Chapter 9

Basic Concepts of Chemical Bonding

9.1 Outline

- Lewis symbols and valence electrons
- Ionic bonding - electrostatic attractions between ions of opposite charge
- Covalent bonding - sharing of one or more electron pairs between atoms
- Bond polarity and electronegativity
- Drawing Lewis structures
- Resonances structures, exceptions to the octet rule, and strengths of covalent bonds

9.2 Chemical Bonds

Chemical bond – a strong attractive fource that exists between atoms in a molecule.
The three types of chemical bonds are as follows:

ionic bond a bond between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons.

covalent bond a bond formed between two or more atoms by sharing of electrons.

metallic bond Bonding, usually in solid metals, in which bonding electrons are relatively free to move throughout the three-dimensional structure.

9.3 Lewis Symbols

- The valence electrons, those that reside in the outermost shell of an atom, are responsible for chemical bonding.
- Lewis symbol (electron dot symbol) The chemical symbol for an element, with a dot for each valence electron.

- Dots are placed on the four sides of the chemical symbol, where each side can accommodate up to two electrons.

Table 9.1: Lewis Symbols

Electron	**Electron Configuration**	**Lewis Symbol**	**Electron**	**Electron Configuration**	**Lewis Symbol**
Li	$[He]2s^1$	$\mathrm{Li}\cdot$	Na	$[Ne]3s^1$	$\mathrm{Na}\cdot$
Be	$[He]2s^2$	$\cdot\mathrm{Be}\cdot$	Mg	$[Ne]3s^2$	$\cdot\mathrm{Mg}\cdot$
B	$[He]2s^22p^1$	$\cdot\dot{\mathrm{B}}\cdot$	Al	$[Ne]3s^23p^1$	$\cdot\dot{\mathrm{Al}}\cdot$
C	$[He]2s^22p^2$	$\cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot$	Si	$[Ne]3s^23p^2$	$\cdot\dot{\underset{\cdot}{\mathrm{Si}}}\cdot$
N	$[He]2s^22p^3$	$\cdot\dot{\underset{\cdot}{\mathrm{N}}}:$	P	$[Ne]3s^23p^3$	$\cdot\dot{\underset{\cdot}{\mathrm{P}}}:$
O	$[He]2s^22p^4$	$:\dot{\underset{\cdot}{\mathrm{O}}}:$	S	$[Ne]3s^23p^4$	$:\dot{\underset{\cdot}{\mathrm{S}}}:$
F	$[He]2s^22p^5$	$\cdot\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:$	Cl	$[Ne]3s^23p^5$	$\cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$
Ne	$[He]2s^22p^6$	$:\ddot{\underset{\cdot\cdot}{\mathrm{Ne}}}:$	Ar	$[Ne]3s^23p^6$	$:\ddot{\underset{\cdot\cdot}{\mathrm{Ar}}}:$

9.4 Ionic Bonding

- The combination of sodium metal and chlorine gas results in a violent reaction. The product of this very exothermic reaction is sodium chloride ($NaCl$).

$$\mathrm{Na}\,(s) + \frac{1}{2}\mathrm{Cl_2}(g) \rightarrow \mathrm{NaCl}(s) \qquad \Delta H_f = -410.9\,\mathrm{kJ}$$

- Sodium chloride is comprised of Na^+ and Cl^- ions (see Figure 9.1).
- Recall that metals (e.g., Na) have a tendency to lose electrons to form cations, whereas nonmetals (e.g., Cl) gain electrons to become anions.

$$\mathrm{Na}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Na}^+ + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^-$$

9.5 Structure of Sodium Chloride (NaCl)

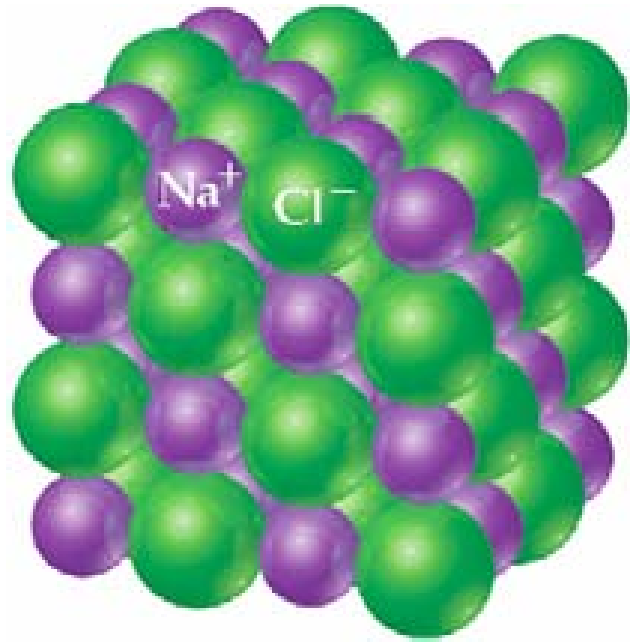


Figure 9.1: Structure of Sodium Chloride (NaCl)

In this three-dimensional array of ions, each Na^+ ion is surrounded by siz Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions.

9.6 Formation of NaCl

- What drives the reaction between Na (s) and Cl_2 (g) to form NaCl?
- Na has a relatively low first ionization energy (i.e., it is perfectly happy to give up its valence electron). Ask yourself, what is the electron configuration of the resulting Na^+ cation?
- Cl has a strong tendency to gain an electron, which is manifested in its large negative electron affinity ($E_a = -349\frac{\text{kJ}}{\text{mol}}$). Ask yourself, what is the electron configuration of the resulting Cl^- cation?
- In addition, as the Na^+ and Cl^- ions are drawn together to form NaCl, a substantial amount of energy is released, known as the lattice energy.

9.7 Lattice Energy

- Lattice energy – The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

- Lattice energies are positive as energy is required to overcome attractive forces between oppositely charged ions. For example,

$$\mathrm{NaCl\,(s) \longrightarrow Na^{+}(g) + Cl{-}(g)} \qquad \Delta H_{\text{lattice}} = +788\,\frac{\text{kJ}}{\text{mol}}$$

- The energy associated with electrostatic interactions is governed by Coulomb's Law:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \tag{9.1}$$

- Lattice energy increases with the charge on the ions.
- It also increases with decreasing size of ions.
- See the worked example entitled Magnitudes of Lattice Energies.

9.8 Magnitudes of Lattice Energies

Which substance would you expect to have the greatest lattice energy, MgF_2, CaF_2, or ZrO_2?

$$\mathrm{MgF_2(s) \longrightarrow Mg^{2+}(g) + 2\,F^{-}(g)}$$

Because the product of the charge, Q_1Q_2, appears in the numerator of the equation above, the lattice energy will increase dramatically when the charges of the ions increase. Thus,

$$\begin{array}{llll} \mathrm{MgF_2} & \mathrm{Q_1{=}^{+}2} & \mathrm{Q_2} & = -1 \\ \mathrm{CaF_2} & \mathrm{Q_1{=}^{+}2} & \mathrm{Q_2} & = -1 \\ \mathrm{ZrO_2} & \mathrm{Q_1{=}^{+}4} & \mathrm{Q_2} & = -2 \end{array}$$

$$\mathrm{CaF_2 < MgF_2 < ZrO_2}$$

Table 9.2: 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		
NaF	910	MgO	3795
		3414	
		3217	
		7547	

9.9 Covalent Bonding

- In covalent bonds, atoms share electrons.
- There are several electrostatic interactions in these bonds:
  - Attractions between electrons and positive nuclei.
  - Repulsions between electrons
  - Repulsions between nuclei
  - Attractive forces must outweigh the repulsive ones

9.10 Lewis Structures

- Consider two Hydrogen atoms coming together to form a covalently bonded H_2 molecule:

$$\mathrm{H}\cdot + \cdot\mathrm{H} \longrightarrow$$

- The H_2 molecule on the right, with its two electrons, exhibits the noble-gas configuration
- Consider two chlorine atoms coming together to form a covalently bonded Cl_2 molecule:

$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot + \cdot\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \longrightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$$

- Each chlorine atom on the right now has a *complete octet* of electrons by sharing the bonding electron pair. It achieves the noble gas configuration of argon (Ar). Again, the shared pair of electrons can be represented by a single bond, as shown below.

9.11 Typical Bonding Motifs

Typical bonding motifs above

9.12 Bond Polarity and Electronegativity

- Molecules such as H_2, N_2, Cl_2, etc are said to be **nonpolar**.
- A nonpolar covalent bond is one in which the electrons are shared equally between two atoms.
- On the other hand, a polar covalent bond is one in which one of the atoms exerts a greater attraction for the bonding electrons than the other.
- In other words, there exists a bond between atoms of different electronegativities.

9.13 Electronegativity

- Electronegativity – the ability of atoms
- On the periodic table

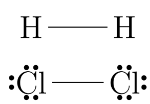
Table 9.3: Electronegativity and Bond Polarity

Compound	**F_2**	**HF**	**LiF**
Electronegativity	4.0 - 4.0 = 0	4.0 - 2.1 = 1.9	4.0 - 1.0 = 3.0
Type of bond	Nonpolar covalent	Polar covalent	Ionic

Table 9.4: Polar Covalent Bonds

Compound	**Bond Length (Å)**	**Electronegativity**	**Dipole Moment (D)**
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

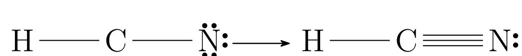
9.14 Writing Lewis Structures



1.

2. The central atom is the least electronegative element that isn't Hydrogen. Connect the other atoms to it by single bonds.

3. Fill the octets of the outer atoms.
   - How many electrons have you accounted for in the above structure? 24
   - How many do you have left? 2
   - Fill in the octet of the central atom.
   - If you run out of electrons before the central atom has an octet: form multiple bonds until it does

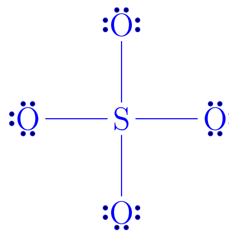


9.15 Lewis Structures for Polyatomic Ions

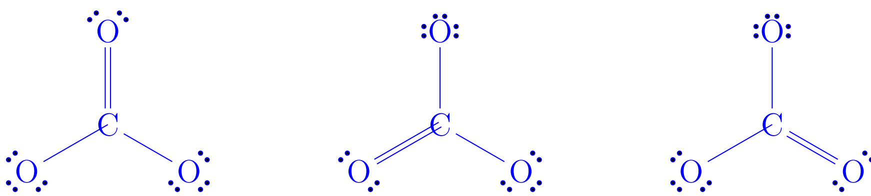
Draw the Lewis structures for:

(a) $ClO_2{}^{-}$

(b) $SO_4{}^{2-}$ $6 + 4(6) + 2 = 32$ valence electrons



(c) $CO_3{}^{2-}$ $4 + 3(6) + 2 = 24$ valence electrons



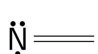
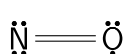
9.16 Resonance

9.17 Exceptions to the Octet Rule

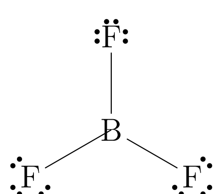
- The three types of systems that don't follow the octet rule are as follows:
  - Ions or molecules with an odd number of electrons
  - Ions or molecules with less than an octet
  - Ions or molecules with more than eight valence electrons (an expanded octet)

9.17.1 Odd Number of Electrons

Ions and molecules with an odd number of electrons (e.g., ClO_2, NO, NO_2, and O_2).

 and 

9.17.2 Fewer than Eight Electrons



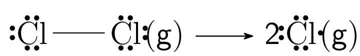
- Consider BF_3
  - Notice how the central boron does not have a complete octet?
  - What about resonance?
  - See worked example below:

Draw the Lewis structure for boron trifluoride, BF_3, and explain why it does not obey the octet rule.
These resonance structures are less important than the first because they put positive charge on the most electronegative fluorine atoms!

9.17.3 More than Eight Electrons

- The only way PCl_5 can exist is if phosphorus has 10 valence electrons around it.
- It is allowed to expand the octet of atoms on or below the 3rd row/period.
- Ask yourself, does NCl_5 exist? No.
- Most likely the *d* orbitals in these atoms participate in bonding.

9.18 Covalent Bond Strength



- The strength of a bond is measured by determining how much energy is required to break the bond.
- This is the bond enthalpy.
- The bond enthalpy for a Cl-Cl bond is measured to be 242 kJ/mol.