Chapter 12: Chemical Bonding

Homework: All questions on the “Multiple-Choice” and the odd-numbered questions on “Exercises” sections at the end of the chapter.

Chemical Bonding

- This chapter focuses on chemical bonding and its role in compound formation
- Virtually everything in nature depends on chemical bonds
  - Proteins, carbohydrates, and fats that make up living matter are complex molecules held by chemical bonds
- Rock/minerals on earth – compounds held together by chemical bonds
- Chemical bonding results from electromagnetic forces between the electrons and nuclei

Law of Conservation of Mass

- *No detectable change in the total mass occurs during a chemical reaction*
- If the total mass involved in a chemical reaction is precisely measured before and after the reaction, there is no difference
- Discovered in 1774 by Frenchman Antoine Lavoisier

Law of Conservation of Mass - Example

- *The complete burning in oxygen (O) of 4.09 g of carbon (C) produces 15.00 g of carbon dioxide (CO₂). How many grams of oxygen reacted?*
- Carbon + oxygen → carbon dioxide
- 4.09 g + ? → 15.00 g
- Obviously the “?” = 10.91 g
- . of the 15.00 g of CO₂
- 4.09 g = C & 10.91 g = O

Formula Mass

- Recall that the *atomic mass (AM)* of an element is the average mass of all its naturally occurring isotopes
  - *Round off these values to the nearest 0.1 u*
- The *formula mass (FM)* of a compound is the sum of the atomic masses given in its formula
- *For example:* CH₄ = 12 u + (4 x 1.0 u) = 16 u
Calculating Formula Masses

• Find the formula mass (FM) of lead chromate, PbCrO$_4$ – used for yellow lines on streets
• Using the Periodic Table, look up the atomic masses of Pb, Cr, and O
  
  - Pb (207.2 u), Cr (52.0 u), O (16.0 u)
  
  • Formula Mass = 207.2 u + 52.0 u + (4 x 16 u)
  
  • FM = 323.2 u

Law of Definite Proportions

• Different samples of a pure compound always contain the same elements in the same proportion by mass.
• For Example:
  
  - 9 g H$_2$O = 8 g Oxygen + 1 g Hydrogen
  - 18 g H$_2$O = 16 g Oxygen + 2 g Hydrogen
  - 36 g H$_2$O = 32 g Oxygen + 4 g Hydrogen

  • In each case the ratio (or proportion) by mass of Oxygen to Hydrogen is 8 to 1

Calculating Percentage by Mass of an Element

% X by mass = \( \frac{\text{atoms of X in formula} \times \text{AM}_X}{\text{FM}_{\text{cpd}}} \times 100 \)

- H$_2$O for example
  
  % O by mass = \( \frac{1 \times 16.0 \text{u}}{18.0} \times 100 = 88.9\% \)
  
  % H by mass = 11.1\%

Calculating Percentage by Mass for CO$_2$

• “Dry Ice” is CO$_2$
• AM (atomic mass) of C = 12.0 u & O = 16.0 u
• FM (formula mass) of CO$_2$ = 12.0 u + (2 x 16.0 u) = 44.0 u
• % mass of C = (1 AM$_C$/FM$_{CO_2}$) x 100 = ??\%
• % mass of O = (3 AM$_O$/FM$_{CO_2}$) x 100 = 72.7\%

Calculating Percentage by Mass for Al$_2$O$_3$

• Mineral corundum (ruby & sapphire) is Al$_2$O$_3$
• AM (atomic mass) of Al = 27.0 u & O = 16.0 u
• FM (formula mass) of Al$_2$O$_3$ = (2 x 27.0 u) + (3 x 16.0 u) = 102.0 u
• % mass of O = (3 AM$_O$/FM$_{Al_2O_3}$) x 100 = ??\%
• % mass of O = (3 x 16.0 u/102.0 u) x 100 = 47.1\%

Definite Proportions

• When a compound is broken down, its elements are found in a definite proportion by mass
• Also, when the same compound is formed, the elements will combine in that same proportion by mass
Limiting & Excess Reactants

- If constituent elements are not mixed in the correct proportions then
- One of the elements will be used completely up and is called the \textit{limiting reactant}
- And one of the elements will only partially be used up and is called the \textit{excess reactant}
- \textit{Let's look at an example} ...

Dalton’s Atomic Theory

- In 1803, John Dalton proposed three hypotheses to explain the following two laws
  - \textit{Law of Conservation of Mass}
  - \textit{Law of Definite Proportions}

Dalton’s Atomic Theory – 1803

Hypothesis #1

1) Each element is composed of small indivisible particles called atoms
   - Atoms are identical for that element, but different from other atoms

Hypothesis #2

2) Chemical combination is simply the bonding of a definite number of atoms to make one molecule of the compound
   - A given compound always has the same relative numbers and types of atoms

Hypothesis #3

3) No atoms are gained/lost/changed in identity during a chemical reaction, they are just rearranged to produce new substances
Dalton’s Atomic Theory - 1803

• Over the years more and more supporting evidence for Dalton’s concept of the atom has accumulated.
• Although there have been many modifications to his basic ideas, they have worked so well and for so long that we now call it the atomic theory.
• Dalton’s atomic theory is the cornerstone of modern chemistry.

A Little Review

• In Chapter 11 we learned that elements in the same group have the same # of valence electrons.
  – Similar compounds → LiCl, NaCl, KCl, RbCl, CsCl
• Because of this behavior, we know that the valence electrons are the ones involved in compound formation.
• Group 8A are the “noble gases” and generally do not bond with other atoms.
• Chemists have concluded that having eight electrons in the outer shell is very stable.

Electron Shell Distribution

Octet Rule

1) Valence electrons are the ones involved in compound formation.
2) Eight electrons in the outer shell is very stable.
   • The vast majority of compounds can be explained by combining these two conclusions.
   • In forming compounds, atoms tend to gain, lose, or share valence electrons to achieve electron configurations with eight electrons in the outer shell. (H is an exception w/ only 2 in outer shell.)

Bonding

• Individual atoms can achieve this “noble gas” electron configuration (8 in outer shell) in two ways:
  – By transferring (gaining or losing) electrons
  – By sharing electrons
• Bonding by transfer of electrons is called ionic bonding and will be discussed in this section.

Ionic Bonding

• In the transfer of electrons:
  – One or more atoms lose their valence electrons
  – Another one or more atoms gain these same electrons
  – In order to achieve noble gas electron configurations
• Compounds formed by this electron transfer process are called ionic compounds.
Ions

• An ion is formed due to the loss or gain of electrons that destroy the electrical neutrality of the atom and produces a net positive or negative electric charge.
• The net electric charge on an ion is the number of protons minus the number of electrons. \( p - e = \text{net charge} \)
• Metals (left side of Periodic Table) tend to lose one or two electrons.
• Nonmetals (right side of Periodic Table) tend to gain electrons.

Pattern of Ionic Charges

Electron Shell Distribution

Results in Ionic Charge Pattern

Sodium Ion \((Na^+)\) (loses the electron from the outer shell)

Chloride Ion \((Cl^-)\) (gains an electron to fill the outer shell)

The Formation of Sodium Chloride

Sodium Chloride (NaCl) – schematic diagram of a crystal showing a formula unit

• Note that it is actually impossible to associate any one \(Na^+\) with one specific \(Cl^-\)
• Thus it is somewhat inappropriate to refer to a “molecule” of any ionic compound.
Lewis Symbol

- Lewis Symbol – the nucleus and inner electrons of an atom/ion represented by the element’s symbol, and the valence electrons shown by dots
  - Cl: or Cl:
  - Na+ or Na+

Ions

- Cations – positive ions, generally metals
  - Elements that tend to lose electrons
  - The positive charge will be equal to the number of valence electrons in the atom (its group number.)
- Anions – negative ions, generally nonmetals
  - Elements that tend to gain electrons
  - The negative charge on the nonmetal’s ion will be the number of valence electrons in the atom (its group number) minus 8.

Pattern of Charges??

- Valence electrons are lost by metals and gained by nonmetals generally to the extent necessary to acquire eight electrons into the most outer shell, that is, to acquire an electron configuration isoelectronic with a noble gas. (same electron configuration)
- For example: Al3+ is isoelectric with Ne
  - or S2− is isoelectronic with Ar.
Ionic Bonds and Compounds

- Ionic bond – electrical forces that hold the ions together in the crystal lattice of an ionic compound
- In every ionic compound, the total charge in the formula adds up to zero and the compound exhibits electrical neutrality.
- In NaCl the ratio of Na\(^+\) to Cl\(^-\) is always 1 to 1.
- In CaCl\(_2\) the ratio of Ca\(^{2+}\) to Cl\(^-\) is always 1 to 2.

Formulas for Ionic Compounds

- The numbers of atoms of the various elements in a compound are determined by:
  1) The total electrical charge for the compound is zero
  2) All the individual atoms have noble gas configurations in their outer shell

Writing formulas for Ionic Compounds – an Example

- Write the formula for calcium phosphate, the major component of bones.
- Ca is in Group 2A → 2+ ionic charge
- Phosphate is the polyatomic ion (section 11.5) PO\(_4\) → 3− ionic charge
- Therefore when combining these two ions neutrality can be attained with three Ca\(^{2+}\) and two PO\(_{4}^{3−}\).
- Ca\(_3\)(PO\(_4\))\(_2\)

Confidence Exercise

- Write in the formulas for the ionic compounds formed by combining each metal ion (M) with each nonmetal ion (X).

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<tr>
<th>X(^-)</th>
<th>X(^2-)</th>
<th>X(^3-)</th>
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<tr>
<td>M(^+)</td>
<td>MX</td>
<td>M(_2)X</td>
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<tr>
<td>M(^{2+})</td>
<td>MX(_2)</td>
<td>MX</td>
</tr>
<tr>
<td>M(^{3+})</td>
<td>MX(_3)</td>
<td>M(_2)X(_3)</td>
</tr>
</tbody>
</table>

Ionic Compounds

- Due to the very strong forces of attraction between oppositely charged ions
  - Ionic compounds are always crystalline solids and also have high melting and boiling points
- Ionic compounds also have a specific property when an electric current is passed through them.
  - Solid ionic compounds DO NOT conduct electricity (because ions cannot move.)
  - Melted ionic compounds will CONDUCT electricity.

Melted Salt (NaCl) Conducts Electricity

Aqueous solutions in which ionic compounds have been dissolved also conduct electricity.
**Stock System – For metals that form two ions**

- Stock System – place in parentheses directly after the metal’s name a Roman numeral giving the value of the metal’s ionic charge
  - $\text{CrCl}_2$ chromium(II) chloride (usually blue)
  - $\text{CrCl}_3$ chromium(III) chloride (usually green)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Stock System Name</th>
<th>Old Name</th>
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<tbody>
<tr>
<td>$\text{Cu}^{+}$</td>
<td>copper(I)</td>
<td>cuprous</td>
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<tr>
<td>$\text{Cu}^{2+}$</td>
<td>copper(II)</td>
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</tr>
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<td>$\text{Fe}^{2+}$</td>
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<tr>
<td>$\text{Cr}^{6+}$</td>
<td>chromium(III)</td>
<td>chromic</td>
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</table>

**Stock System: Example**

- A certain compound of gold and sulfur has the formula $\text{Au}_2\text{S}$. What is the Stock system name?
  - Au = either 2+ or 1+ & S = 2-
  - Therefore the Stock system name = gold(I) sulfide
  - Cu = either 2+ or 1+ & F = 1-
  - CuF = copper(I) fluoride
  - CuF$_2$ = copper(II) fluoride
  - (The old names for these compounds were cuprous fluoride and cupric fluoride.)

**Covalent Bonding**

- When a pair of electrons is shared by two atoms, a covalent bond exists between these atoms
  - The two electrons no longer orbit an individual nucleus, but are shared equally by both nuclei
- If the covalent bond is between atoms of the same element, the molecule formed is that of an element – $\text{H}_2$ (hydrogen gas)
- Covalent bonds between atoms of different elements form molecules of compounds – $\text{HCl}$

**Covalent Bonding in the $\text{H}_2$ molecule**

0.074 nm is the distance at which the two H atoms are the most stable

**Lewis Symbol Use**

- Hydrogen gas ($\text{H}_2$)
- $\text{H} - \text{H} \rightarrow \text{H} : \text{H}$ or $\text{H} - \text{H}$ (shows two hydrogen atoms each sharing both valence electrons – a covalent bond)
- Hydrogen chloride (hydrochloric acid) ($\text{HCl}$)
- $\text{H} - \text{Cl} \rightarrow \text{H} : \text{Cl}$ or $\text{H} - \text{Cl}$ (shows the H and Cl atoms sharing two electrons – a covalent bond)

**Stable Covalent Molecules**

- Stable Covalent Molecules form when the atoms share electrons in such a way as to give all atoms a share in a noble gas configuration
- Recall the Octet Rule – in forming compounds, atoms tend to gain, lose, or share electrons to achieve electron configurations of the noble gases
Covalent Bonds & Groups

- Noble Gases (8A) tend to form 0 bonds
- Hydrogen and Group 7A tend to form 1 bond
- Group 6A tend to form 2 bonds
- Group 5A tend to form 3 bonds
- Group 4A tend to form 4 bonds

Number of Covalent Bonds expected by Common Nonmetals

<table>
<thead>
<tr>
<th>Periods</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
<th>8A</th>
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<tbody>
<tr>
<td>Bonds</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
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</table>

Exceptions are uncommon in Periods 1 & 2, but occur with more frequency starting with Period 3

Double/Triple Bonding

- When an element has 2, 3, or 4 unpaired valence electrons, its atoms will sometimes share more than one of them with another atom
- Double and Triple bonds between two atoms are possible

Double Bond Example – CO₂

\( \cdot \overset{\cdot}{O} \cdot \overset{\cdot}{C} \cdot \overset{\cdot}{O} \)

or

\( \cdot \overset{\cdot}{O} = \overset{\cdot}{O} \cdot \overset{\cdot}{C} \cdot \overset{\cdot}{O} \)

Triple Bond Example – N₂

\( \cdot \overset{\cdot}{N} \cdot \overset{\cdot}{N} \cdot \overset{\cdot}{N} \cdot \overset{\cdot}{N} \cdot \overset{\cdot}{N} \)

or

\( \cdot \overset{\cdot}{N} = \overset{\cdot}{N} \cdot \overset{\cdot}{N} \cdot \overset{\cdot}{N} \)
Drawing Lewis Structures for Simple Covalent Compounds – use board

- Chloroform CHCl₃
- C (four bonds); H (one bond); Cl (one bond) each
- only C can be the central atom
- Hydrogen peroxide H₂O₂
- H (one bond); O(two bonds)
- only O can connect two atoms

Covalent Bonding – Misc. Info.

- Unlike ionic compounds, covalent compounds are composed of individual molecules with a specific molecular formula
- Carbon tetrachloride (CCl₄) consists of many individual CCl₄ molecules
- Within a molecule the covalent bonds are strong, but the individual molecules only weakly attract each other

 Ionic & Covalent??

- Some compounds contain both ionic and covalent bonds – sodium hydroxide (NaOH)
- OH⁻ is a polyatomic ion that has a covalent bond between the O & H
- But there is an ionic bond between the Na⁺ and the OH⁻, holding the whole molecule together
- Na⁺[O–H]⁻

Rules to Predict Ionic or Covalent??

- Compounds formed of only nonmetals are covalent (except ammonium compounds)
- Compounds of metals and nonmetals are generally ionic
- Compounds of metals with polyatomic ions are ionic
- Compounds that are gases, liquids, or low-melting-point solids are covalent
- Compounds that conduct electricity when melted are ionic

Comparison of Properties of Ionic and Covalent Compounds

<table>
<thead>
<tr>
<th>Ionic Compounds</th>
<th>Covalent Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline solids (made of ions)</td>
<td>Gases, liquids, or solids (made of molecules)</td>
</tr>
<tr>
<td>High melting and boiling points</td>
<td>Low melting and boiling points</td>
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<tr>
<td>Conduct electricity when melted</td>
<td>Poor electrical conductors in all phases</td>
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<tr>
<td>Many soluble in water but not in nonpolar liquids</td>
<td>Many soluble in nonpolar liquids but not in water</td>
</tr>
</tbody>
</table>

Predicting Bonding Type – examples

- KF → ionic, a metal and nonmetal
- SiH₄ → covalent, all nonmetals
- Ca(NO₃)₂ → ionic, metal and polyatomic ion
- X (a gas at room temp) → covalent, a gas
- Y (melts at 900°C, then conducts electricity) → ionic
Polar Covalent Bonding

• Remember that in covalent bonding, electrons are shared, but …
  – These bonds are not always shared equally
• Unless the atoms are the same element, the bonding electrons spend more time around the more nonmetallic element
  – The sharing is unequal
• The is called a polar covalent bond, indicating a slightly positive end and a slightly negative end

Electronegativity

• Electronegativity (EN) – a measure of the ability of an atom in a molecule to draw bonding electrons to itself
• Electronegativity also displays definite trends on the Periodic Table
  – Increases across a period
  – Decreases down a group

Electronegativity – an Example

• Consider HCl → H (EN=2.1) & Cl (EN=3.0)
  – Note that the Cl is more electronegative
• The two bonding electrons tend to spend more time at the Cl end ∴ resulting in a polar covalent bond
• Polarity can be represented → H – Cl
  • The head of arrow points to the more electronegative atom and the other side makes a “plus”

Electronegativity Values

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Summary of Ionic and Covalent Bonding

 Showing the Polarity of Bonds - example

• Use arrows to show the polarity of the covalent bonds of H₂O
  • O (EN=3.5) & H (EN=2.1)
  • Cl (EN=3.0) & C (EN=2.5)
Showing the Polarity of Bonds - example

- Use arrows to show the polarity of the covalent bonds of CCl₄
  - O (EN=3.5) & H (EN=2.1)
  - Cl (EN=3.0) & C (EN=2.5)

Polar Bonds and Polar Molecules

- The molecule as a whole, as well as bonds, can have polarity
- A molecule is polar if electrons are more attracted to one end of the molecule
- Such a molecule has a slightly (-) end and a slightly (+) end
- This type of molecule is said to have a dipole or is called a polar molecule

Polar Bonds & Polar Molecules

<table>
<thead>
<tr>
<th>Polar Molecule</th>
<th>Nonpolar Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (EN=2.1) Cl (EN=3.0)</td>
<td>H (EN=2.1) Be (EN=1.5)</td>
</tr>
</tbody>
</table>

Water Molecule – it is polar!

- If water was a linear molecule it would be nonpolar
- BUT →
  - The water molecule is actually angular (105°) and has a positive and negative end (dipole)
  - Therefore, in order to determine if a molecule is polar (dipole), one must know the molecule’s shape

--Summary--

Polar Bonds and Polar Molecules

- If the bonds in a molecule are nonpolar, the molecule can only be nonpolar
- A molecule with only one polar bond has to be polar
- A molecule with more than one polar bond will be nonpolar if the shape of the molecule causes the polarities of the bonds to cancel, otherwise it will be polar

Polar and Nonpolar Liquids

A stream of polar water molecules (left) is deflected by a charge. A stream of nonpolar CCl₄ molecules is not deflected
Types of Molecules with Polar Bonds but No Resulting Dipole

<table>
<thead>
<tr>
<th>Type</th>
<th>Form of Polar Bonds</th>
<th>Example</th>
<th>Ball and Stick Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear molecules with two identical bonds</td>
<td>[ \text{H} - \text{H} ]</td>
<td>CO₂</td>
<td>![CO₂ Ball and Stick Model]</td>
</tr>
<tr>
<td>Plane molecules with three identical bonds (H2O octahedron)</td>
<td>[ \text{H} \quad \text{H} \quad \text{H} ]</td>
<td>SO₃</td>
<td>![SO₃ Ball and Stick Model]</td>
</tr>
<tr>
<td>Tetrahedral molecules with four identical bonds (H2O tetrahedron)</td>
<td>[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} ]</td>
<td>CCl₄</td>
<td>![CCl₄ Ball and Stick Model]</td>
</tr>
</tbody>
</table>

Dissolving

- Why does water dissolve table salt but does not dissolve oil?
- The polar nature of the water molecule causes them to interact with an ionic substance such as salt
  - The positive ends of the water molecules attract negative ions
  - The negative ends of the water molecules attract positive ions

Polar Water Molecules Dissolve

- If the attraction of the polar water molecules overcomes the attraction between the ions in the crystal, the salt dissolves
- This type of attraction is called an ion-dipole interaction

Sodium Chloride Dissolving in Water

- The (-) ends of the polar water molecules attract/surround the (+) Na
- The (+) ends of the polar water molecules attract/surround the (-) Cl

Polar and Nonpolar Substances

- Two polar substances tend to dissolve in each other
  - They are said to have a dipole-dipole interaction
- Two nonpolar substances also tend to mix well, but not for the same reason
  - Nonpolar molecules of two types simply have no affinity for each other and evenly disperse
  - Gas and Oil are nonpolar molecules that mix well

Polar and Nonpolar Substances

- In general like dissolves like
  - Polar substances tend to mix well in other polar substances
  - Nonpolar substance tend to mix well in other nonpolar substances
- Unlike substances do not tend to mix well
  - The polar molecules tend to gather together and exclude the nonpolar molecules
  - For example oil (nonpolar) does not mix well with water (polar)
Hydrogen Bonding

- Hydrogen bond – a special kind of dipole-dipole interaction
- Hydrogen bonding occurs whenever hydrogen atoms are covalently bonded to small, highly electronegative atoms
- In general, O, F, and N meet these criteria

Hydrogen Bonding in Water

The forces of attraction (red dots) exist between the hydrogen (+) atom of one molecule and the oxygen (-) atom of another molecule

Hydrogen Bonding at Work

In general, the boiling points of similar compounds increase with increasing formula mass. Due to hydrogen bonding the boiling points of H₂O, HF, and NH₃ are all anomalously high.

Hydrogen Bonding

- When hydrogen is covalently bonded to one of these three atoms …
- The bond is very polar and the hydrogen atom is comparatively small
- Thus the partial positive charge on the hydrogen is highly concentrated
- Resulting in the hydrogen atom having an electrical attraction for nearby O, F, or N atoms in neighboring molecules

Hydrogen Bonds

- Hydrogen bonds are strong enough to have a significant effect on the properties of the substance
  - Hydrogen bonds are about 5-10% the strength of covalent bonds

Hydrogen Bonding Affects the Properties of a Substance

- One of the most pronounced effects that results from hydrogen bonding is the predicted change in a substance’s boiling point
- Note on the following graph - the three substances with hydrogen bonding have significantly higher boiling points
  - Hydrogen bonding does not occur in CH₄, its boiling point shows a normal pattern relative to the other hydrogen compounds of Group 4A
Hydrogen Bonding and Density

- Hydrogen bonding and the shape of the water molecule result in ice having a more open structure. In most other substances the solid phase is more dense than the liquid phase.