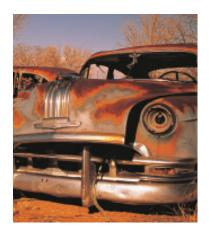
You can also find ionic compounds at home. Iodized table salt consists of sodium chloride with a little potassium iodide added. Antacids contain a variety of compounds, such as magnesium hydroxide and calcium carbonate. Many home cleaning products



Figure 1 Different solids-copper, sulfur, and paraffin wax-behave very differently under mechanical stress.



Figure 2 Clovis points very similar to these are found in hundreds of archaeological sites throughout North America, dating back well over 10 000 years. Considerable skill is required to chip a stone point this way; even experts break more than they finish. Consequently, to the delight of later archaeologists, Aboriginal point makers always left behind many fragments and substandard points. "Clovis" is from the name of the town in New Mexico near the site where these points were first found.



**Figure 3**Rusting is a common and expensive problem.

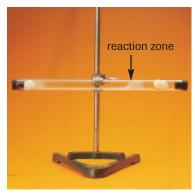


Figure 4

The solid ionic compound ammonium chloride forms from the reaction of ammonia and hydrogen chloride gases when small quantities of concentrated solutions are placed into the ends of a tube such as this.

### Learning Tip

Some confusion may arise from use of the word "particle" in a chemistry textbook. In general use, it often means a tiny bit of a solid, as when we refer to the "smoke" particles of NH<sub>4</sub>Cl(s) that are forming in **Figure 4**. In bonding theory, it more often refers to subatomic particles, such as electrons and protons, and is usually used to distinguish these from chemical entities (molecules, atoms, or ions).

contain sodium hydroxide. Other examples of ionic compounds are the rust (iron(III) hydroxide) that forms on the steel bodies of cars and the tarnish (silver sulfide) that forms on silver. Ionic compounds have low chemical reactivity compared with the elements from which they are formed. Some ionic compounds, such as lime (calcium oxide) and the mineral sylvite (potassium chloride), are so stable that they were classified as elements until the early 1800s. (At that time, elements were defined as pure substances that could not be decomposed by strong heating.)

Reactive metals, such as sodium, magnesium, and calcium, are not found as elements in nature but occur instead in ionic compounds. The least active metals, such as silver, gold, platinum, and mercury, do not react readily to form compounds and may, therefore, be found uncombined in nature.

For thousands of years, metallurgists have used ionic compounds to extract metals from naturally occurring compounds. In these processes, an ionic compound such as hematite ( $Fe_2O_3$ ) in iron ore is reduced to a pure metal, which can then be used to make tools, weapons, and machines. Iron, the main constituent of steel, is the most widely used metal. Unfortunately, iron is reactive and readily corrodes, or reacts with substances in the environment, re-forming to an ionic compound (**Figure 3**). A lot of time and money is spent trying to prevent or slow the corrosion of iron and other metals, for example, by having cars rust-proofed at automotive centres.

## **Formation of Ionic Compounds**

Chemical research shows that ionic compounds are formed in many ways. Binary ionic compounds are the simplest ionic compounds; they may be formed by the reaction of a metal with a nonmetal. For example:

$$2 \text{ Na(s)} + \text{Cl}_2(g) \rightarrow 2 \text{ NaCl(s)}$$

The reaction of ammonia and hydrogen chloride gases produces the ionic compound ammonium chloride, which appears as a white smoke of tiny solid particles (**Figure 4**):

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

The conductivity of molten ionic compounds and aqueous solutions of soluble ionic compounds suggests that charged entities are present. According to atomic theory, the stability of ionic compounds suggests that their electronic structure is similar to that of the noble gases, which have filled energy levels. By tying in these concepts with the collision–reaction theory, scientists explain the formation of an ionic compound as involving collisions between metal and nonmetal atoms that result in a transfer of electrons; the transfer of electrons forms cations and anions that have filled valence energy levels. Scientists believe that the electron transfer is encouraged by the large difference in electronegativity between metal and nonmetal atoms. Lewis formulas represent these concepts. For example, a theoretical description of the formation of sodium fluoride shows how a stable octet structure is formed:

$$Na^{\cdot} + \cdot \ddot{F}^{\cdot} \rightarrow Na^{+}[\ddot{F}^{\cdot}]^{-}$$

Sodium fluoride is added to many toothpastes; research shows that it acts to harden enamel in teeth, so that cavities are less likely to form.

## A Model for Ionic Compounds

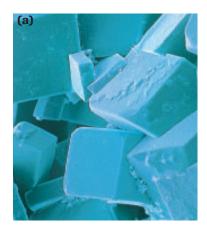
To be acceptable, a theory of bonding must be able to explain the properties of ionic compounds. All ionic compounds are solids at SATP, so the ions must be held together or bonded strongly in a rigid structure. In the model for ionic compounds, ions are

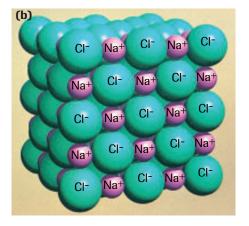
shown as spheres arranged in a regular pattern. Depending on the sizes, shapes, and charges of the ions, different arrangements are possible, but whatever the pattern, it will allow the greatest number of oppositely charged ions to approach each other closely while preventing the close approach of ions with the same charge. In all cases, the model describes any ion as being surrounded by ions of opposite charge. This creates strong attractions and explains why ionic compounds are always solids with high melting and boiling points. The arrangement of ions for a given compound is called its crystal lattice. The model also explains why ionic compounds are brittle—the ions cannot be rearranged without breaking the ordered structure of the crystal lattice apart.

Chemists represent ionic crystals with models, such as the diagram of sodium chloride in Figure 5(b). The diagram shows each ion surrounded by six ions of opposite charge, held firmly within the crystal by strong electrostatic attractions. The observable cubic shape of sodium chloride crystals supports this model. All binary ionic compounds have brittle crystalline forms and medium to high melting and boiling points. These properties vary greatly in degree, however, depending on the nature of the ions forming the compound. Binary ionic compounds have the simplest structures. They are often quite hard solids with very high melting points. Sodium chloride, for example, melts at 800 °C. If you fracture a crystal of salt, it will break along surfaces at 90° to each other, called cubic fracture. These fracture planes follow layers of ions in the crystal lattice.

We have only examined binary ionic compounds here. However, there are also many ionic compounds of polyatomic ions, such as sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>(s). Chemists explain that these compounds have covalent bonds within each polyatomic ion. The bonds hold the polyatomic ion together as a group and cause the whole group to act much like a monatomic ion. Crystal lattices for such ionic compounds are more complex, and the ranges of hardnesses and melting and boiling points vary much more widely. Some of these compounds will decompose before they get hot enough to melt. The theoretical explanation is that the covalent bonds in the polyatomic ions begin to break before the ionic bonding forces in the crystal are overcome.

According to laboratory evidence and the ion model, ion attractions are nondirectional—all positive ions attract all nearby negative ions. There are no distinct neutral molecules in ionic compounds. The chemical formula shows only a formula unit (empirical formula) expressing the simplest whole-number ratio of ions. For example, any crystal of sodium chloride, NaCl(s), contains equal numbers of sodium ions and



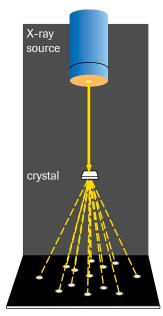


From a cubic crystal of table salt (a) and from X-ray analysis, scientists infer the 3-D arrangement for sodium chloride (b). In this cubic crystal, each ion is surrounded by six ions of opposite charge. The sodium and chloride ions are shown to the correct relative scale in this model.

## DID YOU KNOW F

## X-Rays and 3-D Models

Three-dimensional models of crystals are determined experimentally by X-ray diffraction (Figure 6). When a beam of X-rays is reflected from the top layers of an ionic crystal, a regular pattern is obtained. The wavelength of the X-rays determines the way they are reflected from the spaces between ions. (This is similar to the way in which the wavelength of light determines how it is reflected from the grooves on the surface of a compact disc.) Scientists can use the pattern of either reflected or transmitted X-rays and their knowledge of the wavelength to infer the arrangement, size, and separation of the ions.



photographic plate

Figure 6 Diagram of X-ray diffraction apparatus

chloride ions, and any crystal of calcium fluoride,  $CaF_2(s)$ , contains one calcium ion for every two fluoride ions. Any ionic crystal is explained as being all one structure. You don't know how many positive or negative ions it might contain, but you know exactly how their numbers compare. Logically, ions must always collect to form a crystal lattice in a such way that the total charge balances to zero. In reading chemical formulas, it is very important to remember two things: First, ionic compound formulas do not represent molecules. Second, ion charges are never shown, so they must be referenced or memorized.

## mini Investigation

## **Building an Ionic Crystal Model**

The crystal lattice arrangement for an ionic substance can be quite complex, depending on the sizes, shapes, and charges of the cations and anions that make up the compound. It can get even more complicated when (highly polar) water molecules make up part of the lattice, as happens in hydrated ionic compounds like  $\text{CuSO}_4 \cdot \text{5H}_2\text{O}(\text{s})$ . Interestingly, only about nine common crystal shapes result from all these possible combinations. Of these, the most familiar is the cubic structure seen in common table salt, NaCl(s), which is fairly easy to model.

**Materials:** 18 large Styrofoam spheres, 18 small Styrofoam spheres (half the diameter of the large spheres), toothpicks

- Assemble two separate three-by-three ion layers for the
  lattice by attaching spheres to each other using toothpicks.
  Use large spheres for the chloride ions, and small spheres
  for the sodium ions. Place the chloride ions at the corners
  and centre of each of the two layers. Spheres representing
  oppositely charged ions should be as close as possible, and
  spheres representing like charged ions should not touch
  each other.
- Assemble two more ion layers, but place the sodium ions at the corners.

- Stack the layers alternately, noting how they fit together.
- (a) In the assembled lattice, what are the nearest ions to each chloride? How many of these ions are near any chloride ion that is located completely inside the crystal lattice?
- (b) In the assembled lattice, what are the nearest ions to each sodium? How many of these ions are near any sodium ion that is completely inside the crystal lattice?

The formula for a crystal of sodium chloride could be written as  $Na^+_nCl^-_n$ .

- (c) Why are the ion charges not written in the chemical formula for an ionic compound?
- (d) What number does *n* represent in the above formula?
- (e) Why is this numbering symbolism not normally used?
- (f) What, precisely, do the subscript numbers in an ionic compound formula refer to?
- (g) Observe other models constructed by other groups in your class. Consider and discuss their ion spacing and structural differences and similarities. What theoretical arrangement maximizes attractions of unlike charges and minimizes repulsions of like charges to produce a maximum net attraction?

## Practice

- 1. Draw Lewis formulas for each of the following ions. In each case, begin by first adjusting the number of valence electrons of the central atom to account for the ion charge. Bracket the final formula, and show the net ion charge outside the brackets.
  - (a) CN<sup>-</sup>
- (d) NH<sub>4</sub><sup>+</sup>
- (b) Se<sup>2-</sup>
- (e)  $SO_4^2$
- (c) OH<sup>-</sup>
- (f) Mg<sup>2+</sup>
- **2.** Hydrogen chloride and ammonia gases are mixed in a flask to form a white solid product.
  - (a) Write a balanced chemical equation for the reaction of ammonia and hydrogen chloride gases to form ammonium chloride.
  - (b) Rewrite the equation using Lewis formulas.
- 3. Where are ionic compounds abundant in nature?
- Write a brief explanation for the formation of a binary ionic compound from its constituent elements.
- 5. What evidence suggests that ionic bonds are strong?

- 6. Potassium chloride is a substitute for table salt for people who need to reduce their intake of sodium ions. Use Lewis formulas to represent the formation of potassium chloride from its elements. Show the electronegativities of the reactant atoms.
- 7. Use Lewis formulas to represent the reaction of calcium and oxygen atoms. Name the ionic product.
- 8. The empirically determined chemical formula for magnesium chloride is MgCl<sub>2</sub>. Create Lewis formulas to explain the empirical formula of magnesium chloride.
- 9. Create Lewis formulas to predict the chemical formula of the product of the reaction of aluminium and oxygen.
- 10. Based only on differences in electronegativity, what compound would you expect to be the most strongly ionic of all binary compounds?
- 11. What is the difference between the information communicated by the empirical formula of an ionic compound such as NaCl and the molecular formula of a substance such as H<sub>2</sub>O?

## **Metallic Crystals**

Metals are shiny, silvery, flexible solids with good electrical and thermal conductivity. The hardness varies from soft to hard (e.g., lead to chromium) and the melting points from low to high (e.g., mercury at -39 °C to tungsten at 3410 °C). Further evidence from the analysis of X-ray diffraction patterns shows that all metals have a continuous and very compact crystalline structure (Figure 7). With few exceptions, all metals have closely packed structures.



The crystal structure of metals normally can be seen only under a microscope. On the surface of zinc-plated (galvanized) objects, however, large flat crystals of zinc are plainly visible.



WWW WEB Activity

## Canadian Achievers-Jillian Buriak

Jillian Buriak is a chemistry professor at the University of Alberta and a senior research officer at the NRC's National Institute for Nanotechnology (Figure 8). Dr. Buriak is a leading expert in semiconductor surface chemistry, and she leads a team in basic research essential to developing new technologies such as microelectronics, nano-electromechanical systems, sensors and diagnostics which communicate directly with cells, viruses, and bacteria, and a host of other applications.

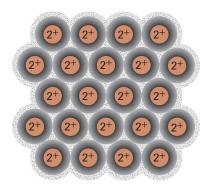
- What is nanotechnology? 1.
- 2. What major award did Buriak win in 2005?
- List five recent projects of Buriak's research group.

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Figure 8 Dr. Jillian Buriak



### Figure 9

This model of bonding in copper shows a continuous (grey) area occupied by mobile valence electrons, attracting all the positive metal ions at once, to hold them together in a regular structure with a net (overall) charge of zero.

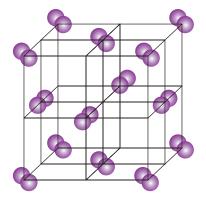


Figure 10
A model of an iodine crystal based on X-ray analysis shows a regular arrangement of iodine molecules.

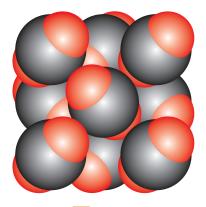


Figure 11 Solid carbon dioxide, or dry ice, also has a crystal structure containing individual carbon dioxide molecules.

An acceptable theory for bonding in metals must describe and explain characteristic metallic properties, provide testable predictions, and be as simple as possible. According to current theory, the properties of metals are the result of metallic bonding. Recall from Section 3.1 that with metallic bonding, the valence electrons are not held strongly by their atoms, so they can easily become mobile. This attraction is not localized or directed between specific entities, as occurs with ionic crystals. Instead, the electrons act like a negative "glue" surrounding the positive metal ions, acting to hold them firmly together. As illustrated in **Figure 9**, valence electrons are believed to occupy the spaces between the positive metal ions. This model incorporates the ideas of

- · low electronegativity of metal atoms to explain loosely held electrons
- · empty valence orbitals to explain electron mobility
- electrostatic attractions of positive ions and the negatively charged mobile valence electrons to explain the strong, nondirectional bonding

The model is used to explain the empirical properties of metals (**Table 2**).

**Table 2** Explaining the Properties of Metals

Property	Explanation
shiny, silvery	valence electrons absorb and re-emit the energy from all wavelengths of visible and near-visible light
flexible	nondirectional bonds mean that the planes of ions can slide over each other while remaining bonded
electrical conductivity	valence electrons can freely move throughout the metal
crystalline	electrons provide the "electrostatic glue" holding the metal ions together producing structures that are continuous and closely packed

The next time you have a rice crisp square, look at it carefully and play with it. The marshmallow is the glue that binds the rice crisps together. If you push on the square, you can easily deform it, without breaking it. The marshmallow acts like the valence electrons in a metal; the crisps represent the metal cations. The mechanical properties are somewhat similar to those of a metal.

## **Molecular Crystals**

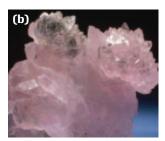
Molecular solids can be elements such as iodine and sulfur, or compounds such as ice and carbon dioxide. Substances with small molecules form solid crystals that have relatively low melting points, are not very hard, and are nonconductors of electricity in their pure form as well as in solution. From X-ray analysis, chemists find that these crystals have molecules arranged in a regular lattice (**Figure 10**). In general, the molecules are packed as close together as their size and shape allow (**Figure 11**).

The properties of molecular crystals can be explained by their structure and the intermolecular forces that hold them together. Chemists understand that London, dipole—dipole, and hydrogen bonding forces are not very strong compared with ionic and covalent bonds. This would explain why molecular crystals have relatively low melting points and a general lack of hardness. Because individual entities are neutral molecules, they cannot conduct an electric current even when the molecules are free to move in the liquid state.

## **Covalent Network Crystals**

Two commonly recognized crystal substances (because they are used in jewellery) are diamond and quartz (Figure 12). These substances are among the hardest materials on Earth and belong to a group known as covalent network crystals. Experiments show that such substances are very hard and brittle, have very high melting points, are insoluble, and are nonconductors of electricity. Covalent network crystals are usually much harder and have much higher melting points than ionic and molecular crystals. They are described as brittle because they do not bend under pressure, but they are so hard they seldom break. One example is silicon carbide (carborundum), SiC(s), used for sandpaper and for grinding stones to sharpen metal tools. Carbide-tipped saw blades (Figure 13) have steel teeth tipped with much harder tungsten carbide, WC(s). However, diamond, C(s), is the classic example of a covalent crystal. It is so hard that it can be used to make drill bits for drilling through the hardest rock on Earth.





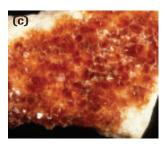


Figure 12 Amethyst (a), rose quartz (b), and citrine (c) are all variations of quartz, which is SiO<sub>2</sub>(s). The different colours are due to tiny amounts of impurities; pure quartz is colourless.

The shape and X-ray diffraction analysis of diamond show that the carbon atoms are in a large tetrahedral network with each carbon covalently bonded to four other carbon atoms (Figure 14). Each diamond is a crystal and can be described theoretically as a single macromolecule with the chemical formula C(s). The network of covalent bonds leads to a common name for these covalent crystals: **covalent network**, a 3-D arrangement of atoms continuously linked throughout the crystal by strong covalent bonds. This term helps differentiate between the covalent bonds within molecules and polyatomic ions and the covalent bonds within covalent network crystals. Like ionic compounds, covalent network compounds have continuous bonding holding every entity in the crystal together. However, covalent network compounds consist of atoms held together by covalent bonds rather than ions held together by ionic bonding. Like ionic compounds, the formulas for covalent network compounds are empirical formulas, showing the simplest whole-number ratio of atoms in the crystalline solid. Most covalent networks involve carbon and/or silicon atoms, which bond strongly (and often) to themselves and to many other atoms, as well.

## **CAREER CONNECTION**



## Geologist/Gemmologist

Geologists explore the Earth's crust for minerals and hydrocarbon formations, such as oil and gas. Gemmologists work specifically with natural gemstones such as diamonds. These scientists work outdoors and in laboratories conducting geological surveys and field research.

Find out what these careers offer and how to train for them.

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Circular saw blades with tungsten carbide-tipped teeth stay sharp much longer.

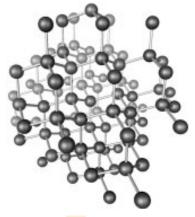


Figure 14

In a model of diamond, each carbon atom has four single covalent bonds to each of four other carbon atoms. As you know from VSEPR theory, four pairs of electrons predict a tetrahedral shape around each carbon atom. This bonding forms a continuous network out to the boundary of the crystal surface.

## DID YOU KNOW ?

## Glass, An Ancient Technology

Glass is one of the oldest, most useful, and versatile materials used by humans. It has been produced for at least four thousand years. Ordinary glass is made from sand (silicon dioxide), limestone (calcium carbonate), and soda ash (sodium carbonate), all very common materials.

## DID YOU KNOW 😭

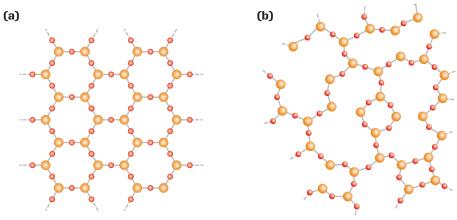
### **Traffic Control**

Semiconductor "sandwiches" that convert electricity directly to light are called LEDs (light-emitting diodes). LEDs are being used increasingly in brake and tail lights of automobiles, and in traffic control signs (**Figure 16**). Small LEDs are used in large groups, so if one fails, the sign/signal is not lost. Although more expensive to produce than conventional lights, LEDs use less energy and last much longer.



Figure 16
The city of Edmonton saves power costs of \$800 000 per year because it converted all red and green traffic signal lights to LEDs.

Crystalline quartz is described theoretically as a covalent network of  $SiO_2(s)$ . The structure can be determined by X-ray analysis (**Figure 15(a)**). When heated above its melting point of 1600 °C and then cooled rapidly, it forms a quartz glass, in which the atoms are quite disordered (**Figure 15(b)**). The properties become more like those of a very stiff liquid rather than a crystalline solid. Common commercial glass has many other compounds mixed with quartz and melts at a much lower temperature. Its properties can be controlled by changing the kinds and amounts of the additives. Purposely, glass is cooled to a rigid state in such a way that it will not crystallize as a regular lattice, so it can be worked into various shapes while hot.



### Figure 15

- (a) X-ray analysis indicates that quartz in its crystalline form has a regular, repeating 3-D network of covalently bonded silicon and oxygen atoms.
- **(b)** Quartz glass is not crystalline because it does not have an extended order; at the atomic level, it is quite disordered and irregular in structure.

The properties of hardness and high melting point provide the evidence that the overall bonding in the large macromolecule of a covalent network is very strong—stronger than most ionic bonding and all intermolecular bonding. Although an individual carbon—carbon bond in diamond is not much different in strength from any other single carbon—carbon covalent bond, it is the interlocking structure that is thought to be responsible for the strength of the material. The final structure is stronger than any individual component. This means that individual atoms are not easily displaced, and that is why the sample is very hard. In order to melt a covalent network crystal, many covalent bonds need to be broken, which requires considerable energy, so the melting points are very high. Electrons in covalent network crystals are held either within the atoms or in the covalent bonds. In either case, they are not free to move through the network. This explains why these substances are nonconductors of electricity.

### Other Covalent Networks of Carbon

Carbon is an extremely versatile atom in terms of its bonding and structures. More than any other atom, carbon can bond to itself to form a variety of pure carbon substances. It can form 3-D tetrahedral arrangements (diamond), layers of sheets (graphite), 60-atom spherical molecules (buckyballs), and long, thin tubes (carbon nanotubes) (Figure 17). Graphite is unlike most covalent crystals in that it readily conducts electricity, but it still has a high melting point. Graphite also acts as a lubricant. All of these properties, plus the X-ray diffraction of the crystals, indicate that the structure for graphite is hexagonal sheets of carbon atoms. Within these planar sheets, the bonding is a covalent network and, therefore, strong, but between the sheets, the bonding is relatively

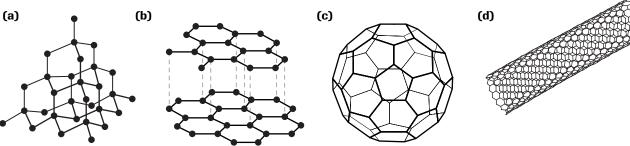


Figure 17

Models of the many forms of pure carbon:

- (a) diamond
- (b) graphite
- (c) buckyball
- (d) carbon nanotube

weak—due to London forces. The lubricating property of graphite can be explained as the covalent network planes sliding over one another easily, like individual sheets of paper in a stack. Powdered graphite makes an excellent lubricant anywhere a dry lubricant is desirable, since it will not attract and hold dust and dirt the way oily lubricants do. The electrical conductivity of graphite is explained by the concept that each carbon atom has only three covalent bonds. The unbonded fourth valence electron of each atom is free to move through the space between the 2-D sheets of atoms. The conductivity of graphite, coupled with a very high melting point, makes it very useful in hightemperature electrical applications, such as contact brushes in electric motors. Another form of carbon, known as buckminsterfullerene (named for the American architect, Buckminster Fuller), is also a very useful dry lubricant. The smallest fullerene is a 60-carbon sphere, affectionately known as a buckyball because of its resemblance to a soccer ball (Figure 17(c)).

### **Semiconductors**

In recent decades we have seen an electronic technological revolution driven by the discovery of the transistor—a solid-state "sandwich" of crystalline semiconductors. Semiconductor material used in transistors is usually pure crystalline silicon or germanium with a tiny quantity (e.g., 5 ppm) of either a Group 13 or 15 element added to the crystal in a process called doping. The purpose of doping is to control the electrical properties of the covalent crystal to produce the conductive properties desired. Transistors are the working components of almost everything electronic (Figure 18).

In an atom of a semiconductor, the highest energy levels may be thought of as being full of electrons that are unable to move from atom to atom. Normally, this would make the substance a nonconductor, like glass or quartz. In a semiconductor, however, electrons require only a small amount of energy to jump to the next higher energy level, which is empty. Once in this level, they may move to another atom easily. Semiconductors are an example of a chemical curiosity where research into atomic structure has turned out to be amazingly useful. Power supplies for many satellites and for the International Space Station (Figure 19) come from solar cells that are semiconductors arranged to convert sunlight directly to electricity. Other arrangements convert heat to electricity, or electricity to heat, or electricity to light—all without moving parts in a small, solid device. Obviously, improving the understanding of semiconductor structure was of great value to society (Figure 16).

## DID YOU KNOW 7

## **Diamond Cutting and Polishing**

Rough diamonds are mined northeast of Yellowknife, Northwest Territories, A copper saw blade pasted with diamond powder and oil is used to cut along the crystal planes. Facets are added by polishing the diamond with a disk impregnated with diamond powder. Only diamond powder is hard enough to cut and polish diamonds.

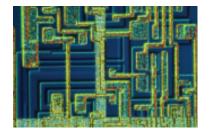


Figure 18

Semiconductors in transistors are covalent crystals that have been manipulated by doping with atoms that have more or fewer electrons than the atoms in the main crystal.



Figure 19 The solar panels that power the International Space Station use semiconductors to change light energy to electric current.

## DID YOU KNOW 😭

### **Canadian Gems**

In recent years. Canada's Northwest Territories have produced excellent quality diamonds, emeralds, and sapphires. Diamonds are a crystallized form of pure carbon and are the hardest natural substance known. Emeralds are a type of beryl (Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>). Ordinary beryl is colourless, but emeralds are green because some of the aluminium has been replaced by either chromium or vanadium. Sapphires are a form of crystallized aluminium oxide (Al<sub>2</sub>O<sub>3</sub>). Trace amounts of titanium in the crystals give sapphires their blue colour. Rubies are another type of corundum that owes its red colour to tiny quantities of chromium.

## DID YOU KNOW 😭

### **The Mohs Hardness Scale**

Geologists often identify minerals by relative hardness. They do a "scratch test" to see whether one substance will scratch another. This is really comparing the relative strengths of bonds in the crystals of the minerals. The most common relative hardness scale is called the Mohs Hardness Scale. Some of the crystal lattices of minerals are very simple, and some are not. Note the range of strengths of ionic and covalent bonds in the crystals, from very soft talc (magnesium silicate) to diamond, the hardest known:

1 talc  $Mg_3Si_4O_{10}\cdot H_2O$ 2 gypsum CaSO<sub>4</sub>·2H<sub>2</sub>O 3 calcite CaCO<sub>3</sub> 4 fluorite CaF<sub>2</sub> CaF<sub>2</sub>·3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> 5 apatite 6 orthoclase  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ 7 quartz (AIF)2SiO4 8 topaz 9 corundum Al<sub>2</sub>O<sub>3</sub> 10 diamond

For comparison purposes, using this scale, the hardness of your fingernail is 2.5, that of a copper penny is 3, and that of a steel knife blade is 5.5. The Mohs scale is not linear: the numbers (1–10) are not proportional to the absolute hardness of these substances.

## Practice

- **12.** In terms of chemical bonds, what are some factors that determine the hardness of a solid?
- 13. Identify the main type of bonding and the type of solid for each of the following:
  - (a) SiO<sub>2</sub>
- (c) CH<sub>4</sub>
- (e) Cr

- (b) Na<sub>2</sub>S
- (d) C
- (f) CaO
- **14.** How does the melting point of a solid relate to the type of entities and forces present?
- 15. Explain why metals are generally malleable, ductile, and flexible.
- **16.** State the similarities and differences in the properties of each of the following pairs of substances. In terms of the entities and forces present, briefly defend each answer.
  - (a) Al(s) and Al<sub>2</sub>O<sub>3</sub>(s)
- (b) CO<sub>2</sub>(s) and SiC(s)
- 17. To cleave or split a crystal, you tap a sharp knife on the crystal surface with a small hammer.
  - (a) Why is the angle of the blade on the crystal important to cleanly split the crystal?
  - (b) If you wanted to cleave a sodium chloride crystal, at what angle to the surface would you place the knife blade?
  - (c) Speculate about what would happen if you tried to cleave a crystal in the wrong location or at the wrong angle.
  - (d) State one technological application of this technique.
- **18.** Match the solids NaBr(s), V(s),  $P_2O_5(s)$ , and SiO<sub>2</sub>(s) to the property listed below:
  - (a) high melting point, conducts electricity
  - (b) low melting point, soft
  - (c) high melting point, soluble in water
  - (d) very high melting point, nonconductor
- **19.** Metals are generally good conductors of heat and electricity. Is there a relationship between a metal's ability to conduct heat and its ability to conduct electricity?
  - (a) Create a hypothesis to answer this question. Include your reasoning.
  - (b) Design an experiment to test your hypothesis and reasoning using common examples of metals.
- 20. Suggest some reasons why graphite may be better than oil in lubricating moving parts of a machine.
- 21. Flint is a form of rock, primarily composed of SiO<sub>2</sub>. Light-coloured forms are called chert, and forms with different colour bands are called agate. Flint can be shaped to produce an extremely sharp edge in a procedure called flintknapping. This technique has been used for millennia by Aboriginal peoples and has now become a popular hobby for many people (Figure 20). Given that flint is very hard and fractures much the same way glass or obsidian does, describe its general bonding in terms of bond type and structural regularity.
- **22.** Write a design for an experiment to measure some physical

Figure 20
Flintknapping is a traditional Aboriginal stoneworking technique that has been taught in North America for thousands of years.

properties of the ionic compounds NaCl(s), NaBr(s), Nal(s), and NaF(s). Write a prediction for a trend you might expect to see in one of the physical properties you will measure for these substances.



## Structures and Properties of Crystals



**How do Molecules Interact?** 

This short quiz will help you figure out whether you have understood the concepts in this unit.

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W W
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Crystal	Entities	Force/Bond	Properties	Examples
ionic	cations anions	ionic	hard; brittle; medium to high melting point; liquid and solution conducts	NaCl(s), Na <sub>3</sub> PO <sub>4</sub> (s), CuSO <sub>4</sub> ·5H <sub>2</sub> O(s)
metallic	cations electrons	metallic	soft to very hard; solid and liquid conducts; ductile; malleable; lustrous	Pb(s), Fe(s), Cu(s), Al(s)
molecular	molecules	London dipole – dipole hydrogen	soft; low melting point; nonconducting solid, liquid, and solution	$H_2O(s)$ (ice), $CO_2(s)$ (dry ice), $I_2(s)$
covalent network	atoms	covalent	very hard; very high melting point; nonconducting	C(s), SiC(s), SiO <sub>2</sub> (s)

**Table 3** Properties of Ionic, Metallic, Molecular, and Covalent Network Crystals



### **INVESTIGATION 3.5 Introduction**

## Classifying Unknown Solids

Design an investigation that enables you to use physical properties, such as conductivity, hardness, solubility, and melting point, to classify four unknown solids as ionic, metallic, molecular, or covalent network.

### **Purpose**

The purpose of this investigation is to use empirical definitions to classify solid substances.

Design Analysis Materials Evaluation (1, 3) Procedure Evidence

### **Problem**

Report Checklist

O Purpose

O Problem

Hypothesis

Prediction

To what class of solids do the four mystery solids belong?

To perform this investigation, turn to page 134. 🧄



### Section 3.5 Questions

- 1. Describe and explain the different electrical conductivity properties of ionic substances under different conditions.
- 2. In terms of entities and forces present, what determines whether a solid substance conducts electricity?
- 3. Calcium oxide (m.p. 2700 °C) and sodium chloride (m.p. 801 °C) have the same crystal structure, and the ions are about the same distance apart in each crystal. Explain the significant difference in their melting points.
- 4. Compare and contrast the bonding forces in carbon dioxide (dry ice) and silicon dioxide (quartz). How does this explain the difference in their properties?

- 5. Why do most metals have a relatively high density?
- 6. State the general order of strength of intermolecular, ionic, covalent network, and metallic bonding. Defend your
- 7. If the zipper on your jacket does not slide easily, how could using your pencil help? Describe what you would do, and explain why this would work.
- 8. Compare diamond and graphite using the following categories: appearance, hardness, electrical conductivity, crystal structure, and uses.

9. Use the evidence in **Table 4** to classify the type of substance and type of bonding for each unknown chloride listed.

Table 4 Physical Properties of Two Chlorides

Unknown chloride	XCI <sub>a</sub>	XCI <sub>b</sub>
Melting point (°C)	750	-25
Boiling point (°C)	1250	92
Solubility in water	high	very low
Solubility in C <sub>6</sub> H <sub>6</sub> (I)	very low	high

10. Describe two areas where research into the structure of molecules has caused a dramatic improvement in materials available to society in general.

### **Extension**

11. Ceramics are products manufactured from earth materials in which silicon oxides and silicate compounds are predominant components. They include products like brick and tile, chinaware, glass (Figure 21), porcelain, and abrasives. How do the structure and bonding change when clay is fired (heated very strongly) to create a ceramic pot or vase? Present your findings, with illustrations.

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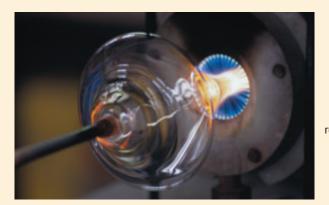




Figure 21
Glass is one special type of ceramic material.

**12.** Research and report on the properties, applications, structure, and bonding in boron nitride, BN(s).

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13. Composite materials combine materials with two or more different types of bonds to produce something with desired properties. For example, concrete embeds rock and sand in a surrounding mix (matrix) of cement to make a building material as strong as stone but easier to work with. Fibreglass embeds glass strands for strength in a plastic matrix for flexibility. New composite materials combine high strength with very light weight, so now they show up everywhere, from graphite golf club shafts to auto engine parts. Research composite materials. Write a brief summary on how the strength and weight of composite materials have dramatically influenced the design of commercial airliners for the 21st century.

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- **14.** Hemoglobin is a very large molecule (more than 9500 atoms) found in red blood cells. It carries oxygen from the lungs to body tissues (**Figure 22**), and carbon dioxide from body tissues to the lungs. Research hemoglobin on the Internet and answer the following questions:
  - (a) How many oxygen molecules can one hemoglobin molecule transport?
  - (b) How does hemoglobin bind to oxygen and to carbon dioxide?
  - (c) How strong are these "transport" bonds compared to each other?

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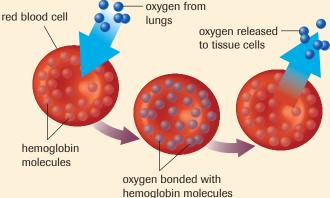


Figure 22
Hemoglobin transports oxygen to body tissue.



## **INVESTIGATION 3.1**

## **Molecular Models**

Chemists use molecular models to explain and predict molecular structure, relating structure to the properties and reactions of substances.

## **Purpose**

The purpose of this investigation is to test the ability of bonding theory to explain some known chemical reactions by using molecular models.

## Problem

How can theory, represented by molecular models, explain the following series of chemical reactions that have been studied in a laboratory?

- (a)  $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
- (b)  $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$
- (c)  $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$
- (d)  $CH_3CH_2CH_2OH \rightarrow CH_3CHCH_2 + H_2O$
- (e)  $HCOOH + CH_3OH \rightarrow HCOOCH_3 + H_2O$

### **Report Checklist**

- Purpose O Design O Problem Materials
- Hypothesis O Procedure Prediction Evidence
- Analysis ○ Evaluation

## Design

Chemical reactions are simulated with model kits to test the ability of bonding theory to explain reaction evidence.

### **Materials**

molecular model kit

## **Procedure**

- 1. For reaction (a), construct a model for each reactant; record the structures in your notebook.
- 2. Rearrange the reactant models to produce structural models of the products, recording the new structures in your notebook.
- 3. Repeat steps 1 and 2 for each chemical reaction.

## **INVESTIGATION 3.2**

## **Evidence for Polar Molecules**

Use the empirical rules (Table 8, page 99) to predict the molecular polarity of the liquids provided.

## **Purpose**

The purpose of this investigation is to test the empirical rules for predicting molecular polarity.

### **Problem**

Which of the liquids provided have polar molecules?



Check the MSDS for all liquids used, and follow appropriate safety precautions.

### **Materials**

lab apron 400 mL beaker eye protection acetate strip (marked +) 50 mL burette vinyl strip (marked −) clamp and stand paper towel burette funnel various liquids

### Report Checklist

- Purpose Design O Problem Materials
- O Hypothesis O Procedure Prediction Evidence
- Analysis Evaluation (1, 2, 3)

### **Procedure**

- 1. Charge an acetate plastic strip by rubbing with a paper towel.
- 2. Allow a thin stream of liquid to flow into a catch beaker.
- 3. Hold the charged strip close to the stream and observe the effect, if any.
- 4. Repeat steps 1 to 3 with the vinyl plastic strip.
- 5. Move to the next station and repeat steps 1 to 4.



## **INVESTIGATION 3.3**

## **Molecular Compound Melting Points**

Intermolecular bonding can be expected to have some effect on the melting (freezing) point of a molecular substance. London force theory suggests that, if other factors are equal, substances composed of larger molecules should have higher melting points. In this investigation, you accurately measure the melting point of one of two molecular compounds. You will then combine your laboratory evidence with that of other research groups to see if a hypothesized relationship between melting point and molecular size is supported.

The molecular compounds used are both saturated fatty acids. One is commonly called lauric acid, and has the molecular formula  $C_{12}H_{24}O_2(s)$ . A molecule of this compound has its 12 carbons joined by single covalent bonds in a continuous "chain." Its IUPAC chemical name is dodecanoic acid ("dodec" is the prefix for 12), and its molecular formula is

CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>COOH(s)

The other compound used for this investigation is stearic (octadecanoic) acid,  $CH_3(CH_2)_{16}COOH(s)$ . As you can see from its formula, a stearic acid molecule is very similar to a molecule of lauric acid, but the carbon chain is longer.

For the Analysis, plot both melting and freezing temperature—time curves on the same axes, and interpret the graph shapes for the most accurate determination of the melting point temperature. The class results for both compounds will then be combined with researched melting points for

- capric acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>COOH(s)
- myristic acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>COOH(s)
- palmitic acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>COOH(s), and
- arachidic acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>COOH(s)

The melting points for these compounds may be found in chemistry reference books and online.

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A plot of melting point versus electron count for the molecules of all six saturated fatty acids can then be used as evidence for a statement of any obvious relationship.

## Report Checklist

- Purpose
- Design
- Analysis

ProblemHypothesis

Prediction

- Materials Procedure Evidence
  - S ...
- Evaluation (1, 2, 3)

## **Purpose**

The purpose of this investigation is to test the hypothesis of a relationship between melting point and molecular size.

## **Problem**

What is the relationship between molecular size and melting point?

## **Hypothesis**

The melting point of similar molecular compounds increases with an increase in molecular size, as described by the total number of electrons in the molecule.

## Design

Hot and cold water baths are used to melt a solid compound and then to freeze and remelt it, with the temperature measured at regular intervals during both the freezing and remelting processes. The phase change (freezing point/melting point) temperature is found from superimposed temperature-versus-time graphs of this evidence. This is combined with evidence from other groups for a second similar compound and with information from other references to test the Hypothesis.

### **Materials**

lab apron

eye protection

sample of lauric acid or stearic acid in a

 $15 \times 150$  mm test tube

laboratory stand

test tube clamp

two thermometers or temperature probes

hotplate

two 400 mL beakers

### **Procedure**



Be careful not to splash the hot water. Avoid touching the hotplate surface with your hands. You may find the compound's odour objectionable; use a fume hood.

The glass of a thermometer bulb is very thin and fragile. Be careful not to bump, pull, or twist the thermometer.

- 1. On the hotplate, heat approximately 300 mL of water in a 400 mL beaker until the temperature is about 80 °C. Control the hotplate (turn it down, or switch it off and on) to keep the water hot but not boiling.
- 2. Set (or hold) the test tube containing the solid sample into the beaker of hot water on the hotplate until the sample is completely melted. Place the second thermometer or probe in the melted compound in the test tube.
- 3. Fill the second 400 mL beaker with cold tap water and set it on the base of a laboratory stand. Adjust a test tube clamp on the stand so that it will hold the test tube with the sample suspended in the water in the beaker (Figure 1).

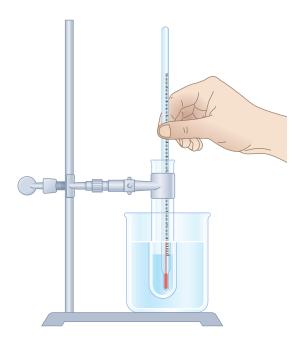


Figure 1 Setup for step 3

- 4. Remove the test tube from the hot water, and place it in the clamp. Hold the thermometer against the side of the test tube so that the bulb is located about halfway between the bottom and the top of the liquid compound in the test tube. The thermometer should be positioned so that it will be held in this position when the liquid compound solidifies. Do *not* attempt to move the thermometer once it is immobilized by the solidified compound.
- 5. Measure and record the temperature as precisely as possible every 15 s as the compound cools. (See Appendix F.3 for a note on precision when reading a thermometer.)
- 6. When the compound has obviously been completely solidified for a few minutes, stop recording measurements.
- 7. Lift the test tube assembly by raising the clamp out of the cold water beaker, and lower the test tube assembly into the beaker of hot water on the hotplate, and begin recording warming measurements by repeating step 5.
- 8. When the compound has obviously been completely liquified for a few minutes, stop recording measurements.
- 9. Remove the thermometer from the melted sample, and wipe it clean with a paper towel. Place the test tube back in the cold water beaker to solidify the sample before returning it.



## **INVESTIGATION 3.4**

## **Hydrogen Bonding**

Breaking bonds absorbs energy, and forming bonds releases energy. Forming new bonds within a liquid should produce a temperature effect. For this investigation, write a Prediction that includes a bonding concept. The Prediction should include reference to a measurable (testable) result of mixing the liquids. Add to the design by identifying the manipulated and responding variables, and the major controlled variable.

## **Purpose**

The purpose of this investigation is to test the concept of hydrogen bonding.

## **Problem**

How does the temperature change upon mixing ethanol,  $C_2H_5OH(1)$ , with water compare with the temperature change upon mixing glycerol (glycerin), C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>(l), with water?

## Design

Equal volumes of ethanol and water, and then of glycerol and water, are mixed. The temperature change is recorded in each case (Figure 2).

## **Materials** lab apron

eye protection distilled water ethanol glycerol

two 10 mL graduated cylinders cup lid with centre hole two thermometers or temperature probes two nested polystyrene cups 250 mL beaker (to support the cups)

## **Report Checklist**

 Purpose O Problem Hypothesis

Prediction

- - O Materials Procedure Evidence

O Design

- Analysis
- Evaluation (1, 2, 3)

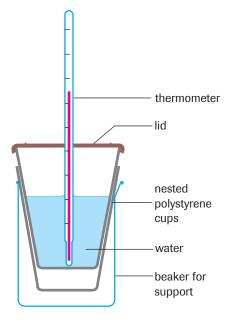


Figure 2 Suggested set-up of apparatus

## **INVESTIGATION 3.5**

## Classifying Unknown Solids

Design an investigation that enables you to use physical properties, such as conductivity, hardness, solubility, and melting point, to classify four unknown solids as ionic, metallic, molecular, or covalent network.

## **Purpose**

The purpose of this investigation is to use empirical definitions to classify solid substances.

## **Report Checklist**

- Purpose
  - O Problem
  - O Hypothesis Procedure Prediction Evidence
- Analysis
- Evaluation (1, 3)

### **Problem**

To what class of solids do the four mystery solids belong?

Design

Materials

134 Chapter 3

# Chapter 3 SUMMARY

### **Outcomes**

## Knowledge

- · explain why formulas for ionic compounds refer to the simplest whole-number ratio of ions that result in a net charge of zero (3.1)
- define valence electron, electronegativity, and ionic bond (3.1, 3.3)
- · use the periodic table and Lewis structures to support and explain ionic bonding theory (3.1)
- · explain how an ionic bond results from the simultaneous attraction of oppositely charged ions (3.1)
- draw or build models of common ionic lattices and relate structures and properties (3.5)
- explain why the formulas for molecular substances refer to the number of atoms of each constituent element (3.2)
- relate electron pairing to covalent bonds (3.1, 3.2)
- build models depicting the structure of simple covalent molecules, including selected organic compounds (3.2)
- · draw electron-dot diagrams of atoms and molecules, writing structural formulas for molecular substances and using Lewis structures to predict bonding in simple molecules (3.2)
- apply VSEPR theory to predict molecular shapes (3.3)
- illustrate, by drawing or building models, the structure of simple molecular substances (3.2)
- explain intermolecular forces, London (dispersion) forces, dipole-dipole attractions, and hydrogen bonding (3.4)
- relate properties of substances to the predicted intermolecular bonding in the substance (3.4, 3.5)
- determine the polarity of a molecule based on simple structural shapes and unequal charge distribution (3.3)
- describe bonding as a continuum ranging from complete electron transfer to equal sharing of electrons. (3.3, 3.4)

### **STS**

- state that the goal of science is knowledge about the natural world (3.1, 3.3, 3.5)
- list the characteristics of empirical and theoretical knowledge (3.1)
- · evaluate scientific knowledge and restrict, revise, or replace it where necessary (3.1, 3.4, 3.5)
- state examples of science leading technology and technology leading science (3.1, 3.5)

### **Skills**

- initiating and planning: design an investigation to determine the properties of ionic compounds (3.5); describe procedures for safe handling, storage, and disposal of laboratory materials (3.3, 3.4, 3.5); state a hypothesis and make a prediction about the properties of molecular substances based on attractive forces (3.3, 3.4)
- performing and recording: draw Lewis formulas and build models of ionic solids (3.5); build models depicting the structure of simple covalent molecules (3.2, 3.4); carry out an investigation to determine the melting points of molecular substances (3.4)
- analyzing and interpreting: identify trends and patterns in the melting points of a related series of molecular substances (3.4); determine the properties of ionic compounds (3.5)
- · communication and teamwork: working cooperatively, critically analyze and evaluate models and graphs constructed by others (3.2, 3.3, 3.5)

## Key Terms



### 3.1

structural formula valence electron orbital valence orbital bonding electron lone pair octet rule Lewis symbol electronegativity covalent bond ionic bond

### 3.2

bonding capacity
empirical formula
molecular formula
Lewis formula
structural formula
stereochemical formula

### 3.3

stereochemistry
VSEPR theory
polar molecule
nonpolar molecule
nonpolar covalent bond
polar covalent bond
bond dipole

### 3.4

intermolecular force van der Waals force dipole-dipole force London force isoelectronic molecules hydrogen bond

### 3.5

crystal lattice covalent network

# + EXTENSION CBC ♣ radioNE QUIRKS QUARKS

### The Big Rip

The Universe will end not with a bang, or a whimper, but with a rip, according to cosmologist Dr. Robert Caldwell. He has been thinking about a mysterious repulsive force often called the "dark energy." Dr. Caldwell's calculations suggest that the dark energy could actually be a different kind of force, previously unknown, and could grow even more powerful as the universe gets older—possibly resulting in the ripping apart of all matter.

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## MAKE a summary

 Covalent bonds and intermolecular forces can be explained in a unified way by describing the central entity that is simultaneously attracted (electrostatically) to the surrounding entities. Copy and complete **Table 1**.

**Table 1** Forces Acting Between Entities

Force or bond	Central entity	Surrounding entities
covalent		
covalent network		
dipole-dipole		
hydrogen		
ionic		
London		
metallic		

**2.** Each class of substance has a characteristic set of properties. Copy and complete **Table 2** using relative descriptions such as low, high, and variable. (Indicate n/a if not applicable.)

Table 2 Summary of Properties of Substances

		Melting	Electrical conductivity		
Substance	Hardness	point	Solid	Liquid	Solution
molecular					
ionic					
covalent network					
metallic					

3. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?



The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 3
- · additional Diploma Exam-style Review questions
- Illustrated Glossary
- · additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

## **► Unit 1 REVIEW**

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.



### DO NOT WRITE IN THIS TEXTBOOK.

### Part 1

- 1. The following scientists made major contributions to bonding theory.
  - 1. Abeaa
  - 2. Kekulé
  - 3. Pauling
  - Lewis

When arranged in chronological order, the order is \_\_\_\_\_, \_\_ , \_\_\_ , and \_\_\_ .

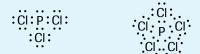
- 2. The most significant new concept of Lewis theory was
  - A. the octet rule for atom stability
  - B. electron gain or loss in ion formation
  - electron sharing in covalent bonds
  - D. different electron energy levels
- 3. The Lewis symbol for a single nitrogen atom would show
  - A. 1 bonding electron and 3 lone pairs
  - B. 2 bonding electrons and 2 lone pairs
  - C. 1 bonding electron and 2 lone pairs
  - 3 bonding electrons and 1 lone pair
- 4. A Lewis formula for the molecule PCl<sub>3</sub> would show
  - A. 13 electron pairs
  - B. 10 electron pairs
  - 8 electron pairs
  - D. 4 electron pairs
- 5. X-ray diffraction evidence led to development of
  - A. Lewis formulas
  - B. crystal lattice models
  - C. VSEPR theory
  - D. the octet rule
- 6. According to VSEPR theory, which molecule has a trigonal pyramidal shape?
  - A. BF<sub>3</sub>
  - B. CO<sub>2</sub>
  - C. NCI<sub>2</sub>
  - D. H<sub>2</sub>S
- 7. When the following covalent bonds are arranged in order
- NR from least polar to most polar, the order is \_\_\_\_, \_\_\_, \_\_\_, and
  - 1. N-0
  - 2. C-I
  - 0-H 3.
  - 4. H-CI

- 8. Intermolecular force theory best explains
  - A. surface tension of a liquid
  - B. electrical conductivity of a metal
  - C. hardness of a covalent network solid
  - D. melting point of an ionic solid
- 9. Theory indicates that metallic bonding depends on
  - A. high electronegativity
  - mobile valence electrons
  - C. polar covalent bonds
  - D. electrical conductivity
- **10.** A molecule of a substance with physical properties primarily explained by London forces is
  - SiC Α.
  - B. **KCI**
  - C. Na₀P
  - D. PH<sub>3</sub>
- 11. Hydrazine, N<sub>2</sub>H<sub>4</sub>(I), is used in rocket fuels. The shape of the bonding around each nitrogen atom in a molecule of hydrazine is predicted to be
  - A. tetrahedral
  - B. linear
  - trigonal pyramidal
  - D. trigonal planar
- **12.** Which of the following molecules is polar?
  - A. C<sub>2</sub>H<sub>6</sub>
  - B. CH<sub>3</sub>OH
  - C. CO<sub>2</sub>
  - D. CCI
- **13.** The *correct* statement about covalent bonding is:
  - A. Almost all covalent bonds involve equally shared electrons and so are normally nonpolar.
  - B. Different covalent bonds can range from equal to extremely unequal electron sharing.
  - C. The total number of electrons shared in covalent bonds by a central atom is always eight.
  - D. Each atom always "contributes" one bonding electron when a covalent bond forms.
- **14.** The compound strontium nitrate, Sr(NO<sub>3</sub>)<sub>2</sub>(s), has which of the following structures?
  - A. covalent bonding and ionic bonding
  - covalent bonding only
  - C. ionic bonding only
  - D. metallic and ionic bonding
- **15.** The shape of permanganate ion,  $MnO_4^-$ , cannot be predicted from the level of VSEPR theory covered in this textbook. However, if you know that the ion's Lewis diagram shows no lone pairs on the central atom, you can conclude that the shape must be
  - A. trigonal pyramidal
  - linear
  - C. trigonal planar
  - D. tetrahedral

### Part 2

Use the information below, **Figure 1**, and **Table 1** to answer questions 16 to 19.

When dry chlorine gas is passed over heated phosphorus, it ignites, and the reaction produces two different products: mostly phosphorus trichloride, with some phosphorus pentachloride mixed in.



### Figure 1

Lewis formulas for phosphorus trichloride and phosphorus pentachloride.

 Table 1
 Physical Properties of Phosphorus Chlorides

Compound	Melting point (°C)	Boiling point (°C)	Colour/State (SATP)
PCl <sub>3</sub>	-112	76	clear, colourless liquid
PCI <sub>5</sub>	148 (under (pressure)	sublimes $(s \rightarrow g)$ at 165	pale yellow crystals

- **16.** Which of the compounds has molecular structure that does not follow the octet rule?
- **17. Explain**, using intermolecular bonding theory, why only one of the compounds is a solid at SATP. Your explanation should state which type of intermolecular bonding is stronger, and why.
- 18. Both compounds are corrosive to skin and tissue, and both react with water. Since human tissue is largely water, the compounds are doubly hazardous because reaction with water produces a very common acid that is also extremely corrosive to tissue. Using each compound's atomic composition, predict which common acid is produced.
- 19. State which compound has a molecular shape that is easily predictable using VSEPR theory, and what shape those molecules will have.
- 20. Empirically, how does the chemical reactivity vary
  - (a) among the elements in Groups 1 and 2 of the periodic table?
  - (b) among the elements in Groups 16 and 17?
  - (c) within Period 3?
  - (d) within Group 18?

- **21. Identify** two generalizations that describe how the trends in atomic electronegativity vary with atom position in the periodic table.
- **22.** How are the positions of two reacting elements in the periodic table related to the type of compound and bond formed? State two generalizations.
- **23.** What is the maximum number of electrons in the valence level of an atom of a representative element?
- **24. Compare** the electronegativities of main group metals with those of main group nonmetals.
- 25. Draw a Lewis formula for each of the following atoms. Then determine the number of bonding electrons and lone pairs for each atom.
  - (a) Ne
  - (b) Al
  - (c) Ge
  - (d) N
  - (e) Br
- **26.** Draw Lewis formulas for atoms of the following elements and **predict** their bonding capacity:
  - (a) calcium
  - (b) chlorine
  - (c) phosphorus
  - (d) silicon
  - (e) sulfur
- **27. Describe** the requirements for valence electrons and orbital occupancy in order for a covalent bond to form between two approaching atoms.
- 28. According to atomic theory, how many lone electron pairs are on the central atom in molecules of the following substances?
  - (a)  $SCl_2(I)$
  - (b) NH<sub>3</sub>(g)
  - (c)  $H_0O(1)$
  - (d)  $CCI_{4}(l)$
  - (e)  $PCl_3(l)$
- 29. Compounds of metals and carbon are used in engineering because of their extreme hardness and strength (Figure 2). The carbon in these metallic carbides behaves as a C<sup>4-</sup> ion, for example, in tungsten carbide, WC(s). Draw the Lewis formula for a carbide ion.



Figure 2
Steel drill bits,
when tipped with
tungsten carbide,
become hard
enough to drill
holes in solid rock,
concrete, and
ceramic tile.

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- **30.** The American chemist Gilbert Lewis suggested that when atoms react, they achieve a more stable electron configuration. Describe the electron arrangement that gives an atom maximum stability.
- 31. Draw a Lewis formula and a structural formula to describe each molecule shown in these unbalanced equations.
  - (a)  $N_2(g) + I_2(s) \rightarrow NI_3(s)$
  - (b)  $H_2O_2(aq) \rightarrow H_2O(1) + O_2(g)$
- 32. Why did scientists create the concept of double and triple covalent bonds?
- 33. What empirical evidence is there for double and triple
- **34.** What information does a boiling point provide about intermolecular forces?
- 35. List three types of intermolecular forces, and give an example of a substance having each type of force.
- 36. Write an empirical definition (based on observable properties) for an ionic compound.
- 37. Summarize the theoretical structure (based on concepts and theory) of ionic compounds.
- 38. Use Lewis formulas to describe the electron rearrangement in the following chemical reactions:
  - (a) magnesium atoms + sulfur atoms  $\rightarrow$

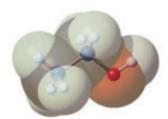
magnesium sulfide

(b) aluminium atoms + chlorine atoms  $\rightarrow$ 

aluminium chloride

- **39.** The VSEPR model includes several concepts related to atomic theory. **Describe** the following concepts:
  - (a) valence shell
  - (b) bonding pair
  - (c) lone pair
  - (d) electron pair repulsion
- **40. Outline** the steps involved in predicting the shape of a molecule using VSEPR theory.
- 41. Using VSEPR theory, predict the shape around the central atom of each of the following molecules:
  - (a) SCI<sub>2</sub>(l)
  - (b) BCl<sub>3</sub>(g)
  - (c) SiH₄(g)
  - (d) CCI<sub>4</sub>(l)
  - (e) HCN(g)
  - (f)  $OCl_2(g)$
  - (g) NCl<sub>3</sub>(g)
  - (h)  $H_2O_2(l)$
- **42.** What is the difference in the meaning of the subscripted numbers in a molecular formula and in an ionic formula?
- 43. List the types of bonds and forces that, according to our current theories, are believed to be present in
  - (a)  $C_6H_{1/4}(I)$
  - (b) Fe(s)
  - (c) CaCl<sub>2</sub>(s)

- (d)  $C_2H_3CI_3(1)$
- (e) C(s) (diamond)
- (f)  $Fe_2O_3(s)$
- (g)  $C_2H_5OH(I)$  (**Figure 3**)
- (h)  $C_{12}H_{22}O_{11}(s)$



### Figure 3

The structure of ethanol molecules results in intermolecular bonding that gives the liquid some very useful properties.

- 44. Draw diagrams of models to describe the following types of bonding:
  - (a) ionic bonding
  - (b) dipole-dipole forces
  - (c) hydrogen bonding
  - (d) metallic bonding
- **45.** Metals are shiny, malleable (bendable) conductors of heat and electricity (Figure 4).
  - (a) Write full electron energy-level diagrams for these metals: magnesium, potassium, lithium, and aluminium.
  - (b) **How** do the valence electron arrangements of metals explain their conductivity and malleability?
- 46. Carbon dioxide is used by green plants in the process of photosynthesis and is also a greenhouse gas produced by fossil fuel combustion.
  - (a) Draw a Lewis formula for carbon dioxide.
  - (b) **Predict** its shape and bond angle.
  - (c) Using appropriate bonding theories, predict and explain the polarity of carbon dioxide.



### Figure 4

Copper is strong, flexible, unreactive, and an excellent conductor of electricity, making it the material of choice for wiring household electric circuits.

- **47.** The polarity of a molecule is determined by theory from bond polarity and molecular shape.
  - (a) **Determine** the polarity of the bonds N–Cl and C–Cl.
  - (b) Predict whether the molecules NCI<sub>3</sub> and CCI<sub>4</sub> are polar or nonpolar. Justify your predictions.
- **48.** Use appropriate bonding theory to **explain** the following:
  - (a) BeH<sub>2</sub> is nonpolar; H<sub>2</sub>S is polar.
  - (b) BH<sub>3</sub> is trigonal planar; NH<sub>3</sub> is trigonal pyramidal.
  - (c) LiH has a melting point of 688 °C; that of HF is -83 °C.
- **49.** Use a theory of intermolecular bonding to **explain** the sequence of boiling points in the following compounds, from a family called alkyl bromides:
  - CH<sub>3</sub>Br(g) (4 °C)
  - C<sub>2</sub>H<sub>5</sub>Br(l) (38 °C)
  - C<sub>3</sub>H<sub>7</sub>Br(l) (71 °C)
- 50. Name the intermolecular forces present in the following compounds, and account for the difference in their boiling points:
  - (a) CH<sub>4</sub>(g) (-164 °C)
  - (b)  $NH_3(g) (-33 °C)$
  - (c)  $BF_3(g) (-100 \,^{\circ}C)$
- 51. All chemical bonds are ultimately thought to be the result of simultaneous attractions between opposite electrostatic charges. For each chemical bond listed below, indicate which types of charged entities and/or particles are involved:
  - (a) covalent bond
  - (b) London forces
  - (c) dipole-dipole forces
  - (d) hydrogen bonds
  - (e) ionic bond
- **52.** Ionic compounds and metals have different physical properties because of the different forces involved. For example, sodium chloride and nickel have nearly identical molar masses; however, their melting points, conductivity, and solubility in water are quite different.
  - (a) **Explain** the large difference in melting point between sodium chloride (801 °C) and nickel metal (1453 °C).
  - (b) Predict the electrical conductivity of each of these substances in the solid state, and provide a theoretical explanation for your prediction.
  - (c) **Predict** the solubility in water of each substance, and provide a theoretical explanation for your prediction.

- 53. Name all the bonding forces acting in each of the following substances:
  - (a) hexane,  $C_6H_{14}(I)$
  - (b) 1-butanol,  $C_4H_9OH(l)$
  - (c) ethylamine, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>(l)
  - (d) chloroethane, C<sub>2</sub>H<sub>5</sub>Cl(l)
  - (e) calcium carbonate, CaCO<sub>3</sub>(s)
  - (f) diamond, C(s)
- **54. Compare** entities and bonding forces in the following pairs of solids:
  - (a) metallic and covalent network
  - (b) molecular and ionic
- **55.** Given the very wide range of boiling points of metal elements, what can be hypothesized about the strength of metallic bonding?
- 56. How can the boiling of water be used as an example to illustrate the relative strengths of hydrogen bonds and covalent bonds?
- 57. Some people find the odour from cooking fish to be unpleasant. Methylamine, CH<sub>3</sub>NH<sub>2</sub>(g), is one of the compounds responsible for the odour (Figure 5).
  - (a) Draw Lewis and structural formulas to describe methylamine.
  - (b) Use VSEPR theory to **predict** the shape around the carbon and nitrogen atoms in methylamine.
  - (c) Methylamine and ethane, C<sub>2</sub>H<sub>6</sub>(g), have similar molar masses. **Explain** why the boiling point of methylamine is -6 °C while that of ethane is much lower. -89 °C.
  - (d) Use structural formulas to rewrite the following equation for the reaction of methylamine with acetic acid:

$$CH_3NH_2(aq) + CH_3COOH(aq) \rightarrow$$

 $CH_3NH_3^+(aq) + CH_3COO^-(aq)$ 

(e) Give a practical reason why vinegar (5% acetic acid) and lemon juice (dilute citric acid) are often served along with cooked fish.



**Figure 5** A "fishy" smell is partly due to the presence of the volatile

substance methylamine.

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58. The most common oxides of Period 2 elements are as follows:

Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>2</sub>, Cl<sub>2</sub>O

- (a) Which oxides are classified as ionic, and which are classified as molecular when using the simple metal-nonmetal or nonmetal-nonmetal combination rule?
- (b) Which oxide is observed to be neither ionic nor molecular, and how does bonding theory explain this?
- (c) Calculate the difference in electronegativity between the two elements in each oxide.
- (d) **How** is the difference in electronegativity related to the properties of the compound?
- 59. Predict the structural formula, molecular formula, and name for the simplest product in each of the following chemical reactions. Which product does not follow the octet rule of covalent bonding?
  - (a)  $H_2(g) + P_n(s) \rightarrow$
  - (b) Si(s) +  $Cl_2(g) \rightarrow$
  - (c)  $C(s) + O_2(g) \rightarrow$
  - (d)  $B(s) + F_2(g) \rightarrow$
- **60.** Chlorine is a very reactive element that forms stable compounds with most other elements. For each of the following chlorine compounds, draw Lewis and structural diagrams, and then **predict** the polarity of the molecules that obey the octet rule. Use the concept of symmetry to speculate about the polarity of the molecules that do not obey the octet rule.
  - (a) NCl<sub>3</sub>
  - (b) SiCl<sub>4</sub>
  - (c) PCI<sub>5</sub>
  - (d) SCI<sub>6</sub>
- 61. Review the focusing questions on page 72. Using the knowledge you have gained from this unit, briefly outline a response to each of these questions.

### Extension

62. Modern technologies like spectroscopy and X-ray diffraction allow scientists to measure indirectly the length of chemical bonds. Use the evidence in Table 2 to create a generalization about the effect of bond type on bond length.

Table 2

Typical compound	Covalent bond type	Bond length (nm)
CH <sub>4</sub>	C-H	0.109
C <sub>2</sub> H <sub>6</sub>	C-C	0.154
C <sub>2</sub> H <sub>4</sub>	C=C	0.134
C <sub>2</sub> H <sub>2</sub>	C≡C	0.120
CH <sub>3</sub> OH	C-0	0.143
CH <sub>3</sub> COCH <sub>3</sub>	C=0	0.123
CH <sub>3</sub> NH <sub>2</sub>	C-N	0.147
CH <sub>3</sub> CN	C≡N	0.116

63. Medical professionals are concerned about the level of saturated and unsaturated fats in the foods we eat. Of even greater concern is the consumption of "trans fats," which are produced by chemically reacting hydrogen with natural oils. Research "saturated fats," "unsaturated fats," and "trans fats," and find out how these terms are related to the concept of single and double bonds. Locate three products such as margarine and snack foods at home or in a grocery store, and list any information printed on the labels or packaging that describes the products' fat content (Figure 6). Briefly summarize the medical concerns about consumption of trans fats.

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Figure 6 Potato chip nutritional data