

# Molecular and Ionic Compound Structure and Properties

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## 2.1 Types of Chemical Bonds

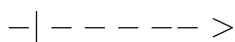
### Types of Bonds

- Ionic bonds: transferring electrons (usually involves a metal and a nonmetal)
- Covalent bonds: sharing electrons (usually involves two nonmetals)
  - Nonpolar: electrons shared equally
  - Polar: electrons shared unequally
- Metallic bond: electrons not associated with a single atom or molecule (delocalized electrons)

### Electronegativity

Electronegativity values for the representative elements increase going from left to right across a period and decrease going down a group. These trends can be understood quantitatively through the electronic structure of the atoms, the shell model, and Coulomb's law. Valence electrons shared between atoms of similar electronegativity constitute a nonpolar covalent bond. For example bonds between carbon and hydrogen are effectively nonpolar even though carbon is slightly more electronegative than hydrogen. Valence electrons shared between atoms of unequal electronegativity constitute a polar covalent bond.

- The atom with a higher electronegativity will develop a partial negative charge ( $\delta^-$ ) relative to the other atom in the bond, which will develop a partial positive ( $\delta^+$ ) charge.
  - Can also use a dipole arrow to denote electronegativity (points towards the more electronegative atom)



- In single bonds, greater differences in electronegativity lead to greater bond dipoles.
- All polar bonds have some ionic character, and the difference between ionic and covalent bonding is not distance but rather a continuum.

The difference in electronegativity is not the only factor in determining if a bond should be designated as ionic or covalent. Generally, bonds between a metal and nonmetal are ionic, and bonds between two nonmetals are covalent. Examination of the properties of a compound is the best way to characterize the type of bonding. In a metallic solid, the valence electrons from the metal atoms are considered to be delocalized and not associated with any individual atom.

## 2.2 Intramolecular Force and Potential Energy

Chemical bonds are an attraction between the nucleus of one atom and the electron of another. There is a balance between the attraction of protons and electrons and the repulsion of proton-proton and electron-electron interactions.

A graph of potential energy versus the distance between atoms is a useful representation for describing the interactions between atoms. Such graphs illustrate both the equilibrium bond length (the separation between atoms at which the potential energy is lowest) and the bond energy (the energy required to separate the atoms). If the potential energy is  $> 0$ , then the atom arrangement is unstable. If it is  $< 0$ , then the atom arrangement is stable.

### Covalent Bonds

In a covalent bond, the bond length is influenced by both the size of the atom's core and the bond order (i.e., single, double, triple). Single bonds have the fewest shared electrons, have a weaker attraction between nucleus of one atom and the bonding electrons, and a weaker and longer bond. Triple bonds have the most shared electrons, have a stronger attraction between nucleus of one atom and the bonding electrons, and a stronger and shorter bond.

BOND ORDER	SINGLE BOND	DOUBLE BOND	TRIPLE BOND
<b>Bond Diagram</b>	X : X	X :: X	X ::: X
<b>Strength</b>	Weakest	Middle	Strongest
<b>Length</b>	Longest	Middle	Shortest

## Ionic Bonds

Ionic bonds result from electrostatic attraction between a cation (positively charged) and anion (negatively charged). Coulomb's law can be used to understand the strength of interactions between cations and anions.

- Because the interaction strength is proportional to the charge of each ion, larger charges lead to stronger interactions.
- Because the interaction strength increases as the distance between the centers of the ions (nuclei) decreases, smaller ions lead to stronger interactions.

## 2.3 Structure of Ionic Solids

An ionic bond is an electrostatic attraction between a cation and an anion. In order to conduct electricity, a substance must have (1) charged particles and (2) particles must be free to move.

The cations and anions in an ionic crystal are arranged in a systematic, periodic 3-D array that maximizes the attractive forces among cations and anions while minimizing the repulsive forces.

*Do not need to know the specific types of crystal structures.*

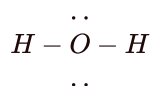
## 2.4 Structure of Metals and Alloys

Metallic bonding can be represented as an array of positive metal ions surrounded by delocalized valence electrons (i.e., a “sea of electrons”).

Alloys are made by combining two or more metallic elements. Interstitial alloys form between atoms of different radii, where the smaller atoms fill the interstitial spaces between the larger atoms. Substitutional alloys form between atoms of comparable radius, where one atom substitutes for the other in the lattice.

## 2.5 Lewis Diagrams

Lewis diagrams can be constructed according to an established set of principles and represent chemical substances. They can show the connectivity between atoms, the bond orders between atoms, and the valence electrons that are not used for bonding.



Dashes (–) represent bonds. Dots (.) represent valence electrons.

## How to Draw a Lewis Diagram

1. Count and sum the valence electrons for all atoms.
2. Add electrons if there is a negative charge and subtract electrons if there is a positive charge (if needed).
3. Determine the central atom. It is usually written first and/or the least electronegative.
4. Place other atoms around the central atom and join with single bonds and add valence electrons so that each atom has an octet.
5. Subtract the electrons from the valence electrons and the bonds from the electron total.
6. Add multiple bonds and count electrons again (if needed).
7. If an ion, add square brackets with charge around the diagram (if needed).

## 2.6 Resonance and Formal Charge

### Resonance

In cases where one or more equivalent Lewis structure can be constructed, resonance must be included as a refinement to the Lewis structure. In many cases, this refinement is needed to provide qualitatively accurate predictions of molecular structure and properties. The octet rule and formal charges can be used as criteria for determining which of several possible valid Lewis diagrams provides the best model for predicting molecular structure and properties. As with any model, there are limitations to the use of the Lewis structure model, particularly in cases with an odd number of valence electrons.

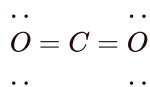
Bonds that have resonance are the same length, regardless of whether they are depicted to have 1 or 2 bonds. Example: the bond lengths of the C–O bonds are identical and the bond order is 1.5.

### Formal Charge

A formal charge is a hypothetical charge the atom would have if all the atoms had the same electronegativity.

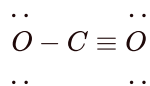
$$\text{formal charge} = (\text{valence electrons}) - (\text{assigned electrons})$$

Example:



Oxygen: formal charge = 6 - 6 = 0

Carbon: formal charge = 4 - 4 = 0



Oxygen (left): formal charge = 6 - 5 = 1

Oxygen (right): formal charge = 6 - 7 = -1

Carbon: 4 - 4 = 0

The top diagram is the most optimal because it has the least amount of nonzero charges.

## Choosing the Best Lewis Diagram

The best diagram will have the minimum number of nonzero formal charges. If nonzero formal charges must remain, the negative charge must be assigned to the most electronegative atom. The sum of all individual formal charges must add up to the charge of the chemical species.

## 2.7 VSEPR and Bond Hybridization

VSEPR theory uses Coulombic repulsion between electrons as a basis for predicting the arrangement of electrons pairs around a central atom. Both Lewis diagrams and VSEPR theory must be used for prediction electronic and structural properties of many covalently bonded molecules and polyatomic ions, including the following:

- Molecular geometry
- Bond angles
- Relative bond energies based on bond order
- Relative bond lengths (multiple bonds, effects of atomic radius)
- Presence of a dipole movement
- Hybridization of valence orbitals of the molecule

## Molecular Geometry

The geometry of molecules will depend on the number of electron domains (bonds and lone pairs) around the central atom. The number of electron domains is sometimes called steric number. Each electron domain will count equally (single/double/triple bonds are considered equivalent). Each molecular shape will have its own name which you must memorize.

Pairs of Electrons	Pairs of Bonding Electrons	Pairs of Lone Electrons	Electron Distribution	Molecular Geometry	Bond Angle	Diagram
2	2	0	linear	linear	180	
3	3	0	trigonal planar	trigonal planar	120	
	2	1		bent	117	
4	4	0	tetrahedral	tetrahedral	109.5	
	3	1		trigonal pyramidal	107	
	2	2		bent	104°	
5	5	0	trigonal bipyramidal	trigonal bipyramidal	120 + 90	
	4	1		seesaw	117 + 90	
	3	2		T-shaped	90	
	2	3		linear	180	
6	6	0	octahedral	octahedral	90	
	5	1		square pyramidal	87	
	4	2		square planar	90	

# Molecular Geometry Affects Polarity

Molecules for which their central atom is symmetrically surrounded by identical atoms are nonpolar. All major shapes—linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral—will produce nonpolar molecules as long as all surrounding atoms are identical. The presence of lone pairs almost always means that the molecule will be polar, exceptions include linear and square planar molecules.

## Hybrid Orbitals

When bonds form, it is possible for these orbitals to morph into new hybrid orbitals. The terms “hybridization” and “hybrid atomic orbital” are used to describe the arrangement of electrons around a central atom.

### 2 Electron Domains

- $sp$  hybridized
- Linear
- Bond angles are  $120^\circ$

### 3 Electron Domains

- $sp^2$  hybridized
- Trigonal planar
- Bond angles are  $120^\circ$

### 4 Electron Domains

- $sp^3$  hybridized
- Tetrahedral
- Bond angles are  $109.5^\circ$

*Do not need to know:*

- *Derivation and depiction of hybrid orbitals*
- *Hybridization involving  $d$  orbitals. When an atom has more than four pairs of electrons surrounding the central atom,  $s$  and  $p$  orbitals are only responsible for the shape of the resulting molecule*



Bond formation is associated with overlap between atomic orbitals. In multiple bonds, such overlap leads to the formation of both sigma and pi bonds. The overlap is stronger in sigma than pi bonds, which is reflected in sigma bonds having greater bond energy than pi bonds. The presence of a pi bond also prevents the rotation of the bond and leads to structural isomers.

*Do not need to know molecular orbital diagrams, filling of molecular orbitals, nor the distinction between bonding, nonbonding, and antibonding orbitals.*