

Chapter 8; Basic Concepts of Chemical Bonding

8.1 Chemical Bonds, Lewis Symbols, and the Octet Rule

When atoms or ions are strongly attracted to one another, we say that there is a **chemical bond** between them.

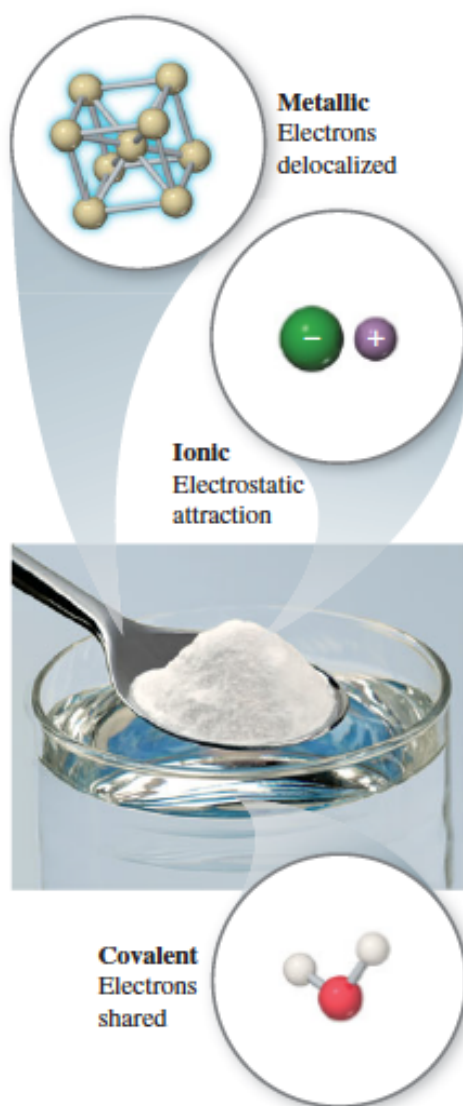
In chemical bonds, electrons are shared or transferred between atoms.

Types of chemical bonds include:

Ionic bonds (electrostatic forces that hold ions together, e.g., NaCl);

Covalent bonds (result from sharing electrons between atoms, e.g., Cl₂)

Metallic bonds (refers to metal nuclei floating in a sea of electrons, e.g. Na).



Lewis Symbols

The electrons involved in bonding are called *valence electrons*.

Valence electrons are found in the incomplete, outermost shell of an atom.

We represent the electrons as dots around the symbol for the element.

The number of valence electrons available for bonding are indicated by unpaired dots.

These symbols are called **Lewis symbols** or Lewis electron-dot symbols.

We generally place the electrons on four sides of a square around the element's symbol.

Sulfur, for example, has the electron configuration $[\text{Ne}]3s^2 3p^4$ and therefore six valence electrons. Its Lewis symbol is



TABLE 8.1 • Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	$[\text{He}]2s^1$	$\text{Li}\cdot$	Na	$[\text{Ne}]3s^1$	$\text{Na}\cdot$
2A	Be	$[\text{He}]2s^2$	$\cdot\text{Be}\cdot$	Mg	$[\text{Ne}]3s^2$	$\cdot\text{Mg}\cdot$
3A	B	$[\text{He}]2s^2 2p^1$	$\cdot\ddot{\text{B}}\cdot$	Al	$[\text{Ne}]3s^2 3p^1$	$\cdot\ddot{\text{Al}}\cdot$
4A	C	$[\text{He}]2s^2 2p^2$	$\cdot\ddot{\text{C}}\cdot$	Si	$[\text{Ne}]3s^2 3p^2$	$\cdot\ddot{\text{Si}}\cdot$
5A	N	$[\text{He}]2s^2 2p^3$	$\cdot\ddot{\text{N}}\cdot$	P	$[\text{Ne}]3s^2 3p^3$	$\cdot\ddot{\text{P}}\cdot$
6A	O	$[\text{He}]2s^2 2p^4$	$:\ddot{\text{O}}:$	S	$[\text{Ne}]3s^2 3p^4$	$:\ddot{\text{S}}:$
7A	F	$[\text{He}]2s^2 2p^5$	$\cdot\ddot{\text{F}}:$	Cl	$[\text{Ne}]3s^2 3p^5$	$\cdot\ddot{\text{Cl}}:$
8A	Ne	$[\text{He}]2s^2 2p^6$	$:\ddot{\text{Ne}}:$	Ar	$[\text{Ne}]3s^2 3p^6$	$:\ddot{\text{Ar}}:$

The Octet Rule

Atoms tend to gain, lose or share electrons until they are surrounded by eight valence electrons; this is known as the **octet rule**.

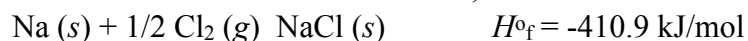
An octet consists of full s and p subshells.

We know that $s^2 p^6$ is a noble gas configuration.

We assume that an atom is stable when surrounded by eight electrons (four electron pairs).

8.2 Ionic Bonding

consider the reaction between sodium and chlorine;



The reaction is violently exothermic

We infer that the NaCl is more stable than its constituent elements.

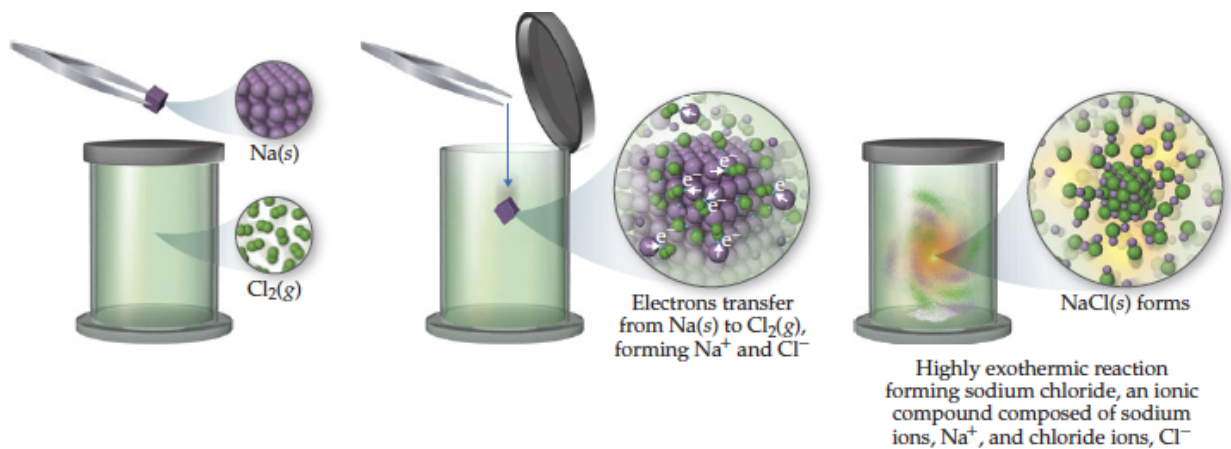
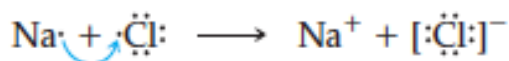
Sodium has lost an electron to become Na^+ and chlorine has gained the electron to become Cl^- .

Note that Na^+ has an Ne electron configuration and Cl^- has an Ar configuration

That is, both Na^+ and Cl^- have an octet of electrons.

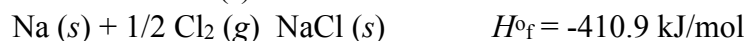
Note that the ions are packed as closely as possible.

Note that it is not easy to find a molecular formula to describe the ionic lattice.

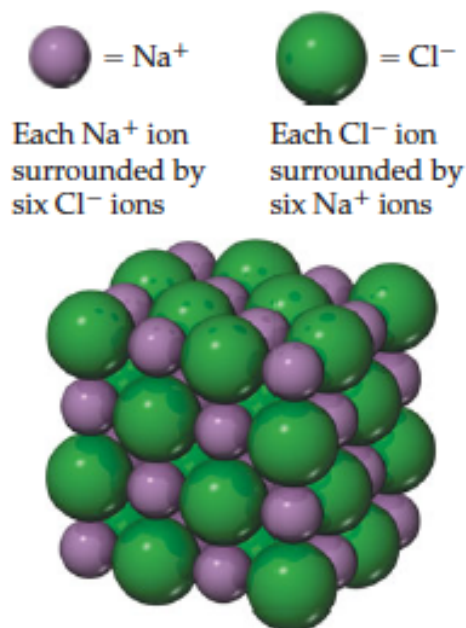


Energetic of Ionic bond Formation

The heat of formation of NaCl (s) is exothermic:



Separation of the NaCl into sodium and chloride ions is endothermic:



The crystal structure of sodium chloride.

The energy required to separate one mole of a solid ionic compound into gaseous ions is called the lattice energy, H_{lattice}

Lattice energy depends on the charge on the ions and the size of the ions. The large positive values indicate that the ions are strongly attracted to one another in ionic solids.

The stability of the ionic compound comes from the attraction between ions of unlike charge.

The specific relationship is given by Coulomb's equation

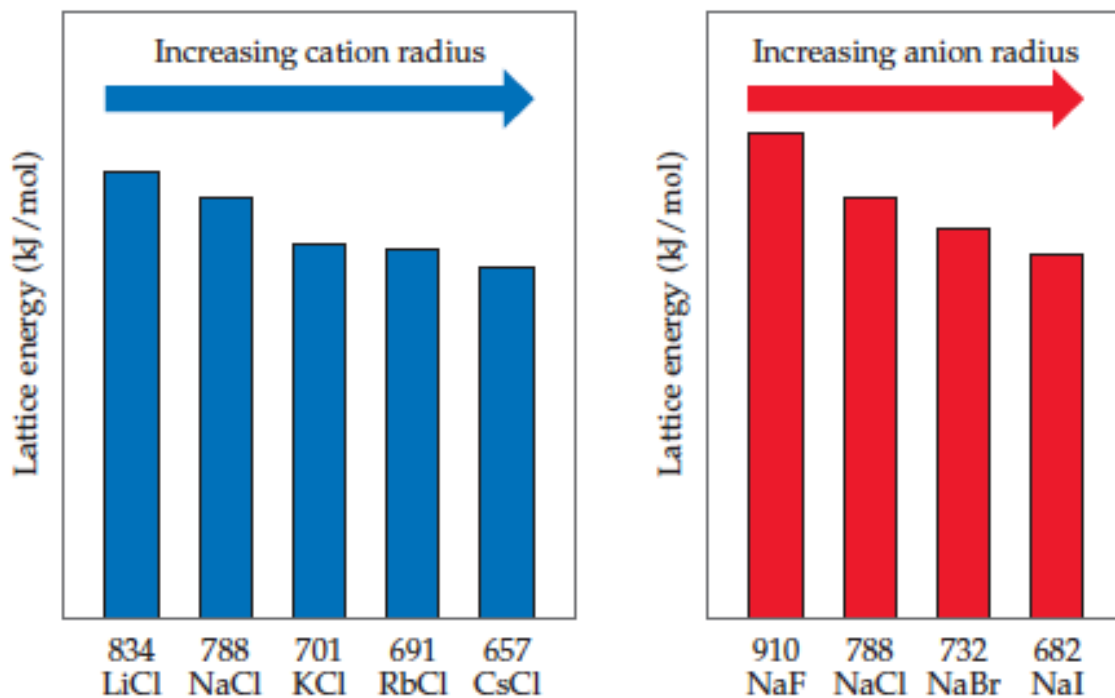
$$E = k \frac{Q_1 Q_2}{D}$$

Where Q_1 and Q_2 are the charges on the particles, d is the distance between their center, and k is a constant.

As Q_1 and Q_2 increase, E increases, and as d increases, E decreases.

TABLE 8.2 • Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2326
LiCl	834	SrCl ₂	2127
LiI	730	MgO	3795
NaF	910	CaO	3414
NaCl	788	SrO	3217
NaBr	732	ScN	7547
NaI	682		
KF	808		
KCl	701		
KBr	671		
CsCl	657		
CsI	600		



Periodic trends in lattice energy as a function of cation or anion radius.

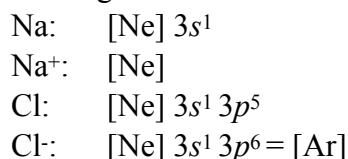
Calculation of the Lattice Energy: The Born-Harber Cycle.

The **Born-Harber cycle** is a thermodynamic cycle that analyzes lattice energy precisely.

Electron Configuration of Ions of the Representative Elements.

These are derived from the electron configuration of elements with the required number of electrons added or removed from the most accessible orbital.

Electron configuration of ions can predict stable ion formation:



Transition-Metal Ions

Lattice energy compensate for the loss of up to three electrons

We often encounter cations with charges of 1+, 2+ or 3+ in ionic compounds

However, transition metals can not attain noble gas conformation (> 3 electrons beyond a noble gas core).

Transition metals tend to lose the valence shell electrons first and then as many *d* electrons as are required to reach the desired charge on the ion.

Thus electrons are removed from 4*s* **before** the 3*d*, etc.

Polyatomic Ions

Polyatomic ions are formed when there is an overall charge on a compound containing covalent bonds

Example: SO_4^{2-} , NO_3^-

In polyatomic ions, two or more atoms are bound together by predominantly covalent bonds.

8.3 Covalent Bonding

The majority of chemical substances do not have characteristics of ionic compounds.

A chemical bond formed by sharing a pair of electrons is called a covalent bond.

Both atoms acquire noble-gas electronic configurations.

This is the 'glue' to bind atoms together.

Lewis Structures

Formation of covalent bonds can be represented using Lewis symbols.

The structures are called **Lewis structures**.

We usually show each electron pair shared between atoms as a line and show unshared electrons as dots.

Each pair of shared electrons constitutes one chemical bond.

Example; $\text{H}\cdot + \text{H}\cdot$ $\text{H}:\text{H}$ has electrons on a line connecting the two H nuclei; HH .

Multiple Bonds

It is possible for more than one pair of electrons to be shared between two atoms (e.g. **multiple bonding**):

One shared pair of electrons is a **single bond** (e.g., H₂);

Two shared pairs of electrons is a **double bond** (e.g., O₂)

Three shared pairs of electrons is a **triple bond** (e.g., N₂)

Generally, bond distance decreases as we move from single through double to triple bonds.

8.4 Bond Polarity and Electronegativity

The electron pairs shared between two different atoms are usually unequally shared.

Bond polarity describes the sharing of the electrons in a covalent bond.

Two extremes:

In a **nonpolar covalent bond**, the electrons are shared equally.

Example: bonding between identical atoms (example: Cl₂).

In a **nonpolar covalent bond**, one of the atoms exerts a greater attraction for bonding electrons than the other (example: HCl).

If the difference is large enough, an ionic bond forms (example: NaCl).

Electronegativity

The ability of an atom in a molecule to attract electrons to itself is its electronegativity.

The electronegativity of an element is related to its ionization energy and electron affinity.

Pauling electronegativity scale: from 0.7 (Cs) to 4.0 (F).

Electronegativity increases across a period and decreases down a group.

Electronegativity and Bond Polarity

Electronegativity difference close to zero results in nonpolar covalent bonds.

The electrons are equally or almost equally shared.

The greater the difference in electronegativity between two atoms, the more polar the bond (polar covalent bond).

There is no sharp distinction between bonding types.

Dipole Moments

Molecules like HF have centers of positive and negative charge that do not coincide.

These are **polar molecules**.

We indicate the polarity of a molecule in two ways

The positive end (or pole) in a polar bond may be represented with a “+” and the negative with a “-”.

We can also place an arrow over the line representing the bond.

The arrow points toward the more electronegative element and shows the shift in electron density toward that atom.

We can quantify the polarity of the molecule.

When charges are separated by a distance, a **dipole** is produced.

The **dipole moment** is the quantitative measure of the magnitude of the dipole ()

$$= Q r$$

The magnitude of the dipole moment is given in Debyes.

8.5 Drawing Lewis Structures

Some simple guidelines for drawing Lewis structures:

Add up all of the valence electrons in all atoms.

For an anion, add electrons equal to the negative charge.

For a cation, subtract electrons equal to the positive charge.

Identify the central atom.

When the central atom has other atoms bound to it, the central atom is usually written first.

Example: in CO₂, the central atom is carbon.

Place the central atom in the center of the molecule and add all other atoms around it.

Place one bond (two electrons) between each pair of atoms

Complete the octets for all atoms connected to the central atom (exception: hydrogen can only have two electrons).

Complete the octet for the central atom; use multiple bonds if necessary.

Formal Charge

Sometimes it is possible to draw more than one Lewis structure with the octet rule obeyed for all the atoms.

To determine which structure is the most reasonable, we use formal charge.

The **formal charge** of an atom is the charge that an atom (in a molecule) would have if all of the atoms had the same electronegativity.

To calculate the formal charge, electrons are assigned as follows:

All nonbonding (unshared) electrons are assigned to the atom on which they are found.

Half of the bonding electrons are assigned to each atom in a bond.

Formal charge is the number of valence electrons in the isolated atom, minus the number of electrons assigned to the atom in the Lewis structure.

For example; consider CN⁻ (cyanide ion):

For carbon:

There are four valence electrons (from periodic table).

In the Lewis structure, there are two nonbonding electrons and three electrons from the triple bond.

There are five electrons from the Lewis structure.

Formal charge: $4 - 5 = -1$.

For nitrogen:

There are five valence electrons (from periodic table).

In the Lewis structure, there are two nonbonding electrons and three electrons from the triple bond.

There are five electrons from the Lewis structure.

Formal charge: $5 - 5 = 0$.

Using formal charge calculations to distinguish between alternative Lewis structures:

The most stable structure has the smallest formal charge on each atom and

The most negative formal charge on the most electronegative atoms.

It is important to keep in mind that formal charges Do NOT represent REAL charges on atoms.

8.6 Resonance Structure

Some molecules are not well described by a single Lewis structure.

Typically, structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.

Example: experimentally, ozone has two identical bonds whereas the Lewis structure requires one single (longer) and one double bond (shorter).

Resonance structures are attempts to represent the real structure that is a mix between several extreme possibilities.

Resonance structures are Lewis structures that differ only with respect to placement of the electrons.

The “true” arrangement is a blend or hybrid of the resonance structures.

Example; in ozone the extreme possibilities have one double and one single bond.

The resonance structure has two identical bonds of intermediate character.

We use a double-headed arrow (\longleftrightarrow) to indicate resonance.

Common example: O_3 , NO_3^- , SO_3 , NO_2 and benzene.

Resonance in Benzene

Benzene belongs to an important category of organic molecules called *aromatic* compounds.

Benzene (C_6H_6) is a cyclic structure.

There are alternative double and single bonds between the carbon atoms

Experimentally, the C-C bonds in benzene are all the same length.

Experimentally, benzene is planar.

To emphasize the resonance between the two Lewis structures, we often represent benzene as a hexagon with a circle in it.

8.7 Exception to the Octet Rule.

There are three classes of exceptions to the octet rule:

- Molecules with an odd number of electrons
- Molecules in which one atom has less than an octet.
- Molecules in which one atom has more than an octet.

[Odd Number of Electrons

Most molecules have an even number of electrons and complete pairing of electrons occurs although some molecules have an odd number of electrons.

Example: ClO_2 , NO and NO_2 .]

Less than an Octet

Molecules with less than an octet are also relatively rare.
Most often encountered in compounds of boron or beryllium
A typical example is BF_3 .

More than an Octet.

This is the largest class of exceptions.
Atoms from the third period on can accommodate more than an octet.
Example; PCl_5 , SF_4 , AsF_6^- and ICl_4^- .

Elements from the third period and beyond have unfilled d orbitals that can be used to accommodate additional electrons.

Size also plays a role.

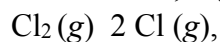
The larger the central atom, the larger the number of atoms that can surround it.
The size of the surrounding atoms is also important.

Expanded octets occur often when the atoms bound to the central atom are the smallest and most electronegative (e.g., F, Cl, O)

8.8 Strengths of Covalent Bonds.

The energy required to break a covalent bond is called the bond **enthalpy**, D .

That is for the Cl_2 molecule, $D(\text{ClCl})$ is given by H for the reaction:



When more than one bond is broken:



The bond enthalpy is a fraction of H for the atomization reaction:

$$D(\text{CH}) = 1/4 H = 1/4 (1660 \text{ kJ}) = 415 \text{ kJ}.$$

The bond enthalpy is always a positive quantity.

Bond Enthalpies and the Enthalpies of Reactions

We can use bond enthalpies to calculate the enthalpy for a chemical reaction.

We recognize that in any chemical reaction bonds need to be broken and then new bonds form.

The enthalpy of the reaction is given by:

The sum of bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed.

Where H_{rxn} is the enthalpy for a reaction

$$H_{\text{rxn}} = D(\text{bonds broken}) - D(\text{bonds formed})$$

We illustrate the concept with the reaction between methane, CH_4 and chlorine:



In this reaction one CH bond and one Cl-Cl bond are broken while one C-Cl bond and one H-Cl bond are formed.

$$\text{So } H_{\text{rxn}} = [D(\text{CH}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})] = -104 \text{ kJ.}$$

The overall reaction is exothermic which means that the bonds formed are stronger than the bonds broken.

The above result is consistent with Hess's law.

Bond Enthalpy and Bond Length

The distance between the nuclei of the atoms involved in a bond is called **bond length**.

Multiple bonds are shorter than single bonds

We can show that multiple bonds are stronger than single bonds.

As the number of bonds between atoms increases, the atoms are held closer and more tightly together.