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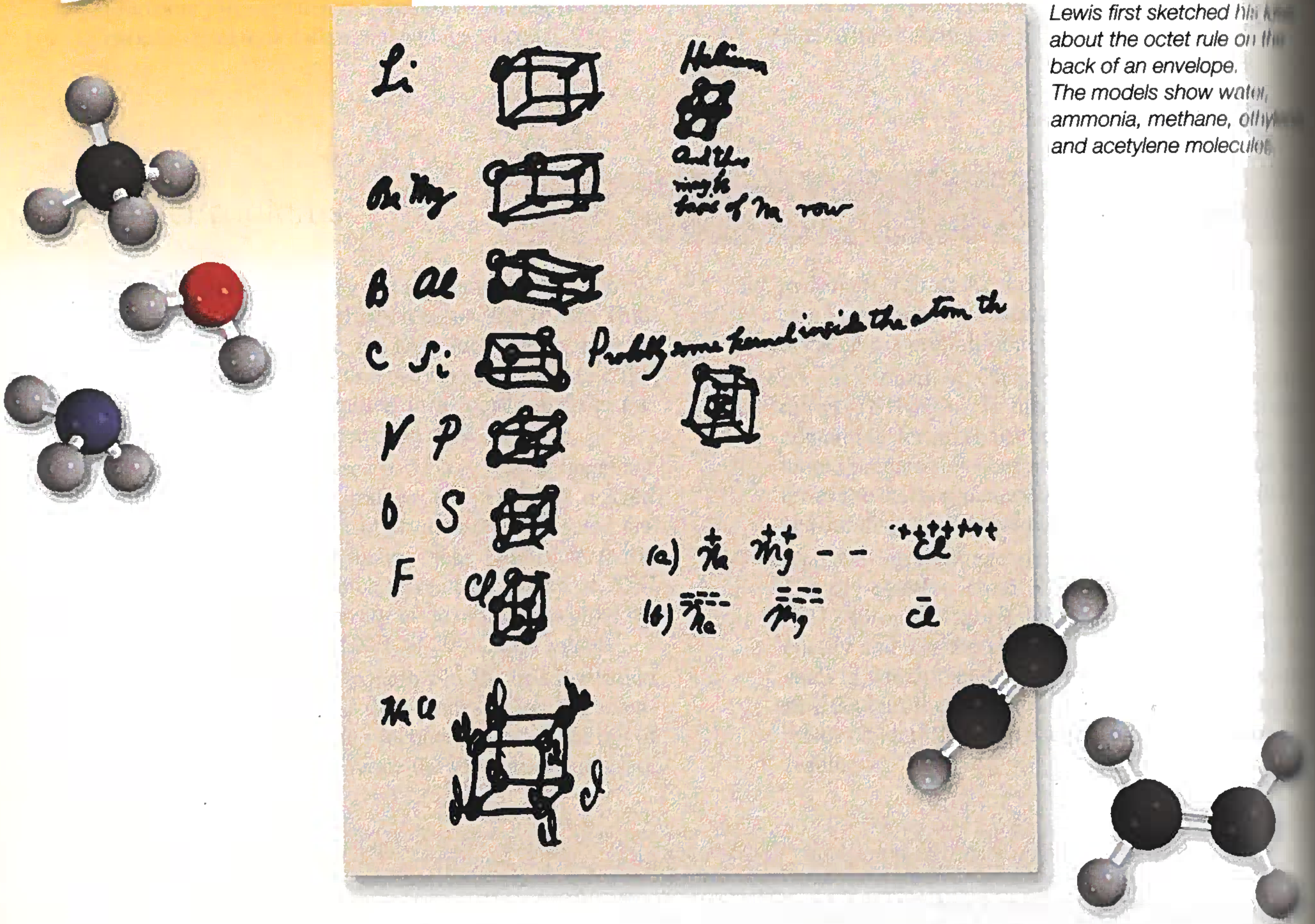


Lewis first sketched his ideas about the octet rule on the back of an envelope. The models show water, ammonia, methane, ethylene and acetylene molecules.

Chemical Bonding I

Basic Concepts

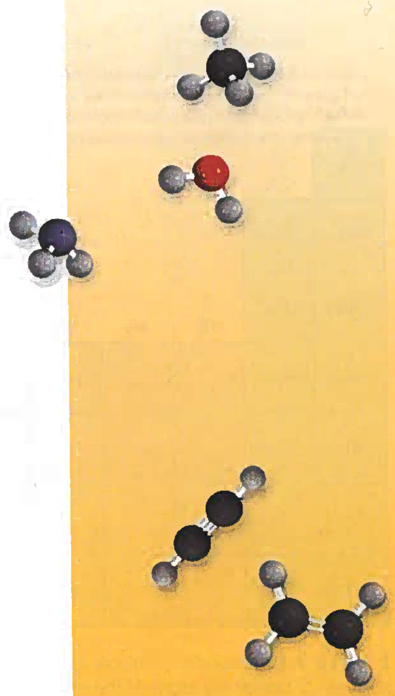
A LOOK AHEAD

- Our study of chemical bonds begins with an introduction to Lewis dot symbols, which shows the valence electrons on an atom. (9.1)
- We then study the formation of ionic bonds and learn the determination of lattice energy, which is a measure of the stability of ionic compounds. (9.2 and 9.3)
- Next, we turn our attention to the formation of covalent bonds. We learn to write Lewis structures, which are governed by the octet rule. (9.4)
- We see that electronegativity is an important concept in understanding the properties of molecules. (9.5)
- We continue to practice writing Lewis structures for molecules and ions and use formal charges to study the distribution of electrons in these species. (9.6 and 9.7)
- We learn further aspects of writing Lewis structures in terms of resonance structures, which are alternate Lewis structures to represent a molecule. We also see that there are important exceptions to the octet rule. (9.8 and 9.9)
- The chapter ends with an examination of the strength of covalent bonds, which leads to the use of bond enthalpies to determine the enthalpy of a reaction. (9.10)

Interactive Activity Summary

1. Interactivity: Ionic Bonds (9.2)
2. Interactivity: Born-Haber Cycle for Lithium Fluoride (9.3)
3. Animation: Ionic vs. Covalent Bonding (9.4)
4. Interactivity: Covalent Bonds (9.4)
5. Interactivity: Lewis Dot Structure (9.6)
6. Interactivity: Resonance (9.8)
7. Animation: Resonance (9.8)
8. Interactivity: Octet Rule Exceptions (9.9)

Why do atoms of different elements react? What are the forces that hold atoms together in molecules and ions in ionic compounds? What shapes do they assume? These are some of the questions addressed in this chapter and in Chapter 10. We begin by looking at the two types of bonds—ionic and covalent—and the forces that stabilize them.



9.1 Lewis Dot Symbols

The development of the periodic table and concept of electron configuration gave chemists a rationale for molecule and compound formation. This explanation, formulated by Gilbert Lewis,[†] is that atoms combine in order to achieve a more stable electron configuration. Maximum stability results when an atom is isoelectronic with a noble gas.

When atoms interact to form a chemical bond, only their outer regions are in contact. For this reason, when we study chemical bonding, we are concerned primarily with the valence electrons of the atoms. To keep track of valence electrons in a chemical reaction, and to make sure that the total number of electrons does not change, chemists use a system of dots devised by Lewis and called Lewis dot symbols. A ***Lewis dot symbol** consists of the symbol of an element and one dot for each valence electron in an atom of the element.* Figure 9.1 shows the Lewis dot symbols for the representative elements and the noble gases. Note that, except for helium, the number of valence electrons each atom has is the same as the group number of the element. For example, Li is a Group 1A element and has one dot for one valence electron; Be, a Group 2A element, has two valence electrons (two dots); and so on. Elements in the same group have similar outer electron configurations and hence similar Lewis dot symbols. The transition metals, lanthanides, and actinides all have incompletely filled inner shells, and in general, we cannot write simple Lewis dot symbols for them.

In this chapter we will learn to use electron configurations and the periodic table to predict the type of bond atoms will form, as well as the number of bonds an atom of a particular element can form and the stability of the product.

[†] Gilbert Newton Lewis (1875–1946). American chemist. Lewis made many important contributions in the areas of chemical bonding, thermodynamics, acids and bases, and spectroscopy. Despite the significance of Lewis's work, he was never awarded a Nobel Prize.

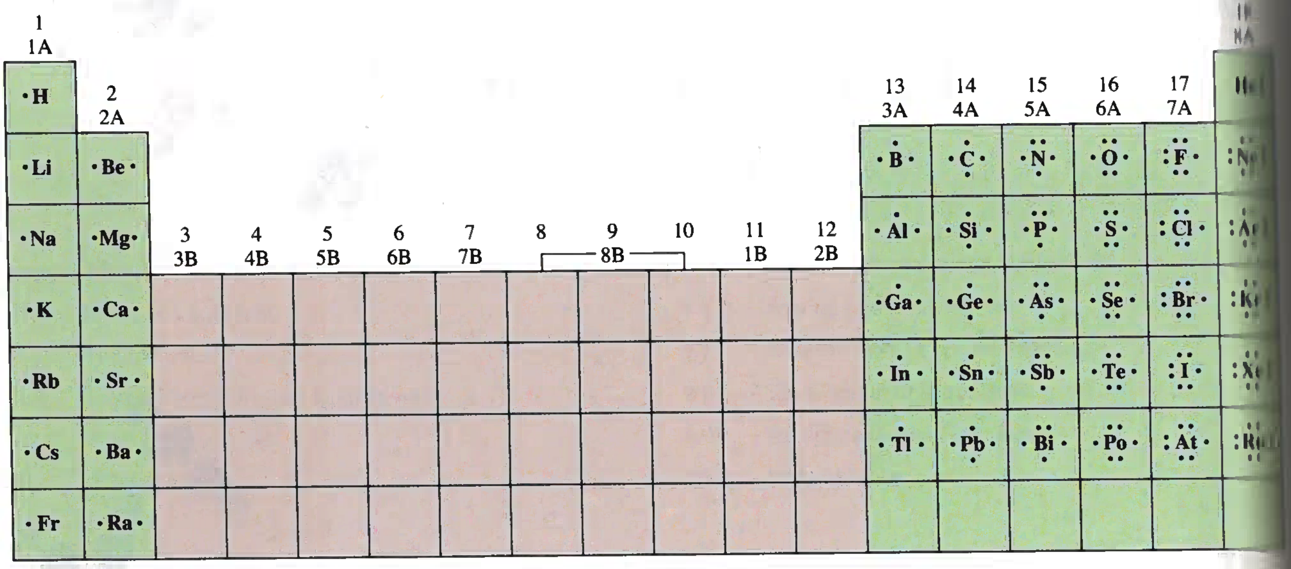
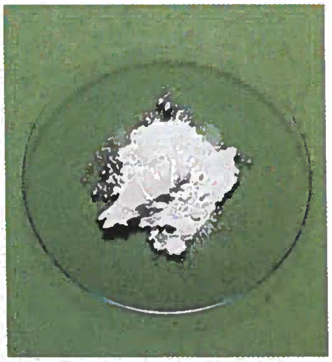


Figure 9.1 *Lewis dot symbols for the representative elements and the noble gases. The number of unpaired dots corresponds to the number of bonds an atom of the element can form in a compound.*

9.2 The Ionic Bond

Interactivity:
Ionic Bonds
ARIS, Interactives

In Chapter 8 we saw that atoms of elements with low ionization energies tend to form cations, while those with high electron affinities tend to form anions. As a rule, the elements most likely to form cations in ionic compounds are the alkali metals and alkaline earth metals, and the elements most likely to form anions are the halogens and oxygen. Consequently, a wide variety of ionic compounds combine a Group 1A or Group 2A metal with a halogen or oxygen. An ***ionic bond*** is *the electrostatic force that holds ions together in an ionic compound.* Consider, for example, the reaction between lithium and fluorine to form lithium fluoride, a poisonous white powder used in lowering the melting point of solders and in manufacturing ceramics. The electron configuration of lithium is $1s^22s^1$, and that of fluorine is $1s^22s^22p^5$. When lithium and fluorine atoms come in contact with each other, the outer $2s^1$ valence electron of lithium is transferred to the fluorine atom. Using Lewis dot symbols, we represent the reaction like this:



Lithium fluoride. Industrially, LiF (like most other ionic compounds) is obtained by purifying minerals containing the compound.

$$\begin{array}{cccccc} \cdot\text{Li} & + & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}\cdot & \longrightarrow & \text{Li}^+ \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:^- & \text{(or LiF)} \\ 1s^22s^1 & & 1s^22s^22p^5 & & 1s^2 \quad 1s^22s^22p^6 & \end{array} \qquad (9.1)$$

For convenience, imagine that this reaction occurs in separate steps—first the ionization of Li:

$$\cdot\text{Li} \longrightarrow \text{Li}^+ + e^-$$

and then the acceptance of an electron by F:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}\cdot + e^- \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:^-$$

Next, imagine the two separate ions joining to form a LiF unit:

$$\text{Li}^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:^- \longrightarrow \text{Li}^+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:^-$$

Note that the sum of these three equations is

$$\cdot\text{Li} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}\cdot \longrightarrow \text{Li}^+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:^-$$

We normally write the empirical formulas of ionic compounds without showing the charges. The + and − are shown here to emphasize the transfer of electrons.

which is the same as Equation (9.1). The ionic bond in LiF is the electrostatic attraction between the positively charged lithium ion and the negatively charged fluoride ion. The compound itself is electrically neutral.

Many other common reactions lead to the formation of ionic bonds. For instance, calcium burns in oxygen to form calcium oxide:

$$2\text{Ca}(s) + \text{O}_2(g) \longrightarrow 2\text{CaO}(s)$$

Assuming that the diatomic O_2 molecule first splits into separate oxygen atoms (we will look at the energetics of this step later), we can represent the reaction with Lewis symbols:

$$\begin{array}{cccccc} \cdot\text{Ca}\cdot & + & \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\cdot & \longrightarrow & \text{Ca}^{2+} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:^{2-} \\ [\text{Ar}]4s^2 & & 1s^22s^22p^4 & & [\text{Ar}] & [\text{Ne}] \end{array}$$

There is a transfer of two electrons from the calcium atom to the oxygen atom. Note that the resulting calcium ion (Ca^{2+}) has the argon electron configuration, the oxide ion (O^{2-}) is isoelectronic with neon, and the compound (CaO) is electrically neutral.

In many cases, the cation and the anion in a compound do not carry the charges. For instance, when lithium burns in air to form lithium oxide (Li_2O), the anced equation is

$$4\text{Li}(s) + \text{O}_2(g) \longrightarrow 2\text{Li}_2\text{O}(s)$$

Using Lewis dot symbols, we write

$$\begin{array}{ccccc} 2\cdot\text{Li} \;+ & \cdot\ddot{\underset{\cdot\cdot}{\text{O}}}\cdot & \longrightarrow\; 2\text{Li}^+ & :\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-} & (\text{or Li}_2\text{O}) \\ 1s^22s^1 & 1s^22s^22p^4 & [\text{He}] & [\text{Ne}] & \end{array}$$

In this process, the oxygen atom receives two electrons (one from each of the lithium atoms) to form the oxide ion. The Li^+ ion is isoelectronic with helium,

When magnesium reacts with nitrogen at elevated temperatures, a white compound, magnesium nitride (Mg_3N_2), forms:

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

or

$$\begin{array}{ccccc} 3\cdot\text{Mg}\cdot \;+ & 2\cdot\ddot{\underset{\cdot}{\text{N}}}\cdot & \longrightarrow\; 3\text{Mg}^{2+} & 2\,:\ddot{\underset{\cdot\cdot}{\text{N}}}:^{3-} & (\text{or Mg}_3\text{N}_2) \\ [\text{Ne}]3s^2 & 1s^22s^22p^3 & [\text{Ne}] & [\text{Ne}] & \end{array}$$

The reaction involves the transfer of six electrons (two from each Mg atom) to nitrogen atoms. The resulting magnesium ion (Mg^{2+}) and the nitride ion (N^{3-}) both isoelectronic with neon. Because there are three +2 ions and two −3 ions, charges balance and the compound is electrically neutral.

In Example 9.1, we apply the Lewis dot symbols to study the formation of ionic compound.

The mineral corundum (Al_2O_3).

Example 9.1

Use Lewis dot symbols to show the formation of aluminum oxide (Al_2O_3).

Strategy We use electroneutrality as our guide in writing formulas for ionic compounds, that is, the total positive charges on the cations must be equal to the total negative charges on the anions.

Solution According to Figure 9.1, the Lewis dot symbols of Al and O are

$$\cdot\dot{\text{Al}}\cdot \qquad \cdot\ddot{\underset{\cdot\cdot}{\text{O}}}\cdot$$

Because aluminum tends to form the cation (Al^{3+}) and oxygen the anion (O^{2-}) in ionic compounds, the transfer of electrons is from Al to O. There are three valence electrons in each Al atom; each O atom needs two electrons to form the O^{2-} ion, which is isoelectronic with neon. Thus, the simplest neutralizing ratio of Al^{3+} to O^{2-} is 2:3; two Al^{3+} ions have a total charge of +6, and three O^{2-} ions have a total charge of −6. So the empirical formula of aluminum oxide is Al_2O_3, and the reaction is

$$\begin{array}{ccccc} 2\cdot\dot{\text{Al}}\cdot \;+ & 3\cdot\ddot{\underset{\cdot\cdot}{\text{O}}}\cdot & \longrightarrow\; 2\text{Al}^{3+} & 3\,:\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-} & (\text{or Al}_2\text{O}_3) \\ [\text{Ne}]3s^23p^1 & 1s^22s^22p^4 & [\text{Ne}] & [\text{Ne}] & \end{array}$$

(Continued)

Check Make sure that the number of valence electrons (24) is the same on both sides of the equation. Are the subscripts in Al_2O_3 reduced to the smallest possible whole numbers?

Practice Exercise Use Lewis dot symbols to represent the formation of barium hydride.

Similar problems: 9.17, 9.18.

9.3 Lattice Energy of Ionic Compounds

We can predict which elements are likely to form ionic compounds based on ionization energy and electron affinity, but how do we evaluate the stability of an ionic compound? Ionization energy and electron affinity are defined for processes occurring in the gas phase, but at 1 atm and 25°C all ionic compounds are solids. The solid state is a very different environment because each cation in a solid is surrounded by a specific number of anions, and vice versa. Thus, the overall stability of a solid ionic compound depends on the interactions of all these ions and not merely on the interaction of a single cation with a single anion. A quantitative measure of the stability of any ionic solid is its ***lattice energy,*** defined as *the energy required to completely separate one mole of a solid ionic compound into gaseous ions.*

The Born-Haber Cycle for Determining Lattice Energies

Lattice energy cannot be measured directly. However, if we know the structure and composition of an ionic compound, we can calculate the compound's lattice energy by using ***Coulomb's***[†] ***law,*** which states that *the potential energy (E) between two ions is directly proportional to the product of their charges and inversely proportional to the distance of separation between them.* For a single Li^+ ion and a single F^- ion separated by distance r, the potential energy of the system is given by

$$\begin{aligned} E &\propto \frac{Q_{Li^+}Q_{F^-}}{r} \\ &= k\frac{Q_{Li^+}Q_{F^-}}{r} \qquad (9.2) \end{aligned}$$

Because energy = force × distance, Coulomb's law can also be stated as

$$F = k\frac{Q_{Li^+}Q_{F^-}}{r^2}$$

where F is the force between the ions.

where Q_{Li^+} and Q_{F^-} are the charges on the Li^+ and F^- ions and k is the proportionality constant. Because Q_{Li^+} is positive and Q_{F^-} is negative, E is a negative quantity, and the formation of an ionic bond from Li^+ and F^- is an exothermic process. Consequently, energy must be supplied to reverse the process (in other words, the lattice energy of LiF is positive), and so a bonded pair of Li^+ and F^- ions is more stable than separate Li^+ and F^- ions.

We can also determine lattice energy indirectly, by assuming that the formation of an ionic compound takes place in a series of steps. This procedure, known as the ***Born-Haber cycle,*** *relates lattice energies of ionic compounds to ionization energies, electron affinities, and other atomic and molecular properties.* It is based on Hess's

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[†] Charles Augustin de Coulomb (1736–1806). French physicist. Coulomb did research in electricity and magnetism and applied Newton's inverse square law to electricity. He also invented a torsion balance.

Interactivity:
Born-Haber Cycle for Lithium Fluoride
ARIS, Interactives

law (see Section 6.6). Developed by Max Born[‡] and Fritz Haber,[§] the Born-Haber cycle defines the various steps that precede the formation of an ionic solid. We will illustrate its use to find the lattice energy of lithium fluoride.

Consider the reaction between lithium and fluorine:

$$\mathrm{Li}(s) + \tfrac{1}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{LiF}(s)$$

The standard enthalpy change for this reaction is −594.1 kJ/mol. (Because the reactants and product are in their standard states, that is, at 1 atm, the enthalpy change is also the standard enthalpy of formation for LiF.) Keeping in mind that the sum of enthalpy changes for the steps is equal to the enthalpy change for the overall reaction (−594.1 kJ/mol), we can trace the formation of LiF from its elements through five separate steps. The process may not occur exactly this way, but this pathway enables us to analyze the energy changes of ionic compound formation, with the application of Hess's law.

1. Convert solid lithium to lithium vapor (the direct conversion of a solid to a gas is called sublimation):

$$\mathrm{Li}(s) \longrightarrow \mathrm{Li}(g) \qquad \Delta H^\circ_1 = 155.2\ \mathrm{kJ/mol}$$

The energy of sublimation for lithium is 155.2 kJ/mol.

2. Dissociate $\frac{1}{2}$ mole of F_2 gas into separate gaseous F atoms:

$$\tfrac{1}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{F}(g) \qquad \Delta H^\circ_2 = 75.3\ \mathrm{kJ/mol}$$

The F atoms in a F_2 molecule are held together by a covalent bond. The energy required to break this bond is called the bond enthalpy (Section 9.10).

The energy needed to break the bonds in 1 mole of F_2 molecules is 150.6 kJ. Here we are breaking the bonds in half a mole of F_2, so the enthalpy change is 150.6/2, or 75.3, kJ.

3. Ionize 1 mole of gaseous Li atoms (see Table 8.3):

$$\mathrm{Li}(g) \longrightarrow \mathrm{Li}^+(g) + e^- \qquad \Delta H^\circ_3 = 520\ \mathrm{kJ/mol}$$

This process corresponds to the first ionization of lithium.

4. Add 1 mole of electrons to 1 mole of gaseous F atoms. As discussed on page 33 the energy change for this process is just the opposite of electron affinity (see Table 8.3):

$$\mathrm{F}(g) + e^- \longrightarrow \mathrm{F}^-(g) \qquad \Delta H^\circ_4 = -328\ \mathrm{kJ/mol}$$

5. Combine 1 mole of gaseous Li^+ and 1 mole of F^- to form 1 mole of solid LiF:

$$\mathrm{Li}^+(g) + \mathrm{F}^-(g) \longrightarrow \mathrm{LiF}(s) \qquad \Delta H^\circ_5 =$$

The reverse of step 5,

$$\text{energy} + \mathrm{LiF}(s) \longrightarrow \mathrm{Li}^+(g) + \mathrm{F}^-(g)$$

[‡] Max Born (1882–1970). German physicist. Born was one of the founders of modern physics. His work covered a wide range of topics. He received the Nobel Prize in Physics in 1954 for his interpretation of the wave function for particles.

[§] Fritz Haber (1868–1934). German chemist. Haber's process for synthesizing ammonia from atmospheric nitrogen kept Germany supplied with nitrates for explosives during World War I. He also did work on gas warfare. In 1918 Haber received the Nobel Prize in Chemistry.

fines the lattice energy of LiF. Thus, the lattice energy must have the same magnitude as ΔH_5° but an opposite sign. Although we cannot determine ΔH_5° directly, we can calculate its value by the following procedure.

$$\begin{array}{lrll}
1. & \mathrm{Li}(s) \longrightarrow & \mathrm{Li}(g) & \Delta H_1^\circ = 155.2\ \mathrm{kJ/mol} \\
2. & \tfrac{1}{2}\mathrm{F}_2(g) \longrightarrow & \mathrm{F}(g) & \Delta H_2^\circ = 75.3\ \mathrm{kJ/mol} \\
3. & \mathrm{Li}(g) \longrightarrow & \mathrm{Li}^+(g) + e^- & \Delta H_3^\circ = 520\ \mathrm{kJ/mol} \\
4. & \mathrm{F}(g) + e^- \longrightarrow & \mathrm{F}^-(g) & \Delta H_4^\circ = -328\ \mathrm{kJ/mol} \\
5. & \mathrm{Li}^+(g) + \mathrm{F}^-(g) \longrightarrow & \mathrm{LiF}(s) & \Delta H_5^\circ = ? \\
\hline
 & \mathrm{Li}(s) + \tfrac{1}{2}\mathrm{F}_2(g) \longrightarrow & \mathrm{LiF}(s) & \Delta H_{\mathrm{overall}}^\circ = -594.1\ \mathrm{kJ/mol}
\end{array}$$

According to Hess's law, we can write

$$\Delta H_{\mathrm{overall}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$

or

$$-594.1\ \mathrm{kJ/mol} = 155.2\ \mathrm{kJ/mol} + 75.3\ \mathrm{kJ/mol} + 520\ \mathrm{kJ/mol} - 328\ \mathrm{kJ/mol} + \Delta H_5^\circ$$

Hence

$$\Delta H_5^\circ = -1017\ \mathrm{kJ/mol}$$

and the lattice energy of LiF is +1017 kJ/mol.

Figure 9.2 summarizes the Born-Haber cycle for LiF. Steps 1, 2, and 3 all require the input of energy. On the other hand, steps 4 and 5 release energy. Because ΔH_5° is a large negative quantity, the lattice energy of LiF is a large positive quantity, which accounts for the stability of solid LiF. The greater the lattice energy, the more stable the ionic compound. Keep in mind that lattice energy is *always* a positive quantity because the separation of ions in a solid into ions in the gas phase is, by Coulomb's law, an endothermic process.

Table 9.1 lists the lattice energies and the melting points of several common ionic compounds. There is a rough correlation between lattice energy and melting point. The larger the lattice energy, the more stable the solid and the more tightly held the ions. It takes more energy to melt such a solid, and so the solid has a higher melting point than one with a smaller lattice energy. Note that $MgCl_2$, Na_2O, and MgO have

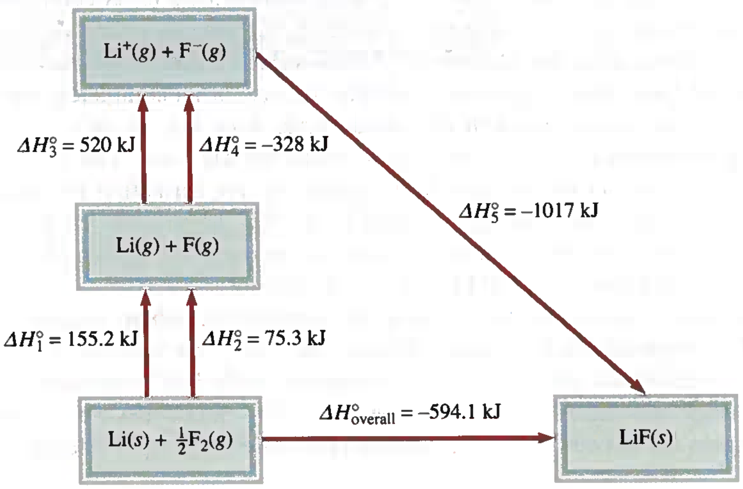


Figure 9.2 *The Born-Haber cycle for the formation of 1 mole of solid LiF.*

TABLE 9.1 Lattice Energies and Melting Points of Some Alkali Metal and Alkaline Earth Metal Halides and Oxides

Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
LiBr	787	550
LiI	732	450
NaCl	788	801
NaBr	736	750
NaI	686	662
KCl	699	772
KBr	689	735
KI	632	680
$MgCl_2$	2527	714
Na_2O	2570	Sub*
MgO	3890	2800

*Na_2O sublimes at 1275°C.

unusually high lattice energies. The first of these ionic compounds has a doubly charged cation (Mg^{2+}) and the second a doubly charged anion (O^{2-}); in the third compound there is an interaction between two doubly charged species (Mg^{2+} and O^{2-}). The coulombic attractions between two doubly charged species, or between a doubly charged ion and a singly charged ion, are much stronger than those between singly charged anions and cations.

Lattice Energy and the Formulas of Ionic Compounds

Because lattice energy is a measure of the stability of ionic compounds, its value can help us explain the formulas of these compounds. Consider magnesium chloride as an example. We have seen that the ionization energy of an element increases rapidly as successive electrons are removed from its atom. For example, the first ionization energy of magnesium is 738 kJ/mol, and the second ionization energy is 1450 kJ/mol, almost twice the first. We might ask why, from the standpoint of energy, magnesium does not prefer to form unipositive ions in its compounds. Why doesn't magnesium chloride have the formula MgCl (containing the Mg^+ ion) rather than $MgCl_2$ (containing the Mg^{2+} ion)? Admittedly, the Mg^{2+} ion has the noble gas configuration [Ne], which represents stability because of its completely filled shells. But the stability gained through the filled shells does not, in fact, outweigh the energy input needed to remove an electron from the Mg^+ ion. The reason the formula is $MgCl_2$ lies in the extra stability gained by the formation of solid magnesium chloride. The lattice energy of $MgCl_2$ is 2527 kJ/mol, which is more than enough to compensate for the energy needed to remove the first two electrons from a Mg atom (738 kJ/mol + 1450 kJ/mol = 2188 kJ/mol).

What about sodium chloride? Why is the formula for sodium chloride NaCl and not $NaCl_2$ (containing the Na^{2+} ion)? Although Na^{2+} does not have the noble gas electron configuration, we might expect the compound to be $NaCl_2$ because Na^{2+} has a higher charge and therefore the hypothetical $NaCl_2$ should have a greater lattice energy. Again the answer lies in the balance between energy input (that is, ionization

CHEMISTRY *in Action*

Sodium Chloride—A Common and Important Ionic Compound

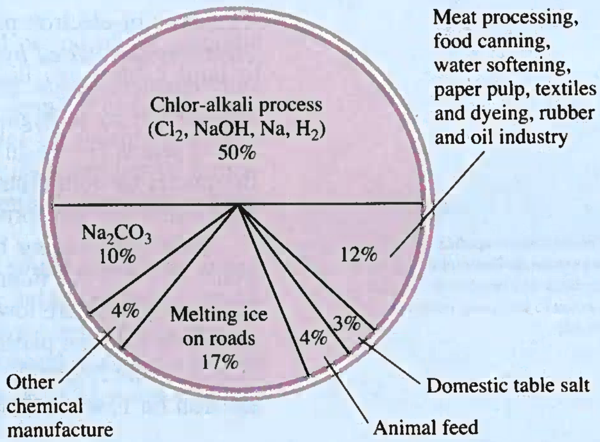
We are all familiar with sodium chloride as table salt. It is a typical ionic compound, a brittle solid with a high melting point (801°C) that conducts electricity in the molten state and in aqueous solution. The structure of solid NaCl is shown in Figure 2.13.

One source of sodium chloride is rock salt, which is found in subterranean deposits often hundreds of meters thick. It is also obtained from seawater or brine (a concentrated NaCl solution) by solar evaporation. Sodium chloride also occurs in nature as the mineral *halite.*

Sodium chloride is used more often than any other material in the manufacture of inorganic chemicals. World consumption of this substance is about 150 million tons per year. The major use of sodium chloride is in the production of other essential inorganic chemicals such as chlorine gas, sodium hydroxide, sodium metal, hydrogen gas, and sodium carbonate. It is also used to melt ice and snow on highways and roads. However, because sodium chloride is harmful to plant life and promotes corrosion of cars, its use for this purpose is of considerable environmental concern.

Solar evaporation process for obtaining sodium chloride.

Underground rock salt mining.



Uses of sodium chloride.

energies) and the stability gained from the formation of the solid. The sum of the first two ionization energies of sodium is

$$496 \text{ kJ/mol} + 4560 \text{ kJ/mol} = 5056 \text{ kJ/mol}$$

The compound $NaCl_2$ does not exist, but if we assume a value of 2527 kJ/mol as its lattice energy (same as that for $MgCl_2$), we see that the energy yield would be far too small to compensate for the energy required to produce the Na^{2+} ion.

What has been said about the cations applies also to the anions. In Sect we observed that the electron affinity of oxygen is 141 kJ/mol, meaning that th lowing process releases energy (and is therefore favorable):

$$O(g) + e^- \longrightarrow O^-(g)$$

As we would expect, adding another electron to the O^- ion

$$O^-(g) + e^- \longrightarrow O^{2-}(g)$$

would be unfavorable because of the increase in electrostatic repulsion. Indeed electron affinity of O^- is negative. Yet compounds containing the oxide ion (O exist and are very stable, whereas compounds containing the O^- ion are not kn Again, the high lattice energy resulting from the presence of O^{2-} ions in compo such as Na_2O or MgO far outweighs the energy needed to produce the O^{2-} ion

9.4 The Covalent Bond

Animation:
Ionic vs. Covalent Bonding
ARIS, Animations

Although the concept of molecules goes back to the seventeenth century, it was until early in the twentieth century that chemists began to understand how and molecules form. The first major breakthrough was Gilbert Lewis's suggestion th chemical bond involves electron sharing by atoms. He depicted the formation chemical bond in H_2 as

$$H\cdot + \cdot H \longrightarrow H:H$$

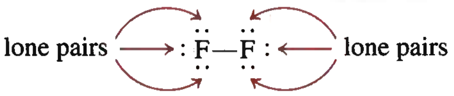
This type of electron pairing is an example of a ***covalent bond,*** *a bond in which electrons are shared by two atoms.* ***Covalent compounds*** *are compounds that con only covalent bonds.* For the sake of simplicity, the shared pair of electrons is represented by a single line. Thus, the covalent bond in the hydrogen molecule be written as H—H. In a covalent bond, each electron in a shared pair is attracted the nuclei of both atoms. This attraction holds the two atoms in H_2 together and responsible for the formation of covalent bonds in other molecules.

This discussion applies only to representative elements. Remember that for these elements, the number of valence electrons is equal to the group number (Groups 1A–7A).

Covalent bonding between many-electron atoms involves only the valence el trons. Consider the fluorine molecule, F_2. The electron configuration of F is $1s^22s$ The $1s$ electrons are low in energy and stay near the nucleus most of the time. For th reason they do not participate in bond formation. Thus, each F atom has seven valen electrons (the $2s$ and $2p$ electrons). According to Figure 9.1, there is only one unpaired electron on F, so the formation of the F_2 molecule can be represented as follows:

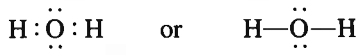
$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \qquad \text{or} \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

Note that only two valence electrons participate in the formation of F_2. The other, non bonding electrons, are called ***lone pairs***—*pairs of valence electrons that are not involved in covalent bond formation.* Thus, each F in F_2 has three lone pairs of electrons:



The structures we use to represent covalent compounds, such as H_2 and F_2, are called Lewis structures. A ***Lewis structure*** is *a representation of covalent bonding in* *which shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms.* Only valence electrons are shown in a Lewis structure.

Let us consider the Lewis structure of the water molecule. Figure 9.1 shows the Lewis dot symbol for oxygen with two unpaired dots or two unpaired electrons, so we expect that O might form two covalent bonds. Because hydrogen has only one electron, it can form only one covalent bond. Thus, the Lewis structure for water is



Interactivity:
Covalent Bonds
ARIS, Interactives

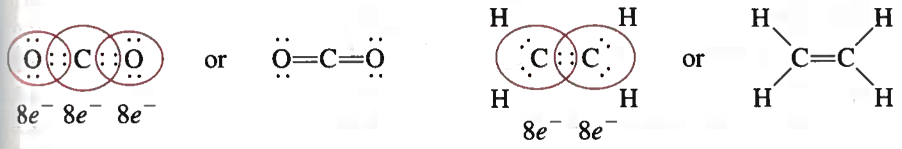
In this case, the O atom has two lone pairs. The hydrogen atom has no lone pairs because its only electron is used to form a covalent bond.

In the F_2 and H_2O molecules, the F and O atoms achieve the stable noble gas configuration by sharing electrons:

The formation of these molecules illustrates the ***octet rule,*** formulated by Lewis: *An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons.* In other words, a covalent bond forms when there are not enough electrons for each individual atom to have a complete octet. By sharing electrons in a covalent bond, the individual atoms can complete their octets. The requirement for hydrogen is that it attain the electron configuration of helium, or a total of two electrons.

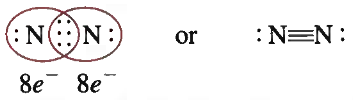
The octet rule works mainly for elements in the second period of the periodic table. These elements have only 2*s* and 2*p* subshells, which can hold a total of eight electrons. When an atom of one of these elements forms a covalent compound, it can attain the noble gas electron configuration [Ne] by sharing electrons with other atoms in the same compound. Later, we will discuss a number of important exceptions to the octet rule that give us further insight into the nature of chemical bonding.

Atoms can form different types of covalent bonds. In a ***single bond,*** *two atoms are held together by one electron pair.* Many compounds are held together by ***multiple bonds,*** that is, bonds formed when *two atoms share two or more pairs of electrons.* If *two atoms share two pairs of electrons,* the covalent bond is called a ***double bond.*** Double bonds are found in molecules of carbon dioxide (CO_2) and ethylene (C_2H_4):



Shortly, you will be introduced to the rules for writing proper Lewis structures. Here we simply want to become familiar with the language associated with them.

A ***triple bond*** arises when *two atoms share three pairs of electrons,* as in the nitrogen molecule (N_2):



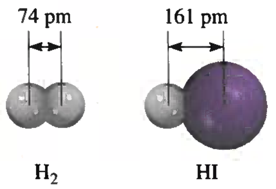
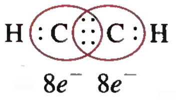


Figure 9.3 *Bond length (in pm) in H_2 and HI.*

The acetylene molecule (C_2H_2) also contains a triple bond, in this case between two carbon atoms:



or H—C≡C—H

Note that in ethylene and acetylene all the valence electrons are used in bonding; there are no lone pairs on the carbon atoms. In fact, with the exception of carbon monoxide, stable molecules containing carbon do not have lone pairs on the carbon atoms.

Multiple bonds are shorter than single covalent bonds. ***Bond length*** is defined as the *distance between the nuclei of two covalently bonded atoms in a molecule* (Figure 9.3). Table 9.2 shows some experimentally determined bond lengths. For a given pair of atoms, such as carbon and nitrogen, triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds. The shorter multiple bonds are also more stable than single bonds, as we will see later.

Comparison of the Properties of Covalent and Ionic Compounds

Ionic and covalent compounds differ markedly in their general physical properties because of differences in the nature of their bonds. There are two types of attractive forces in covalent compounds. The first type is the force that holds the atoms together in a molecule. A quantitative measure of this attraction is given by bond enthalpy, to be discussed in Section 9.10. The second type of attractive force operates *between* molecules and is called an *intermolecular force.* Because intermolecular forces are usually quite weak compared with the forces holding atoms together within a molecule, molecules of a covalent compound are not held together tightly. Consequently covalent compounds are usually gases, liquids, or low-melting solids. On the other hand, the electrostatic forces holding ions together in an ionic compound are usually very strong, so ionic compounds are solids at room temperature and have high melting points. Many ionic compounds are soluble in water, and the resulting aqueous solutions conduct electricity, because the compounds are strong electrolytes. Most

If intermolecular forces are weak, it is relatively easy to break up aggregates of molecules to form liquids (from solids) and gases (from liquids).

TABLE 9.2

Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C=O	121
C—C	154
C=C	133
C≡C	120
C—N	143
C=N	138
C≡N	116
N—O	136
N=O	122
O—H	96

TABLE 9.3 **Comparison of Some General Properties of an Ionic Compound and a Covalent Compound**

Property	NaCl	CCl_4
Appearance	White solid	Colorless liquid
Melting point (°C)	801	−23
Molar heat of fusion* (kJ/mol)	30.2	2.5
Boiling point (°C)	1413	76.5
Molar heat of vaporization* (kJ/mol)	600	30
Density (g/cm^3)	2.17	1.59
Solubility in water	High	Very low
Electrical conductivity		
Solid	Poor	Poor
Liquid	Good	Poor

*Molar heat of fusion and molar heat of vaporization are the amounts of heat needed to melt 1 mole of the solid and to vaporize 1 mole of the liquid, respectively.

covalent compounds are insoluble in water, or if they do dissolve, their aqueous solutions generally do not conduct electricity, because the compounds are nonelectrolytes. Molten ionic compounds conduct electricity because they contain mobile cations and anions; liquid or molten covalent compounds do not conduct electricity because no ions are present. Table 9.3 compares some of the general properties of a typical ionic compound, sodium chloride, with those of a covalent compound, carbon tetrachloride (CCl_4).

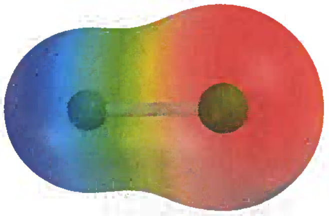


Figure 9.4 *Electrostatic potential map of the HF molecule. The distribution varies according to the colors of the rainbow. The most electron-rich region is red; the most electron-poor region is blue.*

9.5 Electronegativity

A covalent bond, as we have said, is the sharing of an electron pair by two atoms. In a molecule like H_2, in which the atoms are identical, we expect the electrons to be equally shared—that is, the electrons spend the same amount of time in the vicinity of each atom. However, in the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally because H and F are different atoms:

$$\text{H—}\ddot{\underset{\cdot\cdot}{\text{F}}}\text{:}$$

Hydrogen fluoride is a clear, fuming liquid that boils at 19.8°C. It is used to make refrigerants and to prepare hydrofluoric acid.

The bond in HF is called a ***polar covalent bond,*** or simply a *polar bond,* because *the electrons spend more time in the vicinity of one atom than the other.* Experimental evidence indicates that in the HF molecule the electrons spend more time near the F atom. We can think of this unequal sharing of electrons as a partial electron transfer or a shift in electron density, as it is more commonly described, from H to F (Figure 9.4). This "unequal sharing" of the bonding electron pair results in a relatively greater electron density near the fluorine atom and a correspondingly lower electron density near hydrogen. The HF bond and other polar bonds can be thought of as being intermediate between a (nonpolar) covalent bond, in which the sharing of electrons is exactly equal, and an ionic bond, in which the *transfer of the electron(s) is nearly complete.*

A property that helps us distinguish a nonpolar covalent bond from a polar covalent bond is ***electronegativity,*** *the ability of an atom to attract toward itself the electrons in a chemical bond.* Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity. As we might expect, electronegativity is related to electron affinity and ionization energy. Thus, an atom such as fluorine, which has a high electron affinity (tends to pick up electrons easily) and a high ionization energy (does not lose electrons easily), has a high electronegativity. On the other hand, sodium has a low electron affinity, a low ionization energy, and a low electronegativity.

Electronegativity values have no units.

Electronegativity is a relative concept, meaning that an element's electronegativity can be measured only in relation to the electronegativity of other elements. Linus Pauling[†] devised a method for calculating *relative* electronegativities of most elements. These values are shown in Figure 9.5. A careful examination of this chart reveals trends and relationships among electronegativity values of different elements. In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each group,

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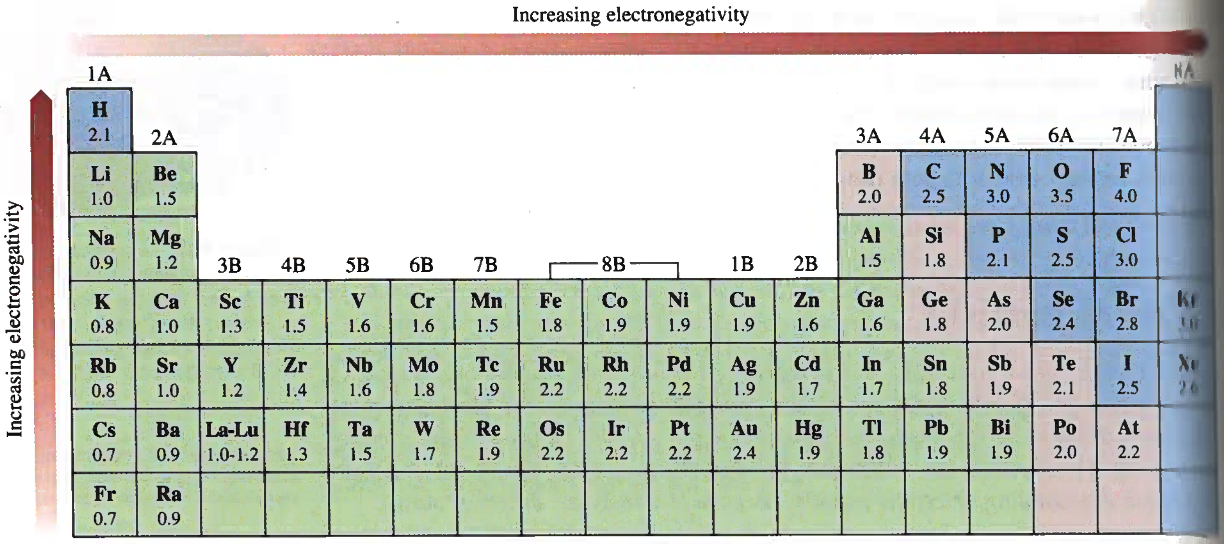
[†] Linus Carl Pauling (1901–1994). American chemist. Regarded by many as the most influential chemist of the twentieth century, Pauling did research in a remarkably broad range of subjects, from chemical physics to molecular biology. Pauling received the Nobel Prize in Chemistry in 1954 for his work on protein structure, and the Nobel Peace Prize in 1962. He is the only person to be the sole recipient of two Nobel Prizes.



1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9															

Figure 9.5 *The electronegativities of common elements.*

electronegativity decreases with increasing atomic number, and increasing metall character. Note that the transition metals do not follow these trends. The most el tronegative elements—the halogens, oxygen, nitrogen, and sulfur—are found in th upper right-hand corner of the periodic table, and the least electronegative eleme (the alkali and alkaline earth metals) are clustered near the lower left-hand corn These trends are readily apparent on a graph, as shown in Figure 9.6.

Atoms of elements with widely different electronegativities tend to form ioni bonds (such as those that exist in NaCl and CaO compounds) with each other beca the atom of the less electronegative element gives up its electron(s) to the atom o the more electronegative element. An ionic bond generally joins an atom of a meta lic element and an atom of a nonmetallic element. Atoms of elements with compa rable electronegativities tend to form polar covalent bonds with each other beca

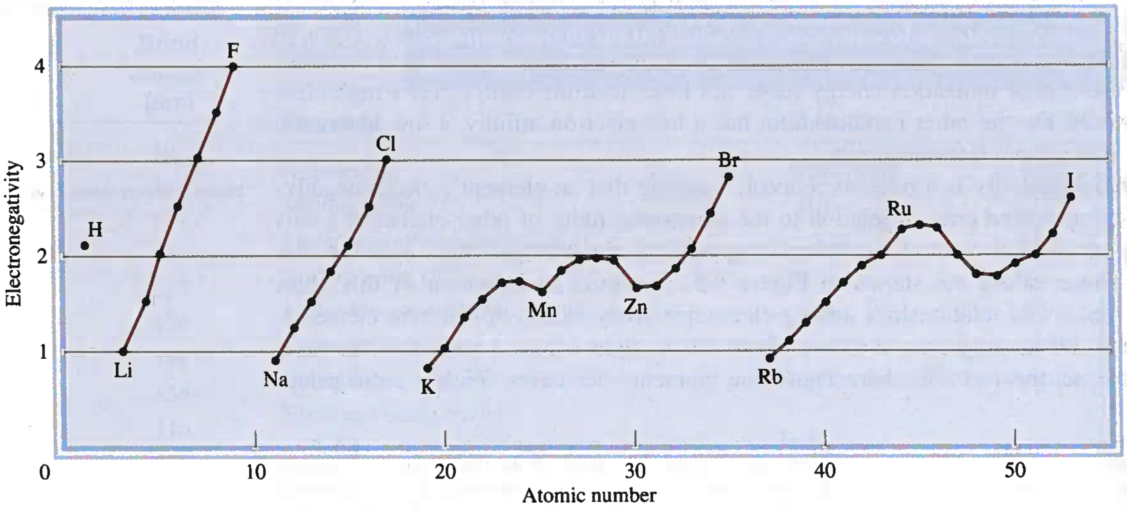


Figure 9.6 *Variation of electronegativity with atomic number. The halogens have the highest electronegativities, and the alkali metals the lowest.*

the shift in electron density is usually small. Most covalent bonds involve atoms of nonmetallic elements. Only atoms of the same element, which have the same electronegativity, can be joined by a pure covalent bond. These trends and characteristics are what we would expect, given our knowledge of ionization energies and electron affinities.

There is no sharp distinction between a polar bond and an ionic bond, but the following general rule is helpful in distinguishing between them. An ionic bond forms when the electronegativity difference between the two bonding atoms is 2.0 or more. This rule applies to most but not all ionic compounds. Sometimes chemists use the quantity *percent ionic character* to describe the nature of a bond. A purely ionic bond would have 100 percent ionic character, although no such bond is known, whereas a nonpolar or purely covalent bond has 0 percent ionic character. As Figure 9.7 shows, there is a correlation between the percent ionic character of a bond and the electronegativity difference between the bonding atoms.

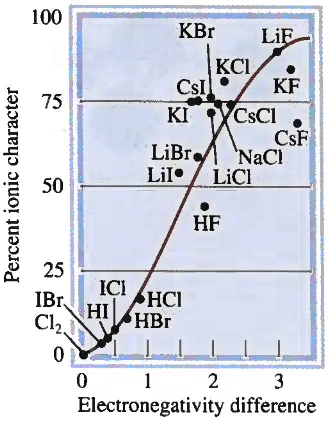


Figure 9.7 *Relation between percent ionic character and electronegativity difference.*

Electronegativity and electron affinity are related but different concepts. Both indicate the tendency of an atom to attract electrons. However, electron affinity refers to an isolated atom's attraction for an additional electron, whereas electronegativity signifies the ability of an atom in a chemical bond (with another atom) to attract the shared electrons. Furthermore, electron affinity is an experimentally measurable quantity, whereas electronegativity is an estimated number that cannot be measured.

Example 9.2 shows how a knowledge of electronegativity can help us determine whether a chemical bond is covalent or ionic.

Example 9.2

Classify the following bonds as ionic, polar covalent, or covalent: (a) the bond in HCl, (b) the bond in KF, and (c) the CC bond in H_3CCH_3.

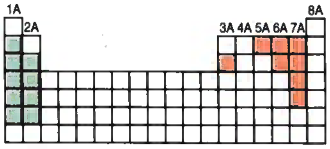
Strategy We follow the 2.0 rule of electronegativity difference and look up the values in Figure 9.5.

Solution (a) The electronegativity difference between H and Cl is 0.9, which is appreciable but not large enough (by the 2.0 rule) to qualify HCl as an ionic compound. Therefore, the bond between H and Cl is polar covalent.

(b) The electronegativity difference between K and F is 3.2, which is well above the 2.0 mark; therefore, the bond between K and F is ionic.

(c) The two C atoms are identical in every respect—they are bonded to each other and each is bonded to three other H atoms. Therefore, the bond between them is purely covalent.

Practice Exercise Which of the following bonds is covalent, which is polar covalent, and which is ionic? (a) the bond in CsCl, (b) the bond in H_2S, (c) the NN bond in H_2NNH_2.



The most electronegative elements are the nonmetals (Groups 5A–7A) and the least electronegative elements are the alkali and alkaline earth metals (Groups 1A–2A) and aluminum. Beryllium, the first member of Group 2A, forms mostly covalent compounds.

Similar problems: 9.39, 9.40.

Electronegativity and Oxidation Number

In Chapter 4 we introduced the rules for assigning oxidation numbers of elements in their compounds. The concept of electronegativity is the basis for these rules. In essence, oxidation number refers to the number of charges an atom would have if electrons were transferred completely to the more electronegative of the bonded atoms in a molecule.

Consider the NH_3 molecule, in which the N atom forms three single bonds with the H atoms. Because N is more electronegative than H, electron density will be shifted from H to N. If the transfer were complete, each H would donate an electron to N, which would have a total charge of −3 while each H would have a charge of +1. Thus, we assign an oxidation number of −3 to N and an oxidation number of +1 to H in NH_3.

Oxygen usually has an oxidation number of −2 in its compounds, except in hydrogen peroxide (H_2O_2), whose Lewis structure is

$$\mathrm{H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H}$$

A bond between identical atoms makes no contribution to the oxidation number of those atoms because the electron pair of that bond is *equally* shared. Because H has an oxidation number of +1, each O atom has an oxidation number of −1.

Can you see now why fluorine always has an oxidation number of −1? It is the most electronegative element known, and it *always* forms a single bond in its compounds. Therefore, it would bear a −1 charge if electron transfer were complete.

9.6 Writing Lewis Structures

Interactivity:
Lewis Dot Structure
ARIS, Interactives

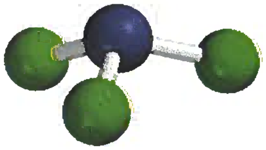
Although the octet rule and Lewis structures do not present a complete picture of covalent bonding, they do help to explain the bonding scheme in many compounds and account for the properties and reactions of molecules. For this reason, you should practice writing Lewis structures of compounds. The basic steps are as follows:

1. Write the skeletal structure of the compound, using chemical symbols and placing bonded atoms next to one another. For simple compounds, this task is fairly easy. For more complex compounds, we must either be given the information or make an intelligent guess about it. In general, the least electronegative atom occupies the central position. Hydrogen and fluorine usually occupy the terminal (end) positions in the Lewis structure.
2. Count the total number of valence electrons present, referring, if necessary, to Figure 9.1. For polyatomic anions, add the number of negative charges to that total. (For example, for the CO_3^{2-} ion we add two electrons because the 2− charge indicates that there are two more electrons than are provided by the atoms.) For polyatomic cations, we subtract the number of positive charges from this total. (Thus, for NH_4^+ we subtract one electron because the 1+ charge indicates a loss of one electron from the group of atoms.)
3. Draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms bonded to the central atom. (Remember that the valence shell of a hydrogen atom is complete with only two electrons.) Electrons belonging to the central or surrounding atoms must be shown as lone pairs if they are not involved in bonding. The total number of electrons to be used is that determined in step 2.
4. After completing steps 1–3, if the central atom has fewer than eight electrons, try adding double or triple bonds between the surrounding atoms and the central atom, using lone pairs from the surrounding atoms to complete the octet of the central atom.

Examples 9.3, 9.4, and 9.5 illustrate the four-step procedure for writing Lewis structures of compounds and an ion.

Example 9.3

Write the Lewis structure for nitrogen trifluoride (NF_3) in which all three F atoms are bonded to the N atom.



NF_3 is a colorless, odorless, unreactive gas.

Solution We follow the preceding procedure for writing Lewis structures.

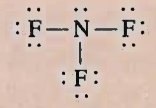
Step 1: The N atom is less electronegative than F, so the skeletal structure of NF_3 is

F N F

F

Step 2: The outer-shell electron configurations of N and F are $2s^22p^3$ and $2s^22p^5$, respectively. Thus, there are $5 + (3 \times 7)$, or 26, valence electrons to account for in NF_3.

Step 3: We draw a single covalent bond between N and each F, and complete the octets for the F atoms. We place the remaining two electrons on N:



Because this structure satisfies the octet rule for all the atoms, step 4 is not required.

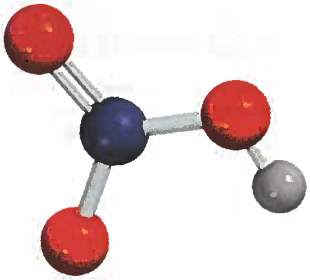
Check Count the valence electrons in NF_3 (in bonds and in lone pairs). The result is 26, the same as the total number of valence electrons on three F atoms ($3 \times 7 = 21$) and one N atom (5).

Similar problem: 9.45.

Practice Exercise Write the Lewis structure for carbon disulfide (CS_2).

Example 9.4

Write the Lewis structure for nitric acid (HNO_3) in which the three O atoms are bonded to the central N atom and the ionizable H atom is bonded to one of the O atoms.



HNO_3 is a strong electrolyte.

Solution We follow the procedure already outlined for writing Lewis structures.

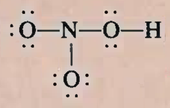
Step 1: The skeletal structure of HNO_3 is

O N O H

O

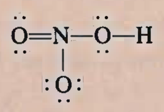
Step 2: The outer-shell electron configurations of N, O, and H are $2s^22p^3$, $2s^22p^4$, and $1s^1$, respectively. Thus, there are $5 + (3 \times 6) + 1$, or 24, valence electrons to account for in HNO_3.

Step 3: We draw a single covalent bond between N and each of the three O atoms and between one O atom and the H atom. Then we fill in electrons to comply with the octet rule for the O atoms:



(Continued)

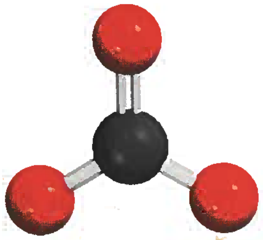
Step 4: We see that this structure satisfies the octet rule for all the O atoms but not the N atom. The N atom has only six electrons. Therefore, we move a lone pair from one of the end O atoms to form another bond with N. Now the octet rule is also satisfied for the N atom:



Check Make sure that all the atoms (except H) satisfy the octet rule. Count the valence electrons in HNO_3 (in bonds and in lone pairs). The result is 24, the same as the total number of valence electrons on three O atoms ($3 \times 6 = 18$), one N atom and one H atom (1).

Similar problem: 9.45.

Practice Exercise Write the Lewis structure for formic acid (HCOOH).



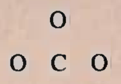
CO_3^{2-}

Example 9.5

Write the Lewis structure for the carbonate ion (CO_3^{2-}).

Solution We follow the preceding procedure for writing Lewis structures and note that this is an anion with two negative charges.

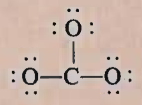
Step 1: We can deduce the skeletal structure of the carbonate ion by recognizing that C is less electronegative than O. Therefore, it is most likely to occupy a central position as follows:



$$\begin{matrix} & O & \\ O & C & O \end{matrix}$$

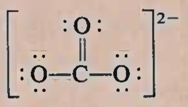
Step 2: The outer-shell electron configurations of C and O are $2s^2 2p^2$ and $2s^2 2p^4$, respectively, and the ion itself has two negative charges. Thus, the total number of electrons is $4 + (3 \times 6) + 2$, or 24.

Step 3: We draw a single covalent bond between C and each O and comply with the octet rule for the O atoms:



This structure shows all 24 electrons.

Step 4: Although the octet rule is satisfied for the O atoms, it is not for the C atom. Therefore, we move a lone pair from one of the O atoms to form another bond with C. Now the octet rule is also satisfied for the C atom:



We use the brackets to indicate that the −2 charge is on the whole molecule.

Check Make sure that all the atoms satisfy the octet rule. Count the valence electrons in CO_3^{2-} (in chemical bonds and in lone pairs). The result is 24, the same as the total number of valence electrons on three O atoms ($3 \times 6 = 18$), one C atom (4), and two negative charges (2).

Similar problem: 9.44.

Practice Exercise Write the Lewis structure for the nitrite ion (NO_2^-).

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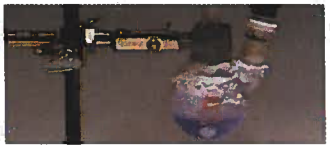
9.7 Formal Charge and Lewis Structure

By comparing the number of electrons in an isolated atom with the number of electrons that are associated with the same atom in a Lewis structure, we can determine the distribution of electrons in the molecule and draw the most plausible Lewis structure. The bookkeeping procedure is as follows: In an isolated atom, the number of electrons associated with the atom is simply the number of valence electrons. (As usual, we need not be concerned with the inner electrons.) In a molecule, electrons associated with the atom are the nonbonding electrons plus the electrons in the bonding pair(s) between the atom and other atom(s). However, because electrons are shared in a bond, we must divide the electrons in a bonding pair equally between the atoms forming the bond. An atom's ***formal charge*** is *the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.*

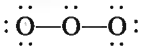
To assign the number of electrons on an atom in a Lewis structure, we proceed as follows:

- All the atom's nonbonding electrons are assigned to the atom.
- We break the bond(s) between the atom and other atom(s) and assign half of the bonding electrons to the atom.

Let us illustrate the concept of formal charge using the ozone molecule (O_3). Proceeding by steps, as we did in Examples 9.3 and 9.4, we draw the skeletal structure of O_3 and then add bonds and electrons to satisfy the octet rule for the two end atoms:

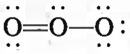


Liquid ozone below its boiling point (−111.3°C). Ozone is a toxic, light-blue gas with a pungent odor.



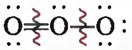
$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-\overset{\cdot\cdot}{O}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

You can see that although all available electrons are used, the octet rule is not satisfied for the central atom. To remedy this, we convert a lone pair on one of the end atoms to a second bond between that end atom and the central atom, as follows:



$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{O}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

The formal charge on each atom in O_3 can now be calculated according to the following scheme:

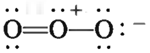


$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{O}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

Assign half of the bonding electrons to each atom.

Valence e^-	6	6	6
e^- assigned to atom	6	5	7
Difference (formal charge)	0	+1	−1

where the wavy red lines denote the breaking of the bonds. Note that the breaking of a single bond results in the transfer of an electron, the breaking of a double bond results in a transfer of two electrons to each of the bonding atoms, and so on. Thus, the formal charges of the atoms in O_3 are



$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{\overset{+}{O}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$$

For single positive and negative charges, we normally omit the numeral 1.

When you write formal charges, these rules are helpful:

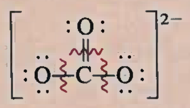
1. For molecules, the sum of the formal charges must add up to zero because molecules are electrically neutral species. (This rule applies, for example, to the O_3 molecule.)
2. For cations, the sum of the formal charges must equal the positive charge.
3. For anions, the sum of the formal charges must equal the negative charge.

Keep in mind that formal charges do not represent actual charge separation within the molecule. In the O_3 molecule, for example, there is no evidence that the central atom bears a net +1 charge or that one of the end atoms bears a −1 charge. Writing these charges on the atoms in the Lewis structure merely helps us keep track of the valence electrons in the molecule.

Example 9.6

Write formal charges for the carbonate ion.

Strategy The Lewis structure for the carbonate ion was developed in Example 9.5:



$$\left[\,\mathrm{O{-}C({=}O){-}O}\,\right]^{2-}$$

The formal charges on the atoms can be calculated using the given procedure.

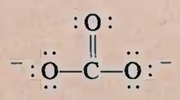
Solution We subtract the number of nonbonding electrons and half of the bonding electrons from the valence electrons of each atom.

The C atom: The C atom has four valence electrons and there are no nonbonding electrons on the atom in the Lewis structure. The breaking of the double bond and two single bonds results in the transfer of four electrons to the C atom. Therefore, the formal charge is $4 - 4 = 0$.

The O atom in C=O: The O atom has six valence electrons and there are four nonbonding electrons on the atom. The breaking of the double bond results in the transfer of two electrons to the O atom. Here the formal charge is $6 - 4 - 2 = 0$.

The O atom in C—O: This atom has six nonbonding electrons and the breaking of the single bond transfers another electron to it. Therefore, the formal charge is $6 - 6 - 1 = -1$.

Thus, the Lewis structure for CO_3^{2-} with formal charges is



$$^{-}\mathrm{O{-}C({=}O){-}O}^{-}$$

Check Note that the sum of the formal charges is −2, the same as the charge on the carbonate ion.

Similar problem: 9.46.

Practice Exercise Write formal charges for the nitrite ion (NO_2^-).

Sometimes there is more than one acceptable Lewis structure for a given species. In such cases, we can often select the most plausible Lewis structure by using formal charges and the following guidelines:

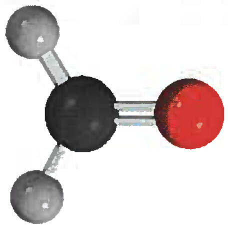
- For molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.

- Lewis structures with large formal charges (+2, +3, and/or −2, −3, and so on) are less plausible than those with small formal charges.
- Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

Example 9.7 shows how formal charges facilitate the choice of the correct Lewis structure for a molecule.

Example 9.7

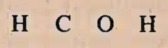
Formaldehyde (CH_2O), a liquid with a disagreeable odor, traditionally has been used to preserve laboratory specimens. Draw the most likely Lewis structure for the compound.



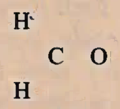
CH_2O

Strategy A plausible Lewis structure should satisfy the octet rule for all the elements, except H, and have the formal charges (if any) distributed according to electronegativity guidelines.

Solution The two possible skeletal structures are

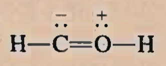


(a)

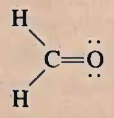


(b)

First we draw the Lewis structures for each of these possibilities



(a)



(b)

To show the formal charges, we follow the procedure given in Example 9.6. In (a) the C atom has a total of five electrons (one lone pair plus three electrons from the breaking of a single and a double bond). Because C has four valence electrons, the formal charge on the atom is 4 − 5 = −1. The O atom has a total of five electrons (one lone pair and three electrons from the breaking of a single and a double bond). Because O has six valence electrons, the formal charge on the atom is 6 − 5 = +1. In (b) the C atom has a total of four electrons from the breaking of two single bonds and a double bond, so its formal charge is 4 − 4 = 0. The O atom has a total of six electrons (two lone pairs and two electrons from the breaking of the double bond). Therefore, the formal charge on the atom is 6 − 6 = 0. Although both structures satisfy the octet rule, (b) is the more likely structure because it carries no formal charges.

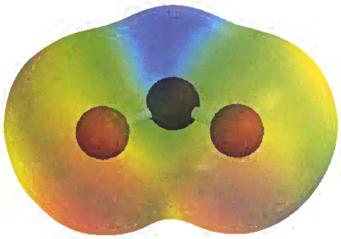
Check In each case make sure that the total number of valence electrons is 12. Can you suggest two other reasons why (a) is less plausible?

Similar problem: 9.47.

Practice Exercise Draw the most reasonable Lewis structure of a molecule that contains a N atom, a C atom, and an H atom.

9.8 The Concept of Resonance

Our drawing of the Lewis structure for ozone (O_3) satisfied the octet rule for the central atom because we placed a double bond between it and one of the two end O



Electrostatic potential map of O_3. The electron density is evenly distributed between the two end O atoms.

atoms. In fact, we can put the double bond at either end of the molecule, as
by these two equivalent Lewis structures:

$$\ddot{\underset{\cdot\cdot}{O}}=\overset{\cdot\cdot +}{O}-\ddot{\underset{\cdot\cdot}{O}}:^{-} \qquad {}^{-}:\ddot{\underset{\cdot\cdot}{O}}-\overset{\cdot\cdot +}{O}=\ddot{\underset{\cdot\cdot}{O}}$$

However, neither one of these two Lewis structures accounts for the known
lengths in O_3.

We would expect the O—O bond in O_3 to be longer than the O=O bond
double bonds are known to be shorter than single bonds. Yet experimental
shows that both oxygen-to-oxygen bonds are equal in length (128 pm). We resolve
discrepancy by using *both* Lewis structures to represent the ozone molecule:

$$\ddot{\underset{\cdot\cdot}{O}}=\overset{\cdot\cdot +}{O}-\ddot{\underset{\cdot\cdot}{O}}:^{-} \longleftrightarrow {}^{-}:\ddot{\underset{\cdot\cdot}{O}}-\overset{\cdot\cdot +}{O}=\ddot{\underset{\cdot\cdot}{O}}$$

Each of these structures is called a resonance structure. A ***resonance structure***,
is *one of two or more Lewis structures for a single molecule that cannot be*
sented accurately by only one Lewis structure. The double-headed arrow indicates
the structures shown are resonance structures.

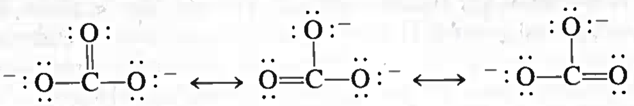
Interactivity:
Resonance
ARIS, Interactives

Animation:
Resonance
ARIS, Animations

The term ***resonance*** itself means *the use of two or more Lewis structures to*
resent a particular molecule. Like the medieval European traveler to Africa
described a rhinoceros as a cross between a griffin and a unicorn, two famili
imaginary animals, we describe ozone, a real molecule, in terms of two famili
nonexistent structures.

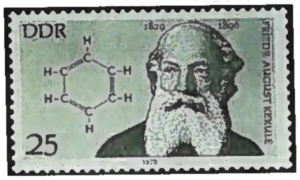
A common misconception about resonance is the notion that a molecule
ozone somehow shifts quickly back and forth from one resonance structure
other. Keep in mind that *neither* resonance structure adequately represents the
molecule, which has its own unique, stable structure. "Resonance" is a human
tion, designed to address the limitations in these simple bonding models. To
the animal analogy, a rhinoceros is a distinct creature, not some oscillation betw
mythical griffin and unicorn!

The carbonate ion provides another example of resonance:

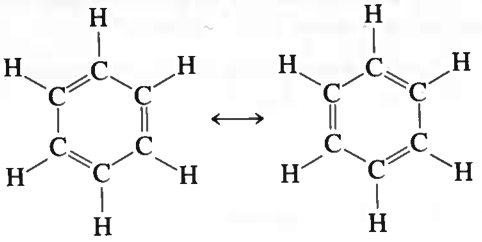


According to experimental evidence, all carbon-to-oxygen bonds in CO_3^{2-} are
alent. Therefore, the properties of the carbonate ion are best explained by consid
ing its resonance structures together.

The concept of resonance applies equally well to organic systems. A good exa
ple is the benzene molecule (C_6H_6):



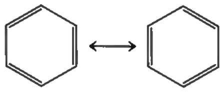
The hexagonal structure of benzene was first proposed by the German chemist August Kekulé (1829–1896).



If one of these resonance structures corresponded to the actual structure of benze
there would be two different bond lengths between adjacent C atoms, one characteri

of the single bond and the other of the double bond. In fact, the distance between all adjacent C atoms in benzene is 140 pm, which is shorter than a C—C bond (154 pm) and longer than a C═C bond (133 pm).

A simpler way of drawing the structure of the benzene molecule and other compounds containing the "benzene ring" is to show only the skeleton and not the carbon and hydrogen atoms. By this convention the resonance structures are represented by



Note that the C atoms at the corners of the hexagon and the H atoms are all omitted, although they are understood to exist. Only the bonds between the C atoms are shown.

Remember this important rule for drawing resonance structures: The positions of electrons, but not those of atoms, can be rearranged in different resonance structures. In other words, the same atoms must be bonded to one another in all the resonance structures for a given species.

Example 9.8 illustrates the procedure for drawing resonance structures of a molecule.

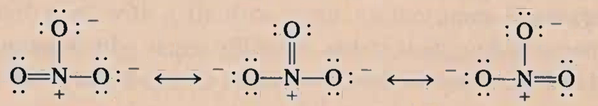
Example 9.8

Draw resonance structures (including formal charges) for the nitrate ion, NO_3^-, which has the following skeletal arrangement:

O
O N O

Strategy We follow the procedure used for drawing Lewis structures and calculating formal charges in Examples 9.5 and 9.6.

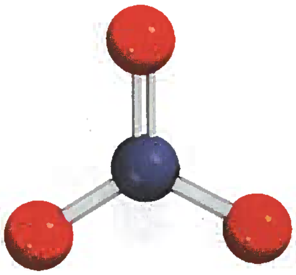
Solution Just as in the case of the carbonate ion, we can draw three equivalent resonance structures for the nitrate ion:



$$\underset{..}{\overset{..}{O}}=\underset{+}{N}(-\underset{..}{\overset{..}{:O:}}^-)-\underset{..}{\overset{..}{O}}:^- \longleftrightarrow {}^-:\underset{..}{\overset{..}{O}}-\underset{+}{N}(=\overset{..}{:O:})-\underset{..}{\overset{..}{O}}:^- \longleftrightarrow {}^-:\underset{..}{\overset{..}{O}}-\underset{+}{N}(-\underset{..}{\overset{..}{:O:}}^-)=\underset{..}{\overset{..}{O}}$$

Check Because N has five valence electrons and each O has six valence electrons and there is a net negative charge, the total number of valence electrons is 5 + (3 × 6) + 1 = 24, the same as the number of valence electrons in the NO_3^- ion.

Practice Exercise Draw resonance structures for the nitrite ion (NO_2^-).



NO_3^-

Similar problems: 9.51, 9.56.

9.9 Exceptions to the Octet Rule

As mentioned earlier, the octet rule applies mainly to the second-period elements. Exceptions to the octet rule fall into three categories characterized by an incomplete octet, an odd number of electrons, or more than eight valence electrons around the central atom.

Interactivity:
Octet Rule Exceptions
ARIS, Interactives

Beryllium, unlike the other Group 2A elements, forms mostly covalent compounds of which BeH_2 is an example.

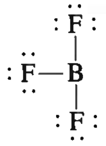
The Incomplete Octet

In some compounds the number of electrons surrounding the central atom in a molecule is fewer than eight. Consider, for example, beryllium, which is a Group (and a second-period) element. The electron configuration of beryllium is $1s^2$ has two valence electrons in the 2*s* orbital. In the gas phase, beryllium hydride (exists as discrete molecules. The Lewis structure of BeH_2 is

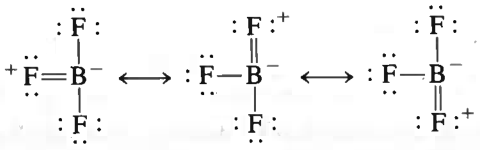
$$H—Be—H$$

As you can see, only four electrons surround the Be atom, and there is no way to isfy the octet rule for beryllium in this molecule.

Elements in Group 3A, particularly boron and aluminum, also tend to form pounds in which they are surrounded by fewer than eight electrons. Take boron example. Because its electron configuration is $1s^22s^22p^1$, it has a total of three val electrons. Boron reacts with the halogens to form a class of compounds having general formula BX_3, where X is a halogen atom. Thus, in boron trifluoride there only six electrons around the boron atom:

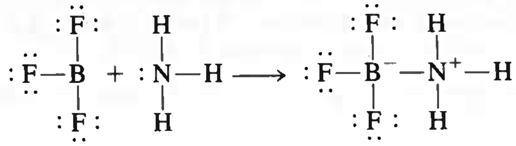


The following resonance structures all contain a double bond between B and satisfy the octet rule for boron:



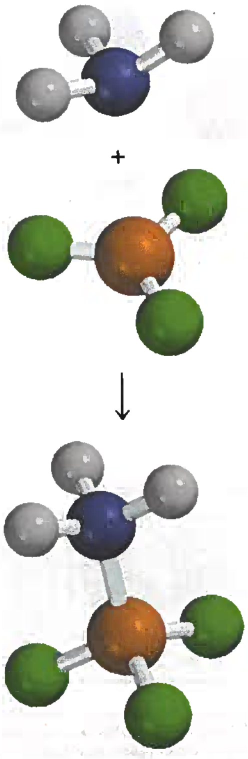
The fact that the B—F bond length in BF_3 (130.9 pm) is shorter than a single (137.3 pm) lends support to the resonance structures even though in each case negative formal charge is placed on the B atom and the positive formal charge on more electronegative F atom.

Although boron trifluoride is stable, it readily reacts with ammonia. This reac is better represented by using the Lewis structure in which boron has only six val electrons around it:



It seems that the properties of BF_3 are best explained by all four resonance structu

The B—N bond in the above compound is different from the covalent bon discussed so far in the sense that both electrons are contributed by the N atom This type of bond is called a ***coordinate covalent bond*** (also referred to as a *da* *bond*), defined as *a covalent bond in which one of the atoms donates both el* *trons.* Although the properties of a coordinate covalent bond do not differ f

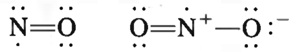


$NH_3 + BF_3 \longrightarrow H_3N—BF_3$

those of a normal covalent bond (because all electrons are alike no matter what their source), the distinction is useful for keeping track of valence electrons and assigning formal charges.

Odd-Electron Molecules

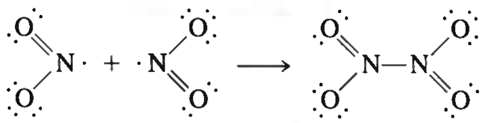
Some molecules contain an *odd* number of electrons. Among them are nitric oxide (NO) and nitrogen dioxide (NO_2):



$\dot{N}=\ddot{O} \quad \ddot{O}=\dot{N}^{+}-\ddot{O}:^{-}$

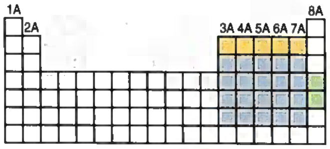
Because we need an even number of electrons for complete pairing (to reach eight), the octet rule clearly cannot be satisfied for all the atoms in any of these molecules.

Odd-electron molecules are sometimes called *radicals*. Many radicals are highly reactive. The reason is that there is a tendency for the unpaired electron to form a covalent bond with an unpaired electron on another molecule. For example, when two nitrogen dioxide molecules collide, they form dinitrogen tetroxide in which the octet rule is satisfied for both the N and O atoms:

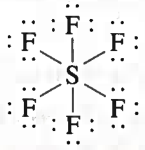


The Expanded Octet

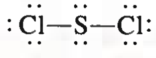
Atoms of the second-period elements cannot have more than eight valence electrons around the central atom, but atoms of elements in and beyond the third period of the periodic table form some compounds in which more than eight electrons surround the central atom. In addition to the 3*s* and 3*p* orbitals, elements in the third period also have 3*d* orbitals that can be used in bonding. These orbitals allow an atom to form an *expanded octet*. One compound in which there is an expanded octet is sulfur hexafluoride, a very stable compound. The electron configuration of sulfur is $[Ne]3s^23p^4$. In SF_6, each of sulfur's six valence electrons forms a covalent bond with a fluorine atom, so there are 12 electrons around the central sulfur atom:



Yellow: second-period elements cannot have an expanded octet. Blue: third-period elements and beyond can have an expanded octet. Green: the noble gases usually only have an expanded octet.



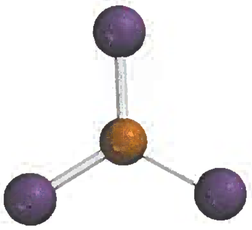
In Chapter 10 we will see that these 12 electrons, or six bonding pairs, are accommodated in six orbitals that originate from the one 3*s*, the three 3*p*, and two of the five 3*d* orbitals. Sulfur also forms many compounds in which it obeys the octet rule. In sulfur dichloride, for instance, S is surrounded by only eight electrons:



$:\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{S}}-\ddot{\underset{..}{Cl}}:$

Sulfur dichloride is a toxic, foul-smelling cherry-red liquid (boiling point: 59°C).

Examples 9.9–9.11 concern compounds that do not obey the octet rule.



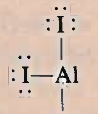
AlI_3 has a tendency to dimerize or form two units as Al_2I_6.

Example 9.9

Draw the Lewis structure for aluminum triiodide (AlI_3).

Strategy We follow the procedures used in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

Solution The outer-shell electron configurations of Al and I are $3s^23p^1$ and $5s^25p^5$, respectively. The total number of valence electrons is $3 + 3 \times 7$ or 24. Because Al is less electronegative than I, it occupies a central position and forms three bonds with the I atoms:

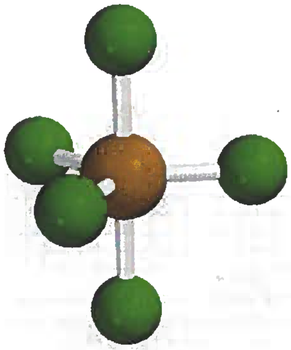


Note that there are no formal charges on the Al and I atoms.

Check Although the octet rule is satisfied for the I atoms, there are only six valence electrons around the Al atom. Thus, AlI_3 is an example of the incomplete octet.

Practice Exercise Draw the Lewis structure for BeF_2.

Similar problem: 9.62.



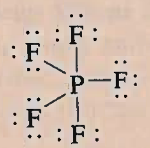
PF_5 is a reactive gaseous compound.

Example 9.10

Draw the Lewis structure for phosphorus pentafluoride (PF_5), in which all five F atoms are bonded to the central P atom.

Strategy Note that P is a third-period element. We follow the procedures given in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

Solution The outer-shell electron configurations for P and F are $3s^23p^3$ and $2s^22p^5$, respectively, and so the total number of valence electrons is $5 + (5 \times 7)$, or 40. Phosphorus, like sulfur, is a third-period element, and therefore it can have an expanded octet. The Lewis structure of PF_5 is



Note that there are no formal charges on the P and F atoms.

Check Although the octet rule is satisfied for the F atoms, there are 10 valence electrons around the P atom, giving it an expanded octet.

Practice Exercise Draw the Lewis structure for arsenic pentafluoride (AsF_5).

Similar problem: 9.64.

Example 9.11

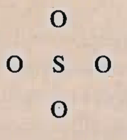
Draw a Lewis structure for the sulfate ion (SO_4^{2-}) in which all four O atoms are bonded to the central S atom.

(Continued)

Strategy Note that S is a third-period element. We follow the procedures given in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

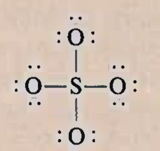
Solution The outer-shell electron configurations of S and O are $3s^23p^4$ and $2s^22p^4$, respectively.

Step 1: The skeletal structure of (SO_4^{2-}) is

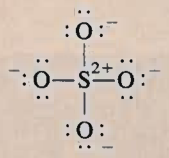


Step 2: Both O and S are Group 6A elements and so have six valence electrons each. Including the two negative charges, we must therefore account for a total of $6 + (4 \times 6) + 2$, or 32, valence electrons in SO_4^{2-}.

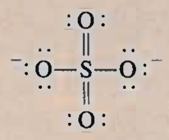
Step 3: We draw a single covalent bond between all the bonding atoms:



Next we show formal charges on the S and O atoms:

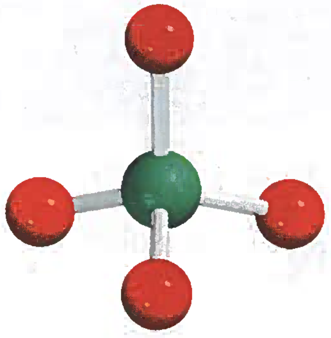


Check One of six other equivalent structures for SO_4^{2-} is as follows:



This structure involves an expanded octet on S but may be considered more plausible because it bears fewer formal charges. However, detailed theoretical calculation shows that the most likely structure is the one that satisfies the octet rule, even though it has greater formal charge separations. The general rule for elements in the third period and beyond is that a resonance structure that obeys the octet rule is preferred over one that involves an expanded octet but bears fewer formal charges.

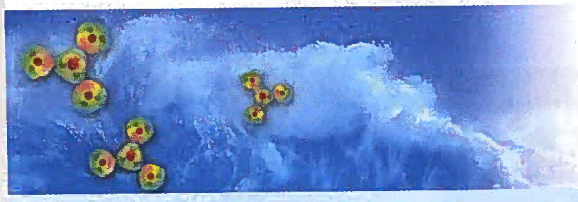
Practice Exercise Draw the Lewis structure of sulfuric acid (H_2SO_4).



SO_4^{2-}

Similar problem: 9.85.

A final note about the expanded octet: In drawing Lewis structures of compounds containing a central atom from the third period and beyond, sometimes we find that the octet rule is satisfied for all the atoms but there are still valence electrons left to place. In such cases, the extra electrons should be placed as lone pairs on the central atom. Example 9.12 shows this approach.



CHEMISTRY in Action

Just Say NO

Nitric oxide (NO), the simplest nitrogen oxide, is an odd-electron molecule, and therefore it is paramagnetic. A colorless gas (boiling point: $-152°C$), NO can be prepared in the laboratory by reacting sodium nitrite ($NaNO_2$) with a reducing agent such as Fe^{2+} in an acidic medium.

$$NO_2^-(aq) + Fe^{2+}(aq) + 2H^+(aq) \longrightarrow NO(g) + Fe^{3+}(aq) + H_2O(l)$$

Environmental sources of nitric oxide include the burning of fossil fuels containing nitrogen compounds and the reaction between nitrogen and oxygen inside the automobile engine at high temperatures

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

Lightning also contributes to the atmospheric concentration of NO. Exposed to air, nitric oxide quickly forms brown nitrogen dioxide gas:

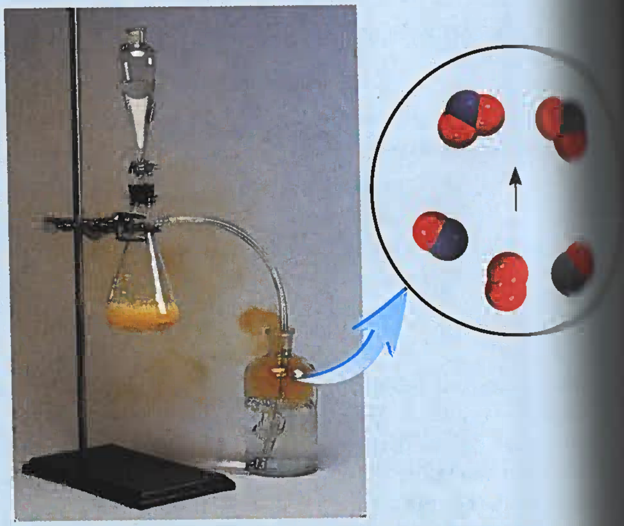
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Nitrogen dioxide is a major component of smog.

About 24 years ago scientists studying muscle relaxation discovered that our bodies produce nitric oxide for use as a neurotransmitter. (A *neurotransmitter* is a small molecule that serves to facilitate cell-to-cell communications.) Since then, it has been detected in at least a dozen cell types in various parts of the body. Cells in the brain, the liver, the pancreas, the gastrointestinal tract, and the blood vessels can synthesize nitric oxide. This molecule also functions as a cellular toxin to kill harmful bacteria. And that's not all: In 1996 it was reported that NO binds to hemoglobin, the oxygen-carrying protein in the blood. No doubt it helps to regulate blood pressure.

The discovery of the biological role of nitric oxide has shed light on how nitroglycerin ($C_3H_5N_3O_9$) works as a drug. For many years, nitroglycerin tablets have been prescribed for heart patients to relieve pain (*angina pectoris*) caused by a brief interference in the flow of blood to the heart, although how it worked was not understood. We now know that nitroglycerin produces nitric oxide, which causes muscles to relax and allows the arteries to dilate. In this respect, it is interesting to note that Alfred Nobel, the inventor of dynamite (a mixture of nitroglycerin and clay that stabilizes the explosive before use), who established the prizes bearing his name, had heart trouble. He refused his doctor's recommendation to ingest a small amount of nitroglycerin to ease the pain.

That NO evolved as a messenger molecule is entirely appropriate. Nitric oxide is small and so can diffuse quickly from cell to cell. It is a stable molecule, but under certain circumstances it is highly reactive, which accounts for its protective function. The enzyme that brings about muscle relaxation contains iron for which nitric oxide has a high affinity. It is the binding of NO to the iron that activates the enzyme. Nevertheless, in the cell, where biological effectors are typically very large molecules, the pervasive effects of one of the smallest known molecules are unprecedented.



Colorless nitric oxide gas is produced by the action of Fe^{2+} on an acidic sodium nitrite solution. The gas is bubbled through water and immediately reacts with oxygen to form the brown NO_2 gas when exposed to air.

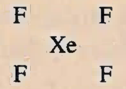
Example 9.12

Draw a Lewis structure of the noble gas compound xenon tetrafluoride (XeF_4) in which all F atoms are bonded to the central Xe atom.

(Continued)

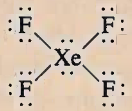
Strategy Note that Xe is a fifth-period element. We follow the procedures in Examples 9.5 and 9.6 for drawing the Lewis structure and calculating formal charges.

Solution *Step 1:* The skeletal structure of XeF_4 is



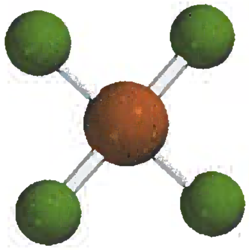
Step 2: The outer-shell electron configurations of Xe and F are $5s^25p^6$ and $2s^22p^5$, respectively, and so the total number of valence electrons is $8 + (4 \times 7)$ or 36.

Step 3: We draw a single covalent bond between all the bonding atoms. The octet rule is satisfied for the F atoms, each of which has three lone pairs. The sum of the lone pair electrons on the four F atoms (4×6) and the four bonding pairs (4×2) is 32. Therefore, the remaining four electrons are shown as two lone pairs on the Xe atom:



We see that the Xe atom has an expanded octet. There are no formal charges on the Xe and F atoms.

Practice Exercise Write the Lewis structure of sulfur tetrafluoride (SF_4).



XeF_4

Similar problem: 9.63.

9.10 Bond Enthalpy

A measure of the stability of a molecule is its ***bond enthalpy,*** which is *the enthalpy change required to break a particular bond in 1 mole of gaseous molecules.* (Bond enthalpies in solids and liquids are affected by neighboring molecules.) The experimentally determined bond enthalpy of the diatomic hydrogen molecule, for example, is

$$H_2(g) \longrightarrow H(g) + H(g) \qquad \Delta H^\circ = 436.4\ \text{kJ/mol}$$

This equation tells us that breaking the covalent bonds in 1 mole of gaseous H_2 molecules requires 436.4 kJ of energy. For the less stable chlorine molecule,

$$Cl_2(g) \longrightarrow Cl(g) + Cl(g) \qquad \Delta H^\circ = 242.7\ \text{kJ/mol}$$

Bond enthalpies can also be directly measured for diatomic molecules containing unlike elements, such as HCl,

$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H^\circ = 431.9\ \text{kJ/mol}$$

as well as for molecules containing double and triple bonds:

$$\begin{aligned} O_2(g) &\longrightarrow O(g) + O(g) \qquad \Delta H^\circ = 498.7\ \text{kJ/mol} \\ N_2(g) &\longrightarrow N(g) + N(g) \qquad \Delta H^\circ = 941.4\ \text{kJ/mol} \end{aligned}$$

The Lewis structure of O_2 is $\underset{\cdot\cdot}{\ddot{\text{O}}}=\underset{\cdot\cdot}{\ddot{\text{O}}}$.

Measuring the strength of covalent bonds in polyatomic molecules is more complicated. For example, measurements show that the energy needed to break the first O—H bond in H_2O is different from that needed to break the second O—H bond:

$$\begin{aligned} H_2O(g) &\longrightarrow H(g) + OH(g) \qquad \Delta H^\circ = 502\ \text{kJ/mol} \\ OH(g) &\longrightarrow H(g) + O(g) \qquad \Delta H^\circ = 427\ \text{kJ/mol} \end{aligned}$$

TABLE 9.4 Some Bond Enthalpies of Diatomic Molecules* and Averag Enthalpies for Bonds in Polyatomic Molecules

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enth (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615	S=S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C=O†	745	Br—Br	192.5
C—P	263	I—I	151.0

*Bond enthalpies for diatomic molecules (in color) have more significant figures than bond enthalpies for bond polyatomic molecules because the bond enthalpies of diatomic molecules are directly measurable quantities and averaged over many compounds.

†The C=O bond enthalpy in CO_2 is 799 kJ/mol.

In each case, an O—H bond is broken, but the first step is more endothermic th the second. The difference between the two ΔH° values suggests that the secon O—H bond itself has undergone change, because of the changes in the chemi environment.

Now we can understand why the bond enthalpy of the same O—H bond in t different molecules such as methanol (CH_3OH) and water (H_2O) will not be the sa their environments are different. Thus, for polyatomic molecules we speak of the *av age* bond enthalpy of a particular bond. For example, we can measure the energy o the O—H bond in 10 different polyatomic molecules and obtain the average O bond enthalpy by dividing the sum of the bond enthalpies by 10. Table 9.4 lists t average bond enthalpies of a number of diatomic and polyatomic molecules. As stat earlier, triple bonds are stronger than double bonds, which, in turn, are stronger th single bonds.

Use of Bond Enthalpies in Thermochemistry

A comparison of the thermochemical changes that take place during a number o reactions (Chapter 6) reveals a strikingly wide variation in the enthalpies of differe reactions. For example, the combustion of hydrogen gas in oxygen gas is fairly exothermic:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -285.8 \text{ kJ/mol}$$

On the other hand, the formation of glucose ($C_6H_{12}O_6$) from water and carbon dioxide, best achieved by photosynthesis, is highly endothermic:

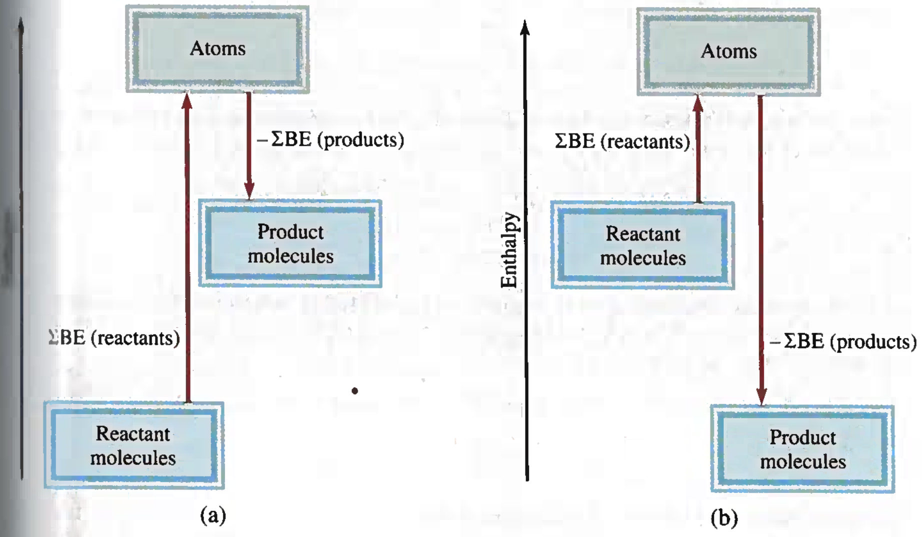
$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H° = 2801 \text{ kJ/mol}$$

We can account for such variations by looking at the stability of individual reactant and product molecules. After all, most chemical reactions involve the making and breaking of bonds. Therefore, knowing the bond enthalpies and hence the stability of molecules tells us something about the thermochemical nature of reactions that molecules undergo.

In many cases, it is possible to predict the approximate enthalpy of reaction by using the average bond enthalpies. Because energy is always required to break chemical bonds and chemical bond formation is always accompanied by a release of energy, we can estimate the enthalpy of a reaction by counting the total number of bonds broken and formed in the reaction and recording all the corresponding energy changes. The enthalpy of reaction in the *gas phase* is given by

$$\begin{aligned}\Delta H° &= \Sigma\text{BE(reactants)} - \Sigma\text{BE(products)}\\ &= \text{total energy input} - \text{total energy released}\end{aligned} \qquad (9.3)$$

where BE stands for average bond enthalpy and Σ is the summation sign. As written, Equation (9.3) takes care of the sign convention for $\Delta H°$. Thus, if the total energy input is greater than the total energy released, $\Delta H°$ is positive and the reaction is endothermic. On the other hand, if more energy is released than absorbed, $\Delta H°$ is negative and the reaction is exothermic (Figure 9.8). If reactants and products are all diatomic molecules, then Equation (9.3) will yield accurate results because the bond enthalpies of diatomic molecules are accurately known. If some or all of the reactants and products are polyatomic molecules, Equation (9.3)

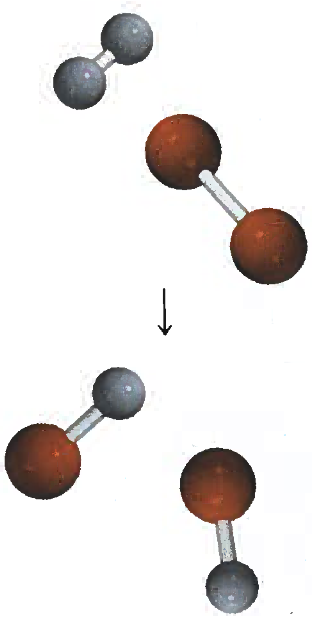


(a) (b)

Figure 9.8 *Bond enthalpy changes in (a) an endothermic reaction and (b) an exothermic reaction.*

will yield only approximate results because the bond enthalpies used will averages.

For diatomic molecules, Equation (9.3) is equivalent to Equation (6.18) results obtained from these two equations should correspond, as Example illustrates.



Example 9.13

Use Equation (9.3) to calculate the enthalpy of reaction for the process

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

Compare your result with that obtained using Equation (6.18).

Strategy Keep in mind that bond breaking is an energy absorbing (endothermic) process and bond making is an energy releasing (exothermic) process. Therefore, the overall energy change is the difference between these two opposing processes, as described by Equation (9.3).

Solution We start by counting the number of bonds broken and the number of bonds formed and the corresponding energy changes. This is best done by creating a table:

Type of bonds broken	*Number of bonds broken*	*Bond enthalpy (kJ/mol)*	*Energy change (kJ/mol)*
H—H (H_2)	1	436.4	436.4
Cl—Cl (Cl_2)	1	242.7	242.7

Type of bonds formed	*Number of bonds formed*	*Bond enthalpy (kJ/mol)*	*Energy change (kJ/mol)*
H—Cl (HCl)	2	431.9	863.8

Refer to Table 9.4 for bond enthalpies of these diatomic molecules.

Next, we obtain the total energy input and total energy released:

$$\text{total energy input} = 436.4\text{ kJ/mol} + 242.7\text{ kJ/mol} = 679.1\text{ kJ/mol}$$
$$\text{total energy released} = 863.8\text{ kJ/mol}$$

Using Equation (9.3), we write

$$\Delta H^\circ = 679.1\text{ kJ/mol} - 863.8\text{ kJ/mol} = -184.7\text{ kJ/mol}$$

Alternatively, we can use Equation (6.18) and the data in Appendix 3 to calculate the enthalpy of reaction:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{HCl}) - [\Delta H_f^\circ(\text{H}_2) + \Delta H_f^\circ(\text{Cl}_2)]\\ &= (2)(-92.3\text{ kJ/mol}) - 0 - 0\\ &= -184.6\text{ kJ/mol}\end{aligned}$$

Check Because the reactants and products are all diatomic molecules, we expect the results of Equations (9.3) and (6.18) to be the same. The small discrepancy here is due to different ways of rounding off.

Similar problem: 9.104.

Practice Exercise Calculate the enthalpy of the reaction

$$H_2(g) + F_2(g) \longrightarrow 2HF(g)$$

using (a) Equation (9.3) and (b) Equation (6.18).

Example 9.14 uses Equation (9.3) to estimate the enthalpy of a reaction involving a polyatomic molecule.

Example 9.14

Estimate the enthalpy change for the combustion of hydrogen gas:

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

Strategy We basically follow the same procedure as that in Example 9.13. Note, however, that H_2O is a polyatomic molecule, and so we need to use the average bond enthalpy value for the O—H bond.

Solution We construct the following table:

Type of bonds broken	*Number of bonds broken*	*Bond enthalpy (kJ/mol)*	*Energy change (kJ/mol)*
H—H (H_2)	2	436.4	872.8
O═O (O_2)	2	498.7	498.7
Type of bonds formed	*Number of bonds formed*	*Bond enthalpy (kJ/mol)*	*Energy change (kJ/mol)*
O—H (H_2O)	4	460	1840

Next, we obtain the total energy input and total energy released:

$$\text{total energy input} = 872.8\text{ kJ/mol} + 498.7\text{ kJ/mol} = 1371.5\text{ kJ/mol}$$
$$\text{total energy released} = 1840\text{ kJ/mol}$$

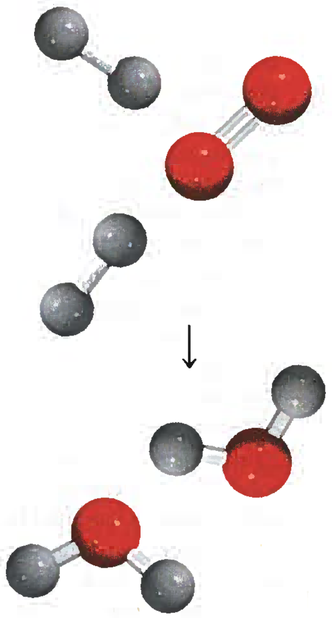
Using Equation (9.3), we write

$$\Delta H° = 1371.5\text{ kJ/mol} - 1840\text{ kJ/mol} = -469\text{ kJ/mol}$$

This result is only an estimate because the bond enthalpy of O—H is an average quantity. Alternatively, we can use Equation (6.18) and the data in Appendix 3 to calculate the enthalpy of reaction:

$$\begin{aligned}\Delta H° &= 2\Delta H_f°(H_2O) - [2\Delta H_f°(H_2) + \Delta H_f°(O_2)]\\ &= 2(-241.8\text{ kJ/mol}) - 0 - 0\\ &= -483.6\text{ kJ/mol}\end{aligned}$$

Check Note that the estimated value based on average bond enthalpies is quite close to the value calculated using $\Delta H_f°$ data. In general, Equation (9.3) works best for reactions that are either quite endothermic or quite exothermic, that is, reactions for which $\Delta H°_{rxn} > 100$ kJ/mol or for which $\Delta H°_{rxn} < -100$ kJ/mol.



Similar problem: 9.72.

Practice Exercise For the reaction

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

(a) Estimate the enthalpy of reaction, using the bond enthalpy values in Table 9.4.
(b) Calculate the enthalpy of reaction, using standard enthalpies of formation. ($\Delta H_f°$ for H_2, C_2H_4, and C_2H_6 are 0, 52.3 kJ/mol, and −84.7 kJ/mol, respectively.)

Summary of Facts and Concepts

1. A Lewis dot symbol shows the number of valence electrons possessed by an atom of a given element. Lewis dot symbols are useful mainly for the representative elements.
2. The elements most likely to form ionic compounds have low ionization energies (such as the alkali metals and the alkaline earth metals, which form cations) or high electron affinities (such as the halogens and oxygen, which form anions).
3. An ionic bond is the product of the electrostatic forces of attraction between positive and negative ions. An ionic compound consists of a large network of ions in which positive and negative charges are balanced. The structure of a solid ionic compound maximizes the net attractive forces among the ions.
4. Lattice energy is a measure of the stability of an ionic solid. It can be calculated by means of the Born-Haber cycle, which is based on Hess's law.
5. In a covalent bond, two electrons (one pair) are shared by two atoms. In multiple covalent bonds, two or three pairs of electrons are shared by two atoms. Some covalently bonded atoms also have lone pairs, that is, pairs of valence electrons that are not involved in bonding. The arrangement of bonding electrons and lone a molecule is represented by a Lewis structure.
6. The octet rule predicts that atoms form enough bonds to surround themselves with eight electro When one atom in a covalently bonded pair do electrons to the bond, the Lewis structure can the formal charge on each atom as a means of track of the valence electrons. There are excep the octet rule, particularly for covalent berylliu pounds, elements in Group 3A, odd–electron cules, and elements in the third period and bey the periodic table.
7. Electronegativity is a measure of an atom's abili tract electrons in a chemical bond.
8. For some molecules or polyatomic ions, two o Lewis structures based on the same skeletal satisfy the octet rule and appear chemically reas Taken together, such resonance structures repre molecule or ion more accurately than any single structure does.
9. The strength of a covalent bond is measured in its bond enthalpy. Bond enthalpies can be used mate the enthalpy of reactions.

Key Words

Bond enthalpy, p. 385
Bond length, p. 368
Born-Haber cycle, p. 361
Coordinate covalent bond, p. 380
Coulomb's law, p. 361
Covalent bond, p. 366
Covalent compound, p. 366
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Resonance, p. 378
Resonance structure, p. 37
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Triple bond, p. 367

Questions and Problems

Lewis Dot Symbols

Review Questions

9.1 What is a Lewis dot symbol? To what elements does the symbol mainly apply?

9.2 Use the second member of each group from Group 1A to Group 7A to show that the number of valence electrons on an atom of the element is the same as its group number.

9.3 Without referring to Figure 9.1, write Lewis dot bols for atoms of the following elements: (a) Be, (b) (c) Ca, (d) Ga, (e) O, (f) Br, (g) N, (h) I, (i) As, (j)

9.4 Write Lewis dot symbols for the following ions Li^+, (b) Cl^-, (c) S^{2-}, (d) Sr^{2+}, (e) N^{3-}.

9.5 Write Lewis dot symbols for the following atoms ions: (a) I, (b) I^-, (c) S, (d) S^{2-}, (e) P, (f) P^{3-}, (g) (h) Na^+, (i) Mg, (j) Mg^{2+}, (k) Al, (l) Al^{3+}, (m) (n) Pb^{2+}.

The Ionic Bond

Review Questions

9.6 Explain what an ionic bond is.

9.7 Explain how ionization energy and electron affinity determine whether atoms of elements will combine to form ionic compounds.

9.8 Name five metals and five nonmetals that are very likely to form ionic compounds. Write formulas for compounds that might result from the combination of these metals and nonmetals. Name these compounds.

9.9 Name one ionic compound that contains only nonmetallic elements.

9.10 Name one ionic compound that contains a polyatomic cation and a polyatomic anion (see Table 2.3).

9.11 Explain why ions with charges greater than 3 are seldom found in ionic compounds.

9.12 The term "molar mass" was introduced in Chapter 3. What is the advantage of using the term "molar mass" when we discuss ionic compounds?

9.13 In which of the following states would NaCl be electrically conducting? (a) solid, (b) molten (that is, melted), (c) dissolved in water. Explain your answers.

9.14 Beryllium forms a compound with chlorine that has the empirical formula $BeCl_2$. How would you determine whether it is an ionic compound? (The compound is not soluble in water.)

Problems

9.15 An ionic bond is formed between a cation A^+ and an anion B^-. How would the energy of the ionic bond [see Equation (9.2)] be affected by the following changes? (a) doubling the radius of A^+, (b) tripling the charge on A^+, (c) doubling the charges on A^+ and B^-, (d) decreasing the radii of A^+ and B^- to half their original values.

9.16 Give the empirical formulas and names of the compounds formed from the following pairs of ions: (a) Rb^+ and I^-, (b) Cs^+ and SO_4^{2-}, (c) Sr^{2+} and N^{3-}, (d) Al^{3+} and S^{2-}.

9.17 Use Lewis dot symbols to show the transfer of electrons between the following atoms to form cations and anions: (a) Na and F, (b) K and S, (c) Ba and O, (d) Al and N.

9.18 Write the Lewis dot symbols of the reactants and products in the following reactions. (First balance the equations.)

(a) $Sr + Se \longrightarrow SrSe$

(b) $Ca + H_2 \longrightarrow CaH_2$

(c) $Li + N_2 \longrightarrow Li_3N$

(d) $Al + S \longrightarrow Al_2S_3$

9.19 For each of the following pairs of elements, state whether the binary compound they form is likely to be ionic or covalent. Write the empirical formula and name of the compound: (a) I and Cl, (b) Mg and F.

9.20 For each of the following pairs of elements, state whether the binary compound they form is likely to be ionic or covalent. Write the empirical formula and name of the compound: (a) B and F, (b) K and Br.

Lattice Energy of Ionic Compounds

Review Questions

9.21 What is lattice energy and what role does it play in the stability of ionic compounds?

9.22 Explain how the lattice energy of an ionic compound such as KCl can be determined using the Born-Haber cycle. On what law is this procedure based?

9.23 Specify which compound in the following pairs of ionic compounds has the higher lattice energy: (a) KCl or MgO, (b) LiF or LiBr, (c) Mg_3N_2 or NaCl. Explain your choice.

9.24 Compare the stability (in the solid state) of the following pairs of compounds: (a) LiF and LiF_2 (containing the Li^{2+} ion), (b) Cs_2O and CsO (containing the O^- ion), (c) $CaBr_2$ and $CaBr_3$ (containing the Ca^{3+} ion).

Problems

9.25 Use the Born-Haber cycle outlined in Section 9.3 for LiF to calculate the lattice energy of NaCl. [The heat of sublimation of Na is 108 kJ/mol and $\Delta H_f^\circ(NaCl) = -411$ kJ/mol. Energy needed to dissociate $\frac{1}{2}$ mole of Cl_2 into Cl atoms $= 121.4$ kJ.]

9.26 Calculate the lattice energy of calcium chloride given that the heat of sublimation of Ca is 121 kJ/mol and $\Delta H_f^\circ(CaCl_2) = -795$ kJ/mol. (See Tables 8.2 and 8.3 for other data.)

The Covalent Bond

Review Questions

9.27 What is Lewis's contribution to our understanding of the covalent bond?

9.28 Use an example to illustrate each of the following terms: lone pairs, Lewis structure, the octet rule, bond length.

9.29 What is the difference between a Lewis dot symbol and a Lewis structure?

9.30 How many lone pairs are on the underlined atoms in these compounds? $H\underline{Br}$, $H_2\underline{S}$, $\underline{C}H_4$

9.31 Compare single, double, and triple bonds in a molecule, and give an example of each. For the same bonding atoms, how does the bond length change from single bond to triple bond?

9.32 Compare the properties of ionic compounds and covalent compounds.

Electronegativity and Bond Type

Review Questions

9.33 Define electronegativity, and explain the difference between electronegativity and electron affinity. Describe in general how the electronegativities of the elements change according to position in the periodic table.

9.34 What is a polar covalent bond? Name two compounds that contain one or more polar covalent bonds.

Problems

9.35 List the following bonds in order of increasing ionic character: the lithium-to-fluorine bond in LiF, the potassium-to-oxygen bond in K_2O, the nitrogen-to-nitrogen bond in N_2, the sulfur-to-oxygen bond in SO_2, the chlorine-to-fluorine bond in ClF_3.

9.36 Arrange the following bonds in order of increasing ionic character: carbon to hydrogen, fluorine to hydrogen, bromine to hydrogen, sodium to chlorine, potassium to fluorine, lithium to chlorine.

9.37 Four atoms are arbitrarily labeled D, E, F, and G. Their electronegativities are as follows: D = 3.8, E = 3.3, F = 2.8, and G = 1.3. If the atoms of these elements form the molecules DE, DG, EG, and DF, how would you arrange these molecules in order of increasing covalent bond character?

9.38 List the following bonds in order of increasing ionic character: cesium to fluorine, chlorine to chlorine, bromine to chlorine, silicon to carbon.

9.39 Classify the following bonds as ionic, polar covalent, or covalent, and give your reasons: (a) the CC bond in H_3CCH_3, (b) the KI bond in KI, (c) the NB bond in H_3NBCl_3, (d) the CF bond in CF_4.

9.40 Classify the following bonds as ionic, polar covalent, or covalent, and give your reasons: (a) the SiSi bond in $Cl_3SiSiCl_3$, (b) the SiCl bond in $Cl_3SiSiCl_3$, (c) the CaF bond in CaF_2, (d) the NH bond in NH_3.

Lewis Structure and the Octet Rule

Review Questions

9.41 Summarize the essential features of the Lewis octet rule. The octet rule applies mainly to the second-period elements. Explain.

9.42 Explain the concept of formal charge. Do formal charges represent actual separation of charges?

Problems

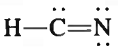
9.43 Write Lewis structures for the following molecules and ions: (a) NCl_3, (b) OCS, (c) H_2O_2, (d) CH_3COO^-, (e) CN^-, (f) $CH_3CH_2NH_3^+$.

9.44 Write Lewis structures for the following molecules and ions: (a) OF_2, (b) N_2F_2, (c) Si_2H_6, (d) OH^-, (e) CH_2ClCOO^-, (f) $CH_3NH_3^+$.

9.45 Write Lewis structures for the following mol (a) ICl, (b) PH_3, (c) P_4 (each P is bonded to thre P atoms), (d) H_2S, (e) N_2H_4, (f) $HClO_3$, (g) CO is bonded to O and Br atoms).

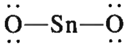
9.46 Write Lewis structures for the following ions: (b) C_2^{2-}, (c) NO^+, (d) NH_4^+. Show formal ch

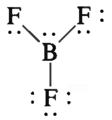
9.47 The following Lewis structures are incorrect. what is wrong with each one and give a corre structure for the molecule. (Relative posit atoms are shown correctly.)

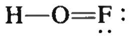
(a)

$H-C=N$

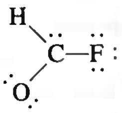
(b)

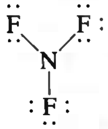
$H=C=C=H$

(c)

$O-Sn-O$

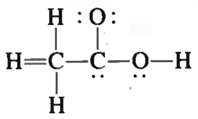
(d)


(e)

$H-O=F$

(f)


(g)


9.48 The skeletal structure of acetic acid shown below rect, but some of the bonds are wrong. (a) Identi incorrect bonds and explain what is wrong wit (b) Write the correct Lewis structure for acetic



The Concept of Resonance

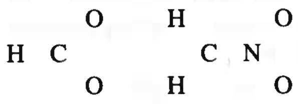
Review Questions

9.49 Define bond length, resonance, and reson structure. What are the rules for writing reson structures?

9.50 Is it possible to "trap" a resonance structure of a pound for study? Explain.

Problems

9.51 Write Lewis structures for the following species, cluding all resonance forms, and show for charges: (a) HCO_2^-, (b) $CH_2NO_2^-$. Relative posit of the atoms are as follows:



9.52 Draw three resonance structures for the chlorate ClO_3^-. Show formal charges.

9.53 Write three resonance structures for hydrazoic HN_3. The atomic arrangement is HNNN. Show for charges.

9.54 Draw two resonance structures for diazomethane, CH_2N_2. Show formal charges. The skeletal structure of the molecule is

$$\begin{array}{lll} \text{H} & & \\ \quad\text{C} & \text{N} & \text{N} \\ \text{H} & & \end{array}$$

9.55 Draw three reasonable resonance structures for the OCN^- ion. Show formal charges.

9.56 Draw three resonance structures for the molecule N_2O in which the atoms are arranged in the order NNO. Indicate formal charges.

Exceptions to the Octet Rule

Review Questions

9.57 Why does the octet rule not hold for many compounds containing elements in the third period of the periodic table and beyond?

9.58 Give three examples of compounds that do not satisfy the octet rule. Write a Lewis structure for each.

9.59 Because fluorine has seven valence electrons ($2s^22p^5$), seven covalent bonds in principle could form around the atom. Such a compound might be FH_7 or FCl_7. These compounds have never been prepared. Why?

9.60 What is a coordinate covalent bond? Is it different from a normal covalent bond?

Problems

9.61 The AlI_3 molecule has an incomplete octet around Al. Draw three resonance structures of the molecule in which the octet rule is satisfied for both the Al and the I atoms. Show formal charges.

9.62 In the vapor phase, beryllium chloride consists of discrete $BeCl_2$ molecules. Is the octet rule satisfied for Be in this compound? If not, can you form an octet around Be by drawing another resonance structure? How plausible is this structure?

9.63 Of the noble gases, only Kr, Xe, and Rn are known to form a few compounds with O and/or F. Write Lewis structures for the following molecules: (a) XeF_2, (b) XeF_4, (c) XeF_6, (d) $XeOF_4$, (e) XeO_2F_2. In each case Xe is the central atom.

9.64 Write a Lewis structure for $SbCl_5$. Does this molecule obey the octet rule?

9.65 Write Lewis structures for SeF_4 and SeF_6. Is the octet rule satisfied for Se?

9.66 Write Lewis structures for the reaction

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

What kind of bond joins Al and Cl in the product?

Bond Enthalpy

Review Questions

9.67 What is bond enthalpy? Bond enthalpies of polyatomic molecules are average values, whereas those of diatomic molecules can be accurately determined. Why?

9.68 Explain why the bond enthalpy of a molecule is usually defined in terms of a gas-phase reaction. Why are bond-breaking processes always endothermic and bond-forming processes always exothermic?

Problems

9.69 From the following data, calculate the average bond enthalpy for the N—H bond:

$$\begin{aligned} NH_3(g) &\longrightarrow NH_2(g) + H(g) & \Delta H^\circ &= 435\text{ kJ/mol} \\ NH_2(g) &\longrightarrow NH(g) + H(g) & \Delta H^\circ &= 381\text{ kJ/mol} \\ NH(g) &\longrightarrow N(g) + H(g) & \Delta H^\circ &= 360\text{ kJ/mol} \end{aligned}$$

9.70 For the reaction

$$O(g) + O_2(g) \longrightarrow O_3(g) \quad \Delta H^\circ = -107.2\text{ kJ/mol}$$

Calculate the average bond enthalpy in O_3.

9.71 The bond enthalpy of $F_2(g)$ is 156.9 kJ/mol. Calculate ΔH_f° for F(g).

9.72 For the reaction

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$$

(a) Predict the enthalpy of reaction from the average bond enthalpies in Table 9.4.

(b) Calculate the enthalpy of reaction from the standard enthalpies of formation (see Appendix 3) of the reactant and product molecules, and compare the result with your answer for part (a).

Additional Problems

9.73 Classify the following substances as ionic compounds or covalent compounds containing discrete molecules: CH_4, KF, CO, $SiCl_4$, $BaCl_2$.

9.74 Which of the following are ionic compounds? Which are covalent compounds? RbCl, PF_5, BrF_3, KO_2, CI_4

9.75 Match each of the following energy changes with one of the processes given: ionization energy, electron affinity, bond enthalpy, and standard enthalpy of formation.

(a) $F(g) + e^- \longrightarrow F^-(g)$

(b) $F_2(g) \longrightarrow 2F(g)$

(c) $Na(g) \longrightarrow Na^+(g) + e^-$

(d) $Na(s) + \frac{1}{2}F_2(g) \longrightarrow NaF(s)$

9.76 The formulas for the fluorides of the third-period elements are NaF, MgF_2, AlF_3, SiF_4, PF_5, SF_6, and ClF_3. Classify these compounds as covalent or ionic.

9.77 Use ionization energy (see Table 8.2) and electron affinity values (see Table 8.3) to calculate the energy change (in kJ/mol) for the following reactions:

(a) $Li(g) + I(g) \longrightarrow Li^+(g) + I^-(g)$

(b) $Na(g) + F(g) \longrightarrow Na^+(g) + F^-(g)$

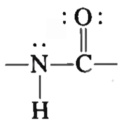
(c) $K(g) + Cl(g) \longrightarrow K^+(g) + Cl^-(g)$

9.78 Describe some characteristics of an ionic compound such as KF that would distinguish it from a covalent compound such as benzene (C_6H_6).

9.79 Write Lewis structures for BrF_3, ClF_5, and IF_7. Identify those in which the octet rule is not obeyed.

9.80 Write three reasonable resonance structures for the azide ion N_3^- in which the atoms are arranged as NNN. Show formal charges.

9.81 The amide group plays an important role in determining the structure of proteins:



Draw another resonance structure for this group. Show formal charges.

9.82 Give an example of an ion or molecule containing Al that (a) obeys the octet rule, (b) has an expanded octet, and (c) has an incomplete octet.

9.83 Draw four reasonable resonance structures for the PO_3F^{2-} ion. The central P atom is bonded to the three O atoms and to the F atom. Show formal charges.

9.84 Attempts to prepare the compounds listed here as stable species under atmospheric conditions have failed. Suggest possible reasons for the failure. CF_2, LiO_2, $CsCl_2$, PI_5

9.85 Draw reasonable resonance structures for the following ions: (a) HSO_4^-, (b) PO_4^{3-}, (c) HSO_3^-, (d) SO_3^{2-}. (*Hint:* See comment on p. 383.)

9.86 Are the following statements true or false? (a) Formal charges represent actual separation of charges. (b) ΔH°_{rxn} can be estimated from the bond enthalpies of reactants and products. (c) All second-period elements obey the octet rule in their compounds. (d) The resonance structures of a molecule can be separated from one another.

9.87 A rule for drawing plausible Lewis structures is that the central atom is invariably less electronegative than the surrounding atoms. Explain why this is so.

9.88 Using the following information and the fact that the average C—H bond enthalpy is 414 kJ/mol, estimate the standard enthalpy of formation of methane (CH_4).

$$C(s) \longrightarrow C(g) \qquad \Delta H^\circ_{rxn} = 716 \text{ kJ/mol}$$
$$2H_2(g) \longrightarrow 4H(g) \qquad \Delta H^\circ_{rxn} = 872.8 \text{ kJ/mol}$$

9.89 Based on energy considerations, which of the fol ing reactions will occur more readily?

(a) $Cl(g) + CH_4(g) \longrightarrow CH_3Cl(g) + H(g)$

(b) $Cl(g) + CH_4(g) \longrightarrow CH_3(g) + HCl(g)$

(*Hint:* Refer to Table 9.4, and assume that the bond enthalpy of the C—Cl bond is 338 kJ/mol

9.90 Which of the following molecules has the sh nitrogen-to-nitrogen bond? Explain. N_2H_4, N_2O, N_2O_4

9.91 Most organic acids can be represented as RCOO where COOH is the carboxyl group and R is th of the molecule. (For example, R is CH_3 in acid, CH_3COOH). (a) Draw a Lewis structu the carboxyl group. (b) Upon ionization, the boxyl group is converted to the carboxylate gr COO^-. Draw resonance structures for the carb late group.

9.92 Which of the following species are isoelectron NH_4^+, C_6H_6, CO, CH_4, N_2, $B_3N_3H_6$

9.93 The following species have been detected in in stellar space: (a) CH, (b) OH, (c) C_2, (d) H (e) HCO. Draw Lewis structures for these spe and indicate whether they are diamagnetic paramagnetic.

9.94 The amide ion, NH_2^-, is a Brønsted base. Repre the reaction between the amide ion and water.

9.95 Draw Lewis structures for the following organic m ecules: (a) tetrafluoroethylene (C_2F_4), (b) prop (C_3H_8), (c) butadiene ($CH_2CHCHCH_2$), (d) propy (CH_3CCH), (e) benzoic acid (C_6H_5COOH). (To dr C_6H_5COOH, replace a H atom in benzene with COOH group.)

9.96 The triiodide ion (I_3^-) in which the I atoms are arran in a straight line is stable, but the corresponding I does not exist. Explain.

9.97 Compare the bond enthalpy of F_2 with the energ change for the following process:

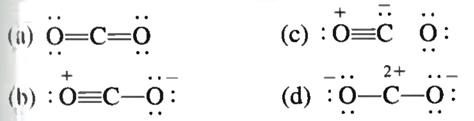
$$F_2(g) \longrightarrow F^+(g) + F^-(g)$$

Which is the preferred dissociation for F_2, energeti cally speaking?

9.98 Methyl isocyanate (CH_3NCO) is used to make cert pesticides. In December 1984, water leaked into tank containing this substance at a chemical plan producing a toxic cloud that killed thousands of pe ple in Bhopal, India. Draw Lewis structures fo CH_3NCO, showing formal charges.

9.99 The chlorine nitrate molecule ($ClONO_2$) is believed be involved in the destruction of ozone in the Antarct stratosphere. Draw a plausible Lewis structure for thi molecule.

9.100 Several resonance structures for the molecule CO_2 ar shown next. Explain why some of them are likely be of little importance in describing the bonding in this molecule.



9.101 For each of the following organic molecules draw a Lewis structure in which the carbon atoms are bonded to each other by single bonds: (a) C_2H_6, (b) C_4H_{10}, (c) C_5H_{12}. For (b) and (c), show only structures in which each C atom is bonded to no more than two other C atoms.

9.102 Draw Lewis structures for the following chlorofluorocarbons (CFCs), which are partly responsible for the depletion of ozone in the stratosphere: (a) $CFCl_3$, (b) CF_2Cl_2, (c) CHF_2Cl, (d) CF_3CHF_2.

9.103 Draw Lewis structures for the following organic molecules. In each there is one C═C bond, and the rest of the carbon atoms are joined by C—C bonds. C_2H_3F, C_3H_6, C_4H_8

9.104 Calculate $\Delta H°$ for the reaction

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

using (a) Equation (9.3) and (b) Equation (6.18), given that $\Delta H_f°$ for $I_2(g)$ is 61.0 kJ/mol.

9.105 Draw Lewis structures for the following organic molecules: (a) methanol (CH_3OH); (b) ethanol (CH_3CH_2OH); (c) tetraethyllead [$Pb(CH_2CH_3)_4$], which is used in "leaded gasoline"; (d) methylamine (CH_3NH_2), which is used in tanning; (e) mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$), a poisonous gas used in World War I; (f) urea [$(NH_2)_2CO$], a fertilizer; and (g) glycine (NH_2CH_2COOH), an amino acid.

9.106 Write Lewis structures for the following four isoelectronic species: (a) CO, (b) NO^+, (c) CN^-, (d) N_2. Show formal charges.

9.107 Oxygen forms three types of ionic compounds in which the anions are oxide (O^{2-}), peroxide (O_2^{2-}), and superoxide (O_2^-). Draw Lewis structures of these ions.

9.108 Comment on the correctness of the statement, "All compounds containing a noble gas atom violate the octet rule."

9.109 Write three resonance structures for (a) the cyanate ion (NCO^-) and (b) the isocyanate ion (CNO^-). In each case, rank the resonance structures in order of increasing importance.

9.110 (a) From the following data calculate the bond enthalpy of the F_2^- ion.

$$F_2(g) \longrightarrow 2F(g) \qquad \Delta H°_{rxn} = 156.9 \text{ kJ/mol}$$
$$F^-(g) \longrightarrow F(g) + e^- \qquad \Delta H°_{rxn} = 333 \text{ kJ/mol}$$
$$F_2^-(g) \longrightarrow F_2(g) + e^- \qquad \Delta H°_{rxn} = 290 \text{ kJ/mol}$$

(b) Explain the difference between the bond enthalpies of F_2 and F_2^-.

9.111 The resonance concept is sometimes described by analogy to a mule, which is a cross between a horse and a donkey. Compare this analogy with the one used in this chapter, that is, the description of a rhinoceros as a cross between a griffin and a unicorn. Which description is more appropriate? Why?

9.112 What are the other two reasons for choosing (b) in Example 9.7?

9.113 In the Chemistry in Action essay on p. 384, nitric oxide is said to be one of about 10 of the smallest stable molecules known. Based on what you have learned in the course so far, write all the diatomic molecules you know, give their names, and show their Lewis structures.

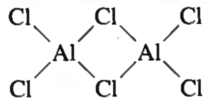
9.114 The N—O bond distance in nitric oxide is 115 pm, which is intermediate between a triple bond (106 pm) and a double bond (120 pm). (a) Draw two resonance structures for NO and comment on their relative importance. (b) Is it possible to draw a resonance structure having a triple bond between the atoms?

9.115 Although nitrogen dioxide (NO_2) is a stable compound, there is a tendency for two such molecules to combine to form dinitrogen tetroxide (N_2O_4). Why? Draw four resonance structures of N_2O_4, showing formal charges.

9.116 Another possible skeletal structure for the CO_3^{2-} (carbonate) ion besides the one presented in Example 9.5 is O C O O. Why would we not use this structure to represent CO_3^{2-}?

9.117 Draw a Lewis structure for nitrogen pentoxide (N_2O_5) in which each N is bonded to three O atoms.

9.118 In the gas phase, aluminum chloride exists as a dimer (a unit of two) with the formula Al_2Cl_6. Its skeletal structure is given by



Complete the Lewis structure and indicate the coordinate covalent bonds in the molecule.

9.119 The hydroxyl radical (OH) plays an important role in atmospheric chemistry. It is highly reactive and has a tendency to combine with a H atom from other compounds, causing them to break up. Thus, OH is sometimes called a "detergent" radical because it helps to clean up the atmosphere. (a) Write the Lewis structure for the radical. (b) Refer to Table 9.4 and explain why the radical has a high affinity for H atoms. (c) Estimate the enthalpy change for the following reaction:

$$OH(g) + CH_4(g) \longrightarrow CH_3(g) + H_2O(g)$$

(d) The radical is generated when sunlight hits water vapor. Calculate the maximum wavelength (in nanometers) required to break an O—H bond in H_2O.

9.120 Experiments show that it takes 1656 kJ/mol to break all the bonds in methane (CH_4) and 4006 kJ/mol to break all the bonds in propane (C_3H_8). Based on these data, calculate the average bond enthalpy of the C—C bond.

9.121 Draw three resonance structures of sulfur dioxide (SO_2). Indicate the most plausible structure(s). (*Hint:* See Example 9.11.)

9.122 Vinyl chloride (C_2H_3Cl) differs from ethylene (C_2H_4) in that one of the H atoms is replaced with a Cl atom. Vinyl chloride is used to prepare poly(vinyl chloride), which is an important polymer used in pipes. (a) Draw the Lewis structure of vinyl chloride. (b) The repeating unit in poly(vinyl chloride) is $—CH_2—CHCl—$. Draw a portion of the molecule showing three such repeating units. (c) Calculate the enthalpy change when 1.0×10^3 kg of vinyl chloride forms poly(vinyl chloride).

9.123 In 1998 scientists using a special type of electron microscope were able to measure the force needed to break a *single* chemical bond. If 2.0×10^{-9} N was needed to break a C—Si bond, estimate the bond enthalpy in kJ/mol. Assume that the bond had to be stretched by a distance of 2 Å (2×10^{-10} m) before it is broken.

9.124 The American chemist Robert S. Mulliken sugg
a different definition for the electronegativity (EN
an element, given by

$$EN = \frac{IE + EA}{2}$$

where IE is the first ionization energy and EA the
tron affinity of the element. Calculate the electro
tivities of O, F, and Cl using the above equation. C
pare the electronegativities of these elements on
Mulliken and Pauling scale. (To convert to the Paul
scale, divide each EN value by 230 kJ/mol.)

9.125 Among the common inhaled anesthetics are:

halothane: $CF_3CHClBr$
enflurane: $CHFClCF_2OCHF_2$
isoflurane: $CF_3CHClOCHF_2$
methoxyflurane: $CHCl_2CF_2OCH_3$

Draw Lewis structures of these molecules.

9.126 A student in your class claims that magnesium o
actually consists of Mg^+ and O^- ions, not Mg^2
O^{2-} ions. Suggest some experiments one could d
show that your classmate is wrong.

Special Problems

9.127 Sulfuric acid (H_2SO_4), the most important industrial chemical in the world, is prepared by oxidizing sulfur to sulfur dioxide and then to sulfur trioxide. Although sulfur trioxide reacts with water to form sulfuric acid, it forms a mist of fine droplets of H_2SO_4 with water vapor that is hard to condense. Instead, sulfur trioxide is first dissolved in 98 percent sulfuric acid to form oleum ($H_2S_2O_7$). On treatment with water, concentrated sulfuric acid can be generated. Write equations for all the steps and draw Lewis structures of oleum based on the discussion in Example 9.11.

9.128 From the lattice energy of KCl in Table 9.1 and the ionization energy of K and electron affinity of Cl in Tables 8.2 and 8.3, calculate the $\Delta H°$ for the reaction

$$K(g) + Cl(g) \longrightarrow KCl(s)$$

9.129 The species H_3^+ is the simplest polyatomic ion. The geometry of the ion is that of an equilateral triangle. (a) Draw three resonance structures to represent the ion. (b) Given the following information

$$2H + H^+ \longrightarrow H_3^+ \quad \Delta H° = -849 \text{ kJ/mol}$$

and

$$H_2 \longrightarrow 2H \quad \Delta H° = 436.4 \text{ kJ/mol}$$

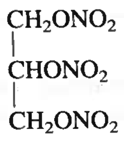
calculate $\Delta H°$ for the reaction

$$H^+ + H_2 \longrightarrow H_3^+$$

9.130 The bond enthalpy of the C—N bond in the amide gro
of proteins (see Problem 9.81) can be treated as an av
age of C—N and C═N bonds. Calculate the maximu
wavelength of light needed to break the bond.

9.131 In 1999 an unusual cation containing only nitrog
(N_5^+) was prepared. Draw three resonance structu
of the ion, showing formal charges. (*Hint:* The N atom
are joined in a linear fashion.)

9.132 Nitroglycerin, one of the most commonly used expl
sives, has the following structure



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

The decomposition reaction is

$$4C_3H_5N_3O_9(l) \longrightarrow$$
$$12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2($$

The explosive action is the result of the heat released
and the large increase in gaseous volume. (a) Calcu
late the $\Delta H°$ for the decomposition of one mole of ni
troglycerin using both standard enthalpy of formation
values and bond enthalpies. Assume that the two O

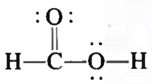
atoms in the NO_2 groups are attached to N with one single bond and one double bond. (b) Calculate the combined volume of the gases at STP. (c) Assuming an initial explosion temperature of 3000 K, estimate the pressure exerted by the gases using the result from (b). (The standard enthalpy of formation of nitroglycerin is −371.1 kJ/mol.)

Answers to Practice Exercises

9.1 $\cdot\mathrm{Ba}\cdot + 2\cdot\mathrm{H} \longrightarrow \mathrm{Ba}^{2+}\ 2\mathrm{H}:^-$ (or BaH_2)
$[\mathrm{Xe}]6s^2$ $1s^1$ [Xe] [He]

9.2 (a) Ionic, (b) polar covalent, (c) covalent.

9.3 $\underset{\cdot\cdot}{\ddot{\mathrm{S}}}=\mathrm{C}=\underset{\cdot\cdot}{\ddot{\mathrm{S}}}$ **9.4**



$\mathrm{H}-\overset{\overset{\displaystyle :\mathrm{O}:}{\|}}{\mathrm{C}}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\mathrm{H}$

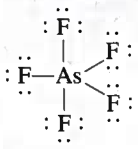
9.5 $\left[\underset{\cdot\cdot}{\ddot{\mathrm{O}}}=\ddot{\mathrm{N}}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\right]^-$

9.6 $\ddot{\mathrm{O}}=\ddot{\mathrm{N}}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^-$ **9.7** $\mathrm{H}-\mathrm{C}\equiv\mathrm{N}:$

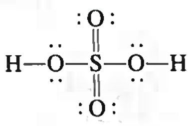
9.8 $\ddot{\mathrm{O}}=\ddot{\mathrm{N}}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^- \longleftrightarrow {}^-:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\ddot{\mathrm{N}}=\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$

9.9 $:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}-\mathrm{Be}-\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$

9.10

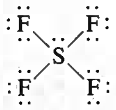


9.11



$\mathrm{H}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\overset{\overset{\displaystyle :\mathrm{O}:}{\|}}{\underset{\underset{\displaystyle :\mathrm{O}:}{\|}}{\mathrm{S}}}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\mathrm{H}$

9.12



9.13 (a) −543.1 kJ/mol, (b) −543.2 kJ/mol.
9.14 (a) −119 kJ/mol, (b) −137.0 kJ/mol.