Chemical bonding describes the attractive forces between atoms that results in the formation of compounds. Only valence electrons are involved in chemical bonding.

**CHEMICAL BONDING BASICS**

Valence electrons are the outermost electrons of an atom and are responsible for chemical bonding. The group number on the periodic table determines the number of valence electrons for the main group elements. Carbon is in Group IVA, therefore it has four valence electrons.

A Lewis dot symbol is a picture representation of an atom and its valence electrons. Valence electrons are drawn one on each side and then paired, built up following Aufbau’s principle (Chapter 6).

\[
\begin{array}{c}
H \cdot \cdot C \cdot \cdot O \cdot : \cdot Cl:
\end{array}
\]

Electronegativity is the measure of the ability of an atom to attract electrons towards itself. Elements with large electronegativity gain electrons to form anions, and those with small electronegativity lose electrons to form cations. Electronegativity increases from left to right across the periodic table, and decreases from top to bottom. Fluorine is the most electronegative element. The difference in electronegativity between two atoms predicts the type of bonding that occurs.

![Electronegativity values, measured on the Pauling scale.](http://cnx.org/contents/85abf193-2bd2-4908-8563-90b8a7ac8df6@9.527)
IONIC BONDING

An ionic bond forms between a cation (metal) and an anion (nonmetal) due to attractive forces between opposite charges. There is a large difference in electronegativity between the metal and nonmetal, which results in the transfer of electrons.

The Lewis dot representation for the formation of the ionic compound sodium chloride is shown below. Chlorine takes an electron from sodium forming the sodium (+1) and chloride (-1) ions. Remember that all elements are trying to achieve noble gas electron configuration with a full valence shell!

\[
\text{Na}^+ + \text{Cl}^- \rightarrow \text{Na}^+ \text{Cl}^- 
\]

COVALENT BONDING

A covalent bond forms between two nonmetals. There is a small or zero difference in electronegativity between two nonmetal elements, which results in the sharing of electrons to form bonds.

The simplest covalent bonding occurs when two hydrogen atoms form the H₂ molecule, shown in Figure 2. Each hydrogen atom has one proton in its nucleus and one electron in the 1s shell. When the atoms are far apart, there is no attractive force between them so a bond cannot form. If the atoms are too close together, the repulsive force between the 1s electrons is too large to form a stable bond. The most stable (lowest energy) bond forms at the distance where attractive and repulsive forces are equal. This distance is called the bond length.

The covalent bond formed between hydrogen atoms is a result of the overlap of 1s orbitals. Each hydrogen atom shares its 1s electrons so that together they have two electrons. Each hydrogen now has electron configuration 1s² – a full valence shell!

Two nonmetal atoms share electrons via orbital overlap to obtain a full valence shell.

Single bond: 2 electrons
Double bond: 4 electrons
Triple bond: 6 electrons

Covalent bonds have different lengths and strengths depending on the atoms involved. The energy required to break a bond is called bond energy (kJ/mol). Stronger bonds are harder to break, therefore have larger bond energies. The length and strength of bonds are inversely proportional.

Bond length: Single > Double > Triple
Bond strength: Triple > Double > Single
LEWIS DOT STRUCTURES OF COVALENT COMPOUNDS

Lewis structures describe the bonding by valence electrons in covalent molecules and polyatomic ions. A line represents a bond and two dots represent a lone pair of electrons not used in bonding. The octet rule states that main group atoms want eight valence electrons in order to attain noble gas configuration. Hydrogen is an exception to the octet rule because it only needs two electrons to fill its valence shell.

Rules for Drawing Lewis Structures

1. Draw the molecular structure by connecting all atoms by a single bond.
   a. The least electronegative atom is usually the central atom.
   b. Hydrogen is never the central atom because it can only form one bond.
   c. Draw the structure as symmetrically as possible.
   d. Ions are drawn with brackets around the structure, with the charge written as a superscript outside of the right bracket.
2. Count the total number of valence electrons in the molecule. For ions, add one electron for each negative charge and subtract one electron for each positive charge.
3. Subtract the number of electrons used in bonding. Remember that 1 bond = 2 electrons.
4. Distribute the remaining electrons as lone pairs around the outer atoms to form octets. Hydrogen does not have an octet, so lone pairs are not placed on hydrogen.
5. If electrons are left over, place remaining electrons around the central atom.
6. If atoms do not have octets, form double or triple bonds to complete octets by moving lone pairs from outer atoms into bonds with the central atom.

Exceptions to the Octet Rule

Incomplete Octet
Some elements are unable to hold eight valence electrons so they form incomplete octets. Already discussed above, hydrogen holds a maximum of two electrons. Elements of Group IIA and IIIA also form incomplete octets when bonding. Beryllium can bond covalently, and may only hold four valence electrons. Boron and aluminum may only hold six valence electrons.

Expanded Octet
Elements in third period and higher have more than four valence electrons and can form more than four bonds with other atoms. The valence shell of these atoms can hold more than eight electrons because they have empty d orbitals that can be used in bonding. When drawing Lewis structures for these hypervalent molecules, there are electrons left over after completing the octets of outer atoms. These additional electrons are placed on the central atom, often expanding octets to 10 or 12. Examples of hypervalent molecules are PCl$_5$, SF$_6$, and BrF$_5$.

Odd-Electron Molecules
Molecules that have an odd number of electrons are called free radicals. When drawing Lewis structures of free radicals there will be one atom that has an incomplete octet. Always complete the octet of the more electronegative atoms first.

RESONANCE AND FORMAL CHARGE

Molecules or ions that have two or more possible Lewis structures with the atoms in the same position exhibit resonance. The carbonate ion, drawn below, has three resonance forms. A double-headed arrow is used to show the relationship between the resonance forms.
The actual structure of carbonate is an average of three resonance forms called a **resonance hybrid**. The bonds between carbon and oxygen are equivalent – intermediate in strength and length between a single and double bond. Resonance hybrids are stabilized by the delocalization of electrons, meaning electrons are more spread out and shared among all atoms.

The **formal charge** of an atom in a molecule is the charge an atom would have if the bonding electrons were shared equally between the atoms. The following formula determines formal charge.

\[
\text{Formal Charge} = \#[\text{valence electrons}] - \#[\text{unshared electrons}] - \#[\text{bonds}]
\]

**Formal Charge Rules**
- The sum of formal charges in a neutral molecule is equal to zero.
- The sum of formal charges in an ion is equal to the charge on the ion.
- The most likely molecular structure has all atoms with formal charge equal to zero.
- If a structure must have nonzero formal charges,
  - the molecular structure with the smallest nonzero formal charges is preferable.
  - the molecular structure with the negative formal charges on the more electronegative atoms is preferable.

Consider three possible Lewis structures for the cyanate ion, NCO\(^{-}\). Which is the best structure? The most stable structure is one in which the formal charge on each atom is minimized. None of the three structures has all zero formal charges. Structure C contains two atoms with formal charge, while Structures A and B have formal charge on only one atom. To decide between Structure A and B, compare the electronegativity of the atoms with negative formal charge. Oxygen is more electronegative than nitrogen, therefore Structure A is the better Lewis structure for the cyanate ion.
Valence Shell Electron Pair Repulsion (VSEPR) theory predicts molecular structure, more specifically the placement of bonds and lone pairs around a central atom. According to VSEPR theory, molecules and ions are the most stable when electron groups are as far apart as possible. Maximum separation of bonds and lone pairs minimizes repulsive interactions between the electron groups. Since lone pairs require more space, they have a greater effect on the shape of a molecule.

The central atom (A) is any atom that is bonded to more than one atom. An electron group is a bonded atom (B) or a lone pair of electrons (E). Each atom bonded to the central atom counts as one bonded atom regardless if the bonding is single, double, or triple. The electron groups around a central atom are represented by an ABE formula.

The number of electron groups determines the geometry of a molecule. Electron group geometry describes the arrangement of bonded atoms and lone pairs in the molecule. There are five electron group geometries: linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral. The electron group geometry is the same as the molecular geometry if the molecule contains no lone pairs around the central atom. The presence of lone pairs around the central atom distorts the molecular shape to minimize repulsion. Molecular geometry describes the three dimensional shape of atoms in the molecule. Bond angles are angles between two atoms and the central atom.

The following tables summarize electron group geometries, molecular geometries, and bond angles for molecules containing 2-6 electron groups.
### Tetrahedral

<table>
<thead>
<tr>
<th>AB₄</th>
<th>Tetrahedral</th>
<th>AB₃E₁</th>
<th>Trigonal Pyramidal</th>
<th>AB₂E₂</th>
<th>Bent</th>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>109.5°</td>
<td></td>
<td></td>
<td>&lt; 109.5°</td>
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</table>

![Tetrahedral structure](image)

### Trigonal Bipyramidal

<table>
<thead>
<tr>
<th>AB₅</th>
<th>Trigonal Bipyramidal</th>
<th>AB₄E₁</th>
<th>See-saw</th>
<th>AB₃E₂</th>
<th>T-Shaped</th>
<th>AB₂E₃</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90°, 120°, 180°</td>
<td></td>
<td></td>
<td>&lt; 90°, &lt; 120°, 180°</td>
<td></td>
<td>&lt; 90°, 180°</td>
<td>180°</td>
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</tr>
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</table>

![Trigonal Bipyramidal structure](image)

### Octahedral

<table>
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<tr>
<th>AB₆</th>
<th>Octahedral</th>
<th>AB₅E₁</th>
<th>Square Pyramidal</th>
<th>AB₄E₂</th>
<th>Square Planar</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
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<td></td>
<td>&lt; 90°</td>
<td></td>
<td>&lt; 90°</td>
</tr>
</tbody>
</table>

![Octahedral structure](image)

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**Polarity**

Polarity arises from the difference in electronegativity between covalently bonded atoms. A nonpolar bond exists between two identical atoms because the difference in electronegativity between the atoms is zero. The electrons are equally shared between the two atoms. Electrons are unequally shared in a polar bond as a result of a difference in electronegativity between the two atoms. The more electronegative atom attracts electron density towards itself creating a separation of charge called a dipole.

The H – F bond is polar. An arrow with a tail (plus sign) shows electron density moving toward the more electronegative atom, fluorine. The fluorine atom is partial negative (\(\delta^-\)) and the hydrogen atom is partial positive (\(\delta^+\)).
Molecules can also be polar or nonpolar depending on their bonds and molecular geometry. A molecule is nonpolar if the bond dipoles cancel one another out. Although carbon dioxide contain polar bonds, the molecule is nonpolar. The dipoles cancel because they point in opposite directions. The molecular geometry of the water molecule is bent, so the dipoles do not cancel. Instead, the dipoles sum to an overall net dipole making water a polar molecule.

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**BOND ENERGY**

**Bond energy** (kJ/mol) is the amount of energy required to break a bond, but is also the amount of energy released in the formation of a bond. Since energy is absorbed to break a bond, bond energies are always positive. The bond energies of various types of bonds are constants, and are found in reference tables.

Bond energies are used to calculate the enthalpy of reaction according to the following equation.

\[ \Delta H_{\text{rxn}} = \sum \text{B.E.}_{\text{reactants}} - \sum \text{B.E.}_{\text{products}} \]

The types and number of bonds in each molecule of the reaction must be known to calculate enthalpy. Recall that a positive enthalpy of reaction indicates the reaction is endothermic, and a negative enthalpy of reaction indicates the reaction is exothermic.

To calculate the enthalpy of reaction for the following equation, appropriate Lewis structures are first drawn. Next, the types and number of bonds are determined for each side of the reaction and plugged into the bond energy equation.

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \rightarrow 2\text{NH}_3 (g) \quad \Delta H_{\text{rxn}} = ? \]

Next, the types and number of bonds are determined for each side of the reaction and plugged into the bond energy equation.

\[ \Delta H_{\text{rxn}} = [(1 \text{ N≡N }) + (3 \text{ H−H})] - [(6 \text{ N−H})] \]

Finally, solve for the enthalpy by plugging in bond energy values in kJ/mol found in reference tables.