A. THE ELECTRONIC NATURE OF CHEMICAL BONDS

a) Electrostatic Forces Between Charged Particles

Definition: An electrostatic force = a force of attraction or repulsion between two charged particles.

All bonding is based on the experimentally-derived relationships of electrostatics:

- Opposite charges attract (ex. electrons and protons)
- Like charges repel. (ex. electrons and electrons)
- The greater the charges, the stronger the attractive or repulsive force.
- The greater the distance between the particles, the weaker the force.

NOTE: When considering two examples, if the charge magnitudes are the same, then distance guides you; if relative distances are the same, then decide according to charge magnitude.

b) Electron Shells Reconsidered

Each period (row) in the periodic table represents an electron shell.

From the 4th shell onwards, the d-orbitals lag by 1 n-value. 

From the 6th shell onwards, the f-orbitals lag by 2 n-values.

When you reach the end of a given period, that electron shell is FULL and therefore "closed".

Definitions:
An open shell is one that contains LESS than the maximum number of electrons
A closed shell is one that contains the maximum number of electrons.

The periodic table shows that patterns in the properties of elements are linked to Atomic number.

Q1: What links atomic number and the properties of elements? electrons

As atomic number increases by one, the number of electrons also increases by one.

This means that the elements in the periodic table are also arranged in order of the number of electrons.

c) What is periodicity?

The Russian chemist Dimitry Mendeleev observed that when the elements are arranged in order of atomic mass, there are recurring patterns in certain properties.

The modern periodic table can be used to analyse trends in properties such as atomic radius across periods and down groups.

(draw this on your diagram)
1. On *graph paper*, construct a grid using the data listed in table 1.
2. Plot the **atomic number** (x-axis) of each element against the **atomic radius** (y-axis) of the same element.
3. Label each point on your graph with the atomic symbol for the element.
4. Can you observe a periodic trend? If so, describe the trend shown by your graph.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>ATOMIC NUMBER</th>
<th>ATOMIC RADIUS</th>
<th>FIRST IONIZATION ENERGY (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>1</td>
<td>0.037</td>
<td>1312</td>
</tr>
<tr>
<td>helium</td>
<td>2</td>
<td>0.05</td>
<td>2372</td>
</tr>
<tr>
<td>lithium</td>
<td>3</td>
<td>0.152</td>
<td>519</td>
</tr>
<tr>
<td>beryllium</td>
<td>4</td>
<td>0.111</td>
<td>900</td>
</tr>
<tr>
<td>boron</td>
<td>5</td>
<td>0.088</td>
<td>799</td>
</tr>
<tr>
<td>carbon</td>
<td>6</td>
<td>0.077</td>
<td>1088</td>
</tr>
<tr>
<td>nitrogen</td>
<td>7</td>
<td>0.070</td>
<td>1406</td>
</tr>
<tr>
<td>oxygen</td>
<td>8</td>
<td>0.066</td>
<td>1314</td>
</tr>
<tr>
<td>fluorine</td>
<td>9</td>
<td>0.064</td>
<td>1682</td>
</tr>
<tr>
<td>neon</td>
<td>10</td>
<td>0.070</td>
<td>2086</td>
</tr>
<tr>
<td>sodium</td>
<td>11</td>
<td>0.186</td>
<td>418</td>
</tr>
<tr>
<td>magnesium</td>
<td>12</td>
<td>0.180</td>
<td>736</td>
</tr>
<tr>
<td>aluminum</td>
<td>13</td>
<td>0.143</td>
<td>577</td>
</tr>
<tr>
<td>silicon</td>
<td>14</td>
<td>0.117</td>
<td>787</td>
</tr>
<tr>
<td>phosphorus</td>
<td>15</td>
<td>0.110</td>
<td>1083</td>
</tr>
<tr>
<td>sulfur</td>
<td>16</td>
<td>0.104</td>
<td>1000</td>
</tr>
<tr>
<td>chlorine</td>
<td>17</td>
<td>0.099</td>
<td>1235</td>
</tr>
<tr>
<td>argon</td>
<td>18</td>
<td>0.094</td>
<td>1518</td>
</tr>
<tr>
<td>potassium</td>
<td>19</td>
<td>0.231</td>
<td>418</td>
</tr>
<tr>
<td>calcium</td>
<td>20</td>
<td>0.137</td>
<td>580</td>
</tr>
</tbody>
</table>
d) The Size of Atoms

The radius of an atom (or ion) = the distance from the centre of the nucleus to the valence electron shell. The radii of atoms and ions is determined by X-Ray diffraction:

- X-Rays are shone through a material producing a diffraction pattern.
- Mathematics is used to translate the pattern into the distances between the atoms or ions.

The atomic radius of an element is difficult to precisely define because of the uncertainty over the size of the electron cloud.

Several definitions are used, depending on the type of bonding.

Another definition is half the shortest internuclear distance found in the structure of the element.

Trends in the Sizes of Atoms

You are expected to know - and be able to explain - the following observed trends in the size of atoms:

The radii of the atoms (atomic radii) DECREASE as atomic number increases along each period.

Reason: Moving with increasing atomic number (from L → R) along a period:

- The number of protons and valence shell electrons are increasing.
- The electrostatic attractive force between protons and electrons increases.
- This increase in the number of protons increases the positive nuclear charge of the atoms, meaning the nucleus has a stronger attraction for the electrons, pulling them in closer.

Increased nuclear charge pulls electrons closer.
The atomic radii INCREASE as the atomic number increases moving down each group.

**Reason:** Moving with increasing atomic number down a group:
- The number of protons and electrons increase dramatically with each new period because a **new valence shell/energy level** is added every time a new period begins.
- However, each new valence shell is **further away from the nucleus** than the one before it (**and the distance between charges is more important than the charge magnitudes**).

Additionally, as the number of **core** electron layers increase, there is increasing interference or "**shielding**" between the nuclear charge and the valence shell charge.

This is known as the **Shielding Effect**. It explains why some atoms are larger than expected.

**What is the Shielding Effect?**

- **outermost e^-** are attracted towards the positive nuclear charge.
- **more protons** = more attraction between nucleus + valence e^-.
- **inner shells of e^- repel the outermost e^-** (core e^-).
- This repulsion cancels out some of the attraction to the nucleus.

- **the reduction in attraction between valence e^- and the nucleus is called "shielding"**.
- **Extra e^- in the same principal energy level have little shielding effect, mostly due to "core e^-"**.
- **the resulting attraction between the valence e^- and the nucleus after shielding is taken into account is called the "effective nuclear charge"**.

Explaining the radius **ACROSS period 3**: what is the role of shielding core electrons?

<table>
<thead>
<tr>
<th>Element</th>
<th>Proton number</th>
<th>Atomic radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>11</td>
<td>0.190</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>0.145</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>0.118</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>0.111</td>
</tr>
<tr>
<td>P</td>
<td>15</td>
<td>0.098</td>
</tr>
<tr>
<td>S</td>
<td>16</td>
<td>0.088</td>
</tr>
<tr>
<td>Cl</td>
<td>17</td>
<td>0.079</td>
</tr>
<tr>
<td>Ar</td>
<td>18</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Proton number **increases** across period 3, but **shielding** remains approximately constant.

This causes an increase in the **effective nuclear charge**, leading to a **greater** attraction between the nucleus and the outermost electrons.

This pulls these electrons **closer** to the nucleus and results in a **smaller** radius.
Ions & Atomic Radius

**Negative Ions:**

As extra **electrons** are added to a neutral atom (e.g., $O$ to make $O^{2-}$) the ion has the **same** positive nuclear charge (due to protons), and an **increased** number of electrons surrounding the nucleus.
- The electrostatic repulsion **increases** ($e^- \text{ repel } e^-$)
- The **volume** occupied by the electrons **increases** (more $e^-$ attracted to same # protons).

**NEGATIVE IONS are LARGER**
than the corresponding neutral atom

**Positive Ions:**

As **electrons** are removed from a neutral atom (e.g., $Mg$ to make $Mg^{2+}$) the ion has the **same** positive nuclear charge (due to protons), and a **decreased** number of negative electrons surrounding the nucleus.
- The electrostatic repulsion **decreases** (fewer $e^-$ attracted to same # protons).
- The **volume** occupied by the electrons **decreases**

**POSITIVE IONS are SMALLER**
than the corresponding neutral atom

---

e) **Valence Electrons Reconsidered**

**Definition:** Valence electrons are now thought of as those electrons found in **open shells**. They are the electrons that are available for, and involved in, chemical bonding.

*(Remember, we are only considering the representative elements for the time being)*

<table>
<thead>
<tr>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>0</td>
</tr>
</tbody>
</table>

An **open shell** is a shell containing less than its maximum number of electrons.

No "open" shells.
f) The Valence of an Atom

When atoms bond their atomic orbitals are blend together into molecular orbitals. For the representative elements, the s and p orbitals blend to form sp-type bonding orbitals (d and f orbitals will not be considered). For our purposes, there will always four sp-type molecular orbitals:

\[ \text{sp orbitals} \]

\[ s \rightarrow 2e^- \]
\[ p \rightarrow 6e^- \]

\[ \text{valence: 1} \]
\[ 2 \]
\[ 3 \]
\[ 4 \]
\[ 3 \]
\[ 2 \]
\[ 1 \]
\[ 0 \]

(* The actual details of hybridized molecular orbitals are beyond the scope of Chemistry 11*)

Definition: The valence of an atom is defined as the number of unpaired \( e^- \) in an atom.

- is also the number of \( e^- \)'s that are normally unavailable for bonding.
- is also sometimes referred to as combining capacity

\[ \text{(how many bonds can be formed)} \]

g) Ionization Energy

Definition: The ionization energy is the amount of energy needed to REMOVE a valence electron from one mole of an element in the gas state.

In order to form a positively charged ion, an electron must be removed from a neutral atom.

**EXAMPLE:** \( \text{Li} + \text{energy} \rightarrow \text{Li}^+ + e^- \)

Comment: Ionization energy is usually expressed in units of \( \text{kJ/mol} \). The element must be in the gas state prior to determining the ionization energy so that we know that the energy input is entirely being used to ionize the atom (and not contributing to, for example, a change of state).

- Ionization energy DECREASES going down a family in the periodic table
- ionization energy INCREASES going from left to right across a period
42. Fill in the blanks using the words "OPEN" or "CLOSED". The entries in the 1st and 3rd columns refer to the TOTAL NUMBER of electrons possessed by an atom.

<table>
<thead>
<tr>
<th>If an atom has:</th>
<th>Then its outermost shell is:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 electron</td>
<td>10 electrons</td>
</tr>
<tr>
<td>2 electrons</td>
<td>11 electrons</td>
</tr>
<tr>
<td>3 electrons</td>
<td>16 electrons</td>
</tr>
<tr>
<td>8 electrons</td>
<td>18 electrons</td>
</tr>
</tbody>
</table>

43. Which family of elements appears to possess only CLOSED SHELLS? Which elements have open shells?

44. Which of the following have an OPEN SHELL and which have ALL SHELLS CLOSED?
   (a) Cl   (c) Mg   (e) Na⁺   (g) O⁻   (i) I
   (b) Ne   (d) Si   (f) Cl⁻   (h) Ca²⁺   (j) Al⁺

45. Fill in the number of valence electrons corresponding to each atom.

<table>
<thead>
<tr>
<th>atom</th>
<th># of valence electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td></td>
</tr>
<tr>
<td>Ne⁺</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td></td>
</tr>
<tr>
<td>S⁻</td>
<td></td>
</tr>
<tr>
<td>S²⁻</td>
<td></td>
</tr>
</tbody>
</table>

48. (a) What happens to the distance between the nucleus and outermost electrons going down a chemical family?
   (b) What happens to the electrostatic attraction of the nucleus to an electron in the outermost shell going down a family?
   (c) What happens to the ionization energy going down a family?

49. (a) What happens to the distance between the nucleus and the outermost electrons going left to right across a period? (Hint: see exercise 41.)
   (b) What happens to the nuclear charge going across the period?
   (c) What happens to the electrostatic attraction of the nucleus to an electron in the outermost shell going across a period?
   (d) What happens to the ionization energy going across the period?

50. Place arrowheads in the correct direction on the horizontal and vertical lines below.

   Ionization energy INCREASES
   Periodic Table
   Ionization energy INCREASES

51. Which member of each of the following pairs should have a greater ionization energy?
   (a) Br or Cl   (b) Al or Cl   (c) Cs or Xe   (d) Mg or Ba   (e) F or Ne   (f) Rb or I

53. Consider two atoms: O and Te.
   (a) Which atom has a larger atomic radius?
   (b) Which atom has the larger ionization energy?
   (c) Which atom has more shells?
   (d) How many valence electrons does Te have?
   (e) What is the valence of Te?
   (f) Which atom has a greater electrostatic attraction between its nucleus and outermost electrons: O or Te?

54. Which ion pair has a greater electrostatic attraction between ions: Li⁺ and F⁻ or Na⁺ and Cl⁻?

55. Consider two atoms: Ga and Br.
   (a) Which atom has a larger atomic radius?
   (b) Which atom has the larger ionization energy?
   (c) Which atom has more shells?
   (d) How many valence electrons does each atom have?
   (e) What is the valence of each atom?
   (f) Which atom has a greater electrostatic attraction between its nucleus and outermost electrons?

56. Which of the following have open shells?
   (a) Se   (b) Br⁻   (c) S²⁻   (d) Kr⁺   (e) Xe   (f) Sb³⁻   (g) Ge
SPECIAL NOTE: The following must be remembered when examining trends down or across the periodic table.

When going DOWN a family in the periodic table, properties are affected by the INCREASING SIZE of the atoms and the INCREASING DISTANCE between the nuclei and the valence electrons.

When going ACROSS a period in the periodic table, properties are affected by the DIFFERING VALENCE, NUCLEAR CHARGE and CHARGE ON THE SPECIES.

B. ELECTRONEGATIVITY

Electronegativity (χ) is defined as the ability of an atom in a molecule to steal electrons from another atom (attract e- to itself).

Electronegativity is a function of two properties of isolated atoms:

i. The atom’s ionization energy (how strongly an atom holds onto its own electrons)
ii. The atom’s electron affinity (how strongly the atom attracts other electrons)

For example, an element which has a large (negative) electron affinity and a high ionization (always endothermic, or positive for neutral atoms)...  
...Will attract e- from other atoms and resist having electrons taken away.

We say these atoms are “highly electronegative”

• atoms with ↑ χ are very attractive to the valence electrons of neighbouring atoms
• atoms with ↑ χ strongly attract their own valence e- (almost never lose one)
• values of χ range from a low of 0.7 (Fr) to a high of 3.9 (F):

The difference in electronegativity between two atoms, Δχ, tells you what type of bond will form.

Electronegativity increases across a period because:

1. The atomic radius decreases
2. The charge on the nucleus increases without significant extra shielding. New electrons do not contribute much to shielding because they are added to the same principal energy level across the period.

(valence) e- held tightly/strongly

Electronegativity decreases down a group because:

1. The atomic radius increases
2. Although the charge on the nucleus increases, shielding also increases significantly. This is because electrons added down the group fill new principal energy levels.

(valence) e- held more weakly
Electronegativities

Table 6.3.3 Relationship of ΔEN and Bond Designation

<table>
<thead>
<tr>
<th>ΔEN</th>
<th>Bond Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>non-polar covalent</td>
</tr>
<tr>
<td>&lt; 0.4</td>
<td>mostly covalent</td>
</tr>
<tr>
<td>0.4 - 1.7</td>
<td>polar covalent</td>
</tr>
<tr>
<td>&gt; 1.7</td>
<td>ionic</td>
</tr>
</tbody>
</table>

C. TYPES OF CHEMICAL BONDS

An IONIC BOND is formed by the electrostatic attraction between a cation and an anion.

- results when Δχ ≥ 1.7
- usually involves a metal (low χ) and non-metal (high χ)
- relatively strong bonds (strength depends on ionic radii and charges of the ions).

e.g. NaCl is an ionic bond because...

\[
\begin{align*}
\chi_{\text{Na}} & : 0.9 \\
\chi_{\text{Cl}} & : 3.0 \\
\end{align*}
\]

\[
\Delta \chi = 3.0 - 0.9 = 2.1
\]

It is this electrostatic attraction that forms ionic bonds in sodium chloride and other ionic compounds.

Electronegativity & Ionic Bonds:

- Formed between two atoms with large differences in their ionization energies and electronegativities

An electronegativity difference of greater than 1.7 can be classified as an ionic bond

- In this case we can essentially say electrons are transferred from one atom to another
**Practice Problems — Ionic Compounds**

Write formulas for the ionic compounds formed when the following elements combine. Using the ΔEN values, arrange the compounds in order of the increasing ionic character of the bonds in each compound.

(a) Na and N  
(b) Sr and Br  
(c) Li and Cl  
(d) Cs and F  
(e) Rb and O

**How do ionic bonds form?**

a) Pre-existing Ions Get Together  *e.g.* double replacement reaction (maybe ppt formation)

b) Atoms React To Form Ions Which Then Combine (Electron transfer)

- The **metal atom** **LOSES** one (or more) electrons to establish a **closed outer shell**
- The **non-metal atom** **GAINS** one (or more) electrons to establish a **closed outer shell**
- both ions are then **isoelectronic** to their nearest **noble gas**.(\* The Octet Rule)
- the ions are held together by the **attraction of their opposite charges**

**Lewis Structures** show the electrons in the valence shell of an atom, ion, or molecule.

*example 1:*

\[
\text{Li}^+ + \text{F}^- \rightarrow \text{Li}^{+}\text{F}^- \text{[isoelectronic to noble gas]}
\]

*example 2:*

\[
\text{K}^+ + \text{Br}^- \rightarrow \text{K}^{+}\text{Br}^- \text{[isoelectronic to noble gas]}
\]

**Predicting Ion Charges**

<table>
<thead>
<tr>
<th>Group (Family)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge on the Ion</td>
<td>+1</td>
<td>+2</td>
<td>+3</td>
<td>/ /</td>
<td>-3</td>
<td>-2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

When atoms form ions, they lose or gain electrons to get a closed shell.

Groups 14 and 15 are only partially predictable.

- C, Si, and Ge **usually do not form ions** while Sn and Pb **form ions** \(\Rightarrow\) generally +2 or +4, +5 cations

For Ionic Bonds:
Pretend that each ion’s charge is at its centre. Compare distances between the centres.

**Which ionic bond is stronger?**

\[
\text{LiF} \quad \text{BrCl}
\]

**Why?**

**Smaller distance between ions \(\Rightarrow\) larger force**

- isoatomic to noble gases
Properties of Ionic Compounds

What is an ionic lattice?

In an ionic compound when any macroscopic sample ions react together, countless atoms will transfer electrons to form countless oppositely charged ions.

These oppositely charged species being produced in close proximity are drawn together into an giant, 3D, ordered, solid, three-dimensional array of cations and anions called a crystal lattice.

The smallest whole number cation-anion ratio in this structure represents the chemical formula for the ionic compound.

The structure of the ionic lattice affects the properties of the ionic compound.

All ionic compounds form lattices and crystals when (s) solid.

Heating ionic compounds

Why are ionic compounds solid at room temperature and have high melting points and boiling points?

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ion charges</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium chloride</td>
<td>1⁺ and 1⁻</td>
<td>801</td>
<td>1,413</td>
</tr>
<tr>
<td>magnesium oxide</td>
<td>2⁺ and 2⁻</td>
<td>2,852</td>
<td>3,600</td>
</tr>
</tbody>
</table>

- Ionic bonds are strong and a lot of heat is needed to break them.
- Larger ionic charges produce stronger ionic bonds and so much more heat is required to break the ionic bonds in magnesium oxide than in sodium chloride.

How can ionic compounds conduct electricity?

- As solids, ionic compounds cannot conduct electricity because their ions are bonded together in the lattice.
- When liquid (molten), the ions can break free of the lattice and are able to move. The ions are charged particles and so carry an electric current.
- Ionic compounds are usually soluble in water because water molecules have a slight electrical charge and so can attract the ions away from the lattice. When dissolved, the ions are free to move and can carry an electric current.

Why are ionic compounds brittle? - they shatter when they are hit.

- When the lattice is hit, a layer of ions is shifted so that ions with the same charges are lined up together.
- These like charges repel each other and so split the ionic lattice causing it to shatter.
1. Ionic compounds are electrically neutral. For this reason, the total amount of charge must equal total charge.

2. All ionic compounds are solid and brittle at room temperature. How does the model above help to explain this fact?

3. The higher the melting point of an ionic compound, the stronger the ionic bond.

**Homework**

Assignment #3 Hebden pg. 172 #57ace, pg. 173 #58-61 pg 175 #63-64adf pg. 176 #65-67

_all assignments are to be completed on a separate page with the assignment number & heading_

**EXERCISE:**

57. Which of the following atom pairs would you expect to form ionic bonds when they join?
   (a) Ba and S  (b) P and Cl  (c) Ca and O  (d) Rb and I  (e) O and H  (f) S and O

58. This exercise compares Li and F.
   (a) Which atom is larger: Li or F? (Hint: see exercise 41.)
   (b) Which atom has the stronger attraction to the outer electrons on a neighbouring atom, based only on the atomic radius?
   (c) Which atom has the greater nuclear charge?
   (d) Which atom can attract electrons from an adjacent atom most strongly, based on both size and nuclear charge?
   (e) Summarize the above by filling in the blank below.

   **IN GENERAL, when going from left to right across the periodic table the electronegativity of the atoms will**

59. This exercise compares F and I.
   (a) Which atom is larger: F or I?
   (b) Which atom has a stronger attraction to the outer electrons of another atom?
   (c) Summarize the above by filling in the blank below.

   **IN GENERAL, when going down a family of the periodic table the electronegativity of the atoms will**

60. Place arrowheads in the correct direction on the horizontal and vertical arrows below.

   ![Electronegativity Increases Diagram]

61. (a) Ignoring the noble gases, which atom is the most electronegative?
    (b) Ignoring the noble gases, which atom is the least electronegative?
    (c) Which is more electronegative: K or Be?
    (d) Which is more electronegative: Pb or S?
63. Mg$^{2+}$ and Na$^+$ have roughly the same ionic radius. O$^{2-}$ and F$^-$ have roughly the same ionic radius. Which substance should have a higher melting temperature: NaF or MgO? Why?

64. Which member of each following pair would you expect to have the higher melting point?
   (a) CaO or RbCl  
   (b) BeO or BN  
   (c) LiF or NaCl  
   (d) CsCl or BaS  
   (e) RbI or KCl  
   (f) BeO or MgS

65. **NEGATIVE IONS**: Assume extra electrons are added to a neutral atom of O to make O$^{2-}$. The resulting ion has the same positive nuclear charge and an increased number of negative electrons surrounding the nucleus.
   (a) What happens to the amount of electrostatic repulsion existing between the electrons?
   (b) What happens to the volume occupied by the electrons due to the change in the amount of electron–electron repulsion?
   (c) Fill in the appropriate word.

   **NEGATIVE IONS are** ________________ than the corresponding neutral atom.

66. **POSITIVE IONS**: Assume electrons are removed from a neutral atom of Mg to make Mg$^{2+}$. The resulting ion has the same positive nuclear charge and a decreased number of negative electrons surrounding the nucleus.
   (a) What happens to the amount of electrostatic repulsion existing between the electrons?
   (b) What happens to the volume occupied by the electrons due to the change in repulsion?
   (c) Fill in the appropriate word.

   **POSITIVE IONS are** ________________ than the corresponding neutral atom.

67. Examine the diagram below, which shows a section of a crystal of NaCl.

Which circles represent Na$^+$:
the larger or smaller ones?
WHY DO ATOMS FORM BONDS?

- Bond formation begins with atoms "colliding"

- For example as two hydrogen atoms approach each other, their **kinetic energy** increases as each electron cloud is attracted to the other's approaching **positive nucleus**.

- Atoms continue moving together until the **repulsive forces** of the two negative electron clouds and the two positive nuclei slow the atoms and convert their kinetic energy into **potential energy (bond energy)**.

**Shared electron pair = covalent bond**

- As the atoms get close to each other, their **electron clouds** overlap enough to cause an **attractive** force to exceed the **repulsive** ones.

- The two valence electrons will move into the region of space between the atoms nuclei.

- This force of attraction of a pair of valence electrons between two adjacent nuclei constitutes a single **covalent bond**.

The atoms of noble gases have completely full outer shells and so are stable.

This makes the noble gases very unreactive and so they do not usually form bonds.

The atoms of other elements have incomplete outer electron shells and so are unstable.

By forming bonds, the atoms of these elements are able to have filled outer shells and become stable.

Non-metal elements usually just need one or two electrons to fill their outer shells. So how do they form a bond?

The two non-metal atoms cannot form a bond by transferring electrons from one to another. Instead, they **share electrons**.

Each atom now has a full, stable outer shell.

The shared electrons join the atoms together. This is called a **covalent bond**.

**A COVALENT BOND** is formed when two atoms complete their octets by **sharing** one or more **pairs of electrons**.

- results when \( \Delta \chi < 1.7 \)

- usually involves a non-metal and a **non-metal**

- both nuclei get to be attracted to more electrons

- both atoms complete their **valence** shells.

- Covalent bonds are **VERY strong**
I. Single (Covalent) Bonds

- formed when two atoms share a single pair of electrons.
- simplest examples are the homogeneous diatomic molecules. (HOFBrINCl elements)

Many non-metal elements, such as hydrogen, exist as simple diatomic molecules that contain covalent bonds.

**How is a covalent bond formed in diatomic molecules?**

**Example 1**

\[ \text{H} \cdot + \cdot \text{H} \rightarrow \text{H} : \text{H} \]

Each H atom has 1 valence e\(^{-}\) \(\Rightarrow\) only s-orbitals (no sp-blended orbitals)

**Example 2**

\[ \text{F} \cdot + \cdot \text{F} \rightarrow \text{F} : \text{F} \]

As they bond, the s and p orbitals "bend" to form sp-orbitals (2e\(^{-}\)) \(\Rightarrow\) 4 sp orbitals

- The overlapping of orbitals to share e\(^{-}\) is the bond.
- 6 "sigma" bond (single bond)
- sp overlap is the bond

The number of electrons that an atom can share is usually the same as its valence.

**Example 3** How many single bonds would you think Carbon could form? Oxygen? Bromine?

\[ \text{C} : [\text{He}] 2s^2 \text{p}^2 \quad \frac{7}{2} \frac{7}{2} \rightarrow \frac{7}{2} \frac{7}{2} \]

\(\Rightarrow\) 4 sp orbitals

\(\therefore\) 4 single bonds possible

\[ \text{O} : [\text{He}] 2s^2 \text{p}^4 \quad \frac{7}{2} \frac{7}{2} \rightarrow \frac{7}{2} \frac{7}{2} \]

\(\Rightarrow\) sp orbitals

\(\therefore\) 2 single bonds possible

\[ \text{Br} : [\text{Ar}] 4s^2 \text{p}^{10} \text{d}^5 \text{p}^5 \quad \frac{7}{4} \frac{7}{4} \rightarrow \frac{7}{4} \frac{7}{4} \]

\(\Rightarrow\) sp orbitals

\(\therefore\) 1 single bond possible
II. Double & Triple (Covalent) Bonds: Non-metal atoms with less than 7 valence e' s are able to share more than single pair of e' s.

Examples:

Oxygen

\[ \text{O}_2 \]

\[ \text{O} = \text{O} \]

\[ \sigma = \text{single bond} \]

\[ \sigma + \pi = \text{double bond} \]

\[ \sigma + 2\pi = \text{triple bond} \]

Carbon Dioxide

\[ \text{O} = \text{C} = \text{O} \]

III. Coordinate Covalent Bonds – atoms that have a non-bonding e' pair in their octet can share to allow an "electron-deficient partner" to complete its octet/duet.

Examples: Ammonium

\[ \text{NH}_4^+ \]

\[ \text{NH}_3 \cdot \text{H}^+ \Rightarrow [\text{H}^- \cdot \text{N} \cdot \text{H}]^+ \]

*NH\textsubscript{3} donated a non-bonding pair of e' to H\textsuperscript{+} ion to form bond.

Hydronium

\[ \text{H}_2\text{O}^+ \]

\[ \text{H}_2\text{O} \cdot \text{H}^+ \Rightarrow [\text{H}^- \cdot \text{O} \cdot \text{H}]^+ \]

*H\textsubscript{2}O donated a non-bonding pair of e' to H\textsuperscript{+} ion to form bond.

In "normal" covalent bonding, each atom contributes an electron to the bond.

In Coordinate covalent bonding both electrons are donated to the bond from a single atom...

...the other just "shows up"
Orbital "blending" during bonding is complex, and certainly extension. It can be helpful in determining the bond type: i.e. single, double or triple bond.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>No. of σ bond</th>
<th>No. of π bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single (C-H)</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Double (C=C)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Triple (C≡C)</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

\[
\text{H—Cl:} \quad \text{:O=O:} \quad \text{:N≡N:}
\]

One σ bond
No π bonds
One σ bond
One π bond
Two π bonds

How is the ratio of atoms calculated?

To calculate the ratio of atoms in a stable covalent compound:

1. Work out how many electrons are needed by each non-metal element to complete its outer electron shell.
2. Work out the ratio of atoms that will provide enough shared electrons to fill all the outer shells.

EXAMPLE:

How do carbon and hydrogen atoms form covalent bonds in a molecule of methane?

<table>
<thead>
<tr>
<th>element</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron configuration</td>
<td>$\text{He} \rightarrow \text{He}^2$</td>
<td>$\text{He}^2$</td>
</tr>
<tr>
<td>electrons needed</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>ratio of atoms</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

$\text{HOOH} \Rightarrow \text{H—C—H}$

\(4\) single bonds

...not an effective method for ions, neutral compounds only.
EXERCISE:

68. Which of the following atom pairs would you expect to form covalent bonds when they join?
   (a) S and O          (c) Fe and Cl          (e) H and S
   (b) Ba and O         (d) N and O           (f) C and H

69. (a) When the distance between two covalently-bonded atoms increases, what happens to the electrostatic attraction of their nuclei to the shared electrons in a covalent bond?
   (b) What would you expect to happen to the strength of the covalent bond between two identical halogen atoms when going down the halogen family from F₂ to I₂?

70. What would you expect to happen to the strength of a covalent bond when the number of shared electrons increases?

71. The distance between the nuclei of two atoms involved in a bond is called the BOND LENGTH. What should happen to the bond length as the number of shared electrons in the bond increases? Why will this happen?

72. Predict the formula of the compound formed by bonding together the following.
   (a) P and Cl          (d) P and O          (g) H and O          (j) C and Cl
   (b) B and O           (e) H and Se         (h) N and I           (k) Si and P
   (c) C and S           (f) F and O          (i) B and C           (l) Si and S
D. PREDICTING MOLECULAR STRUCTURES

How to Draw Lewis Structures

1. Determine the total number of valence electrons in the molecule
   - if species is a molecular ion, then adjust number accordingly
     (add for anions; subtract for cations)

2. Determine which atoms are bonded together and put two electrons into each bond.
   
   **Tips:**
   1) The central atom is usually the highest valence, most electropositive species.
   2) Unless necessary (see next section), do not exceed the valence of each atom!

3. Use the remaining valence electrons to complete the octets of the surrounding atom(s).
   
   - additional de- can complete octet for 'O' atoms?
   - no more than 8e-

4. Place any remaining electrons in pairs on the central atom.
   
   - none remaining.

5. If a central atom has less than an octet of electrons, then have an adjacent atom share an additional pair of its non-bonding electrons with the electron deficient atom (results in a double bond).
   If necessary (and appropriate), assign a triple bond.

6. Replace all bonding electron pairs with dashes.

---

a) The Lewis Structures of Simple Ionic Compounds

The Lewis Structure of an ionic compound is simple to construct. You previously have been shown some example structures for such compounds; this section extends the previous work.

**EXAMPLE:** Draw the Lewis Structure of MgCl₂.

First, determine the charge expected for each ion. In this case, the ions are Mg²⁺ and Cl⁻.

For the purposes of Chemistry 11, the nonmetal ions are symmetrically arranged around the metal ion. Remove the two electrons from the Mg atom to form the Mg²⁺ ion. Add one electron to each Cl atom to form the Cl⁻ ion.

```
: Cl⁻  : Mg²⁺  : Cl⁻  :
```

must show ion!
b) The Lewis Structures of Covalent Compounds that Obey the Octet Rule

Lewis Structures show how the \textit{valence} electrons are distributed in a molecule. The octet rule states that most atoms, other than hydrogen, tend to attain an octet of electrons as a result of forming covalent bonds.

\textbf{Example:} The Lewis structure of H$_2$O is shown below.

```
      H : O : H
```

For water, above, H and O contribute one electron each to the covalent bonds between them and share the two electrons in the bond. Each H can then "lay claim" to a closed shell of 2 electrons. The O atom has 4 electrons which it does not share with the H's in addition to the 4 electrons shared with the H's, for a total of 8 electrons: a closed shell and a "full octet".

Drawing the Lewis Structures of molecules follows a simple set of rules.

\textbf{Example 3} Draw the Lewis Structures for the methane, CH$_4$, and ethene, C$_2$H$_4$.

\textbf{a) Methane: CH$_4$}

\#valence e$^-$: 4 + 4(1) = 8

\textit{not an ion} \textbf{ratio: C : H (swap val. \#)}

\[\text{C} : \text{H} = 1 : 4\]

\textbf{b) Ethene: C$_2$H$_4$}

\#valence e$^-$: 2(4) + 4(1) = 12$^-$

\textbf{Example 4} Draw the Lewis diagram for the nitrate ion, NO$_3^-$.

\#valence e$^-$: 5 + 3(6) + 1 = 24$^-$

\textbf{ratio N : O}

\[\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array}\]
Exceptions to the Octet Rule:

1. Fewer than 8 valence electrons
   Such molecules are called **electron-deficient molecules**

   Examples:
   - $\text{BeH}_2$
   - $\text{BF}_3$
   - $\text{H}_2\text{BeH}_2$

2. Expanded Valence
   - Central atoms from the third and fourth periods can be surrounded by more than 8 valence $e^-$'s. (The extra $e$'s get promoted to low-level d-orbitals)
   - Please remember these two: $\text{P}$ (up to 10 e$^-$'s) and $\text{S}$ (up to 12 e$^-$'s)
   - The good news is that the rules given earlier still apply!

   Examples:
   - $\text{PCl}_5$
   - $\text{SCl}_6$

---

**Homework**

Assignment #4 Hebden pg. 183 #85, pg 188 #86 & Lewis Diagrams / Bonding Worksheet (next page)

all assignments are to be completed on a separate page with the assignment number & heading

**EXERCISE:**

85. Draw the Lewis Structure of each of the following ionic compounds.
   (a) $\text{KBr}$   (b) $\text{AlCl}_3$   (c) $\text{MgO}$   (d) $\text{Li}_2\text{S}$   (e) $\text{K}_3\text{P}$

86. Assign Lewis structures to the following molecules.
   (a) $\text{H} \quad \text{Cl}$   (b) $\text{I} \quad \text{I}$   (c) $\text{I} \quad \text{Cl}$
   (d) $\text{H} \quad \text{H} \quad \text{C} \quad \text{C}$
   (e) $\text{C} \quad \text{C}$
   (f) $\text{H} \quad \text{C} \quad \text{C} \quad \text{H}$
1. Draw electron dot diagrams for the following atoms: (1 mark each)
   a. C
   b. H
   c. Na
   d. Cl
   e. P
   f. Kr
   g. Fr
   h. Mg
   i. Al
   j. O

2. Draw electron dot diagrams for the following ions: (1 mark each)
   a. Na⁺
   b. Cl⁻
   c. Fr⁺
   d. Mg²⁺
   e. Si⁴⁺

3. Draw Lewis structures for the following compounds: (1 mark each)
   a. CO₂
   b. PBr₃
   c. SeF₂
   d. KI
   e. CH₄
   f. C₂H₄
   g. N₂
   h. H₂O
   i. O₂
   j. N₂Br₄
   k. SeCl₂
   l. H₂S
   m. CH₃CH₂CH₃
   n. SO₃²⁻
   o. H₂
E. BOND ENERGY; RELATIVE BOND STRENGTH & REACTIVITY

To break a bond the \( E_p \) (stored in the bond) must be increased.

\[ \Rightarrow \text{bond breaking requires energy (endothermic)} \]

\[ \Rightarrow E_p \text{ converted into } E_k \text{ as bond forms} \]

\[ \therefore \text{bond formation results in energy output} \]

If energy input > energy output, then reaction is \textit{endothermic}.

If energy input < energy output, then reaction is \textit{exothermic}.

**Bond Energy** = the energy (kJ/mol) required to separate two bonded atoms

**Example**: One mole of \( \text{H}_2(\text{g}) \) requires 436 kJ of energy input to separate the two H atoms. Conversely, when two H atoms form a bond, \( \Delta H = 436 \text{ kJ/mol} \times 2 \text{ mol} = 872 \text{ kJ} \) energy is released.

The bond energies have been determined for every kind of covalent bond. We can look them up!

**Significance**: Allows chemists to predict \( \Delta H \) for a given chemical reaction, which is done as follows:

\[ \Delta H = \text{Sum of the bond energies of broken bonds} - \text{Sum of the bond energies of bonds formed} \]

**Bond Characteristics**

<table>
<thead>
<tr>
<th></th>
<th>Single Bonds</th>
<th>Double Bonds</th>
<th>Triple Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td>lonest</td>
<td>snarest</td>
<td>least</td>
</tr>
<tr>
<td><strong>Strength</strong></td>
<td>weakest</td>
<td>strongest</td>
<td></td>
</tr>
<tr>
<td><strong>Reactivity</strong></td>
<td>most reactive</td>
<td>least reactive</td>
<td></td>
</tr>
</tbody>
</table>

Examples

- **Bond Length:**
  - \( \text{C} \equiv \text{C} \) 154 pm
  - \( \text{C} \equiv \text{C} \) 134 pm
  - \( \text{C} \equiv \text{C} \) 120 pm

- **Bond Energy:**
  - \( \text{C} \equiv \text{C} \) 348 kJ/mol
  - \( \text{C} \equiv \text{C} \) 614 kJ/mol
  - \( \text{C} \equiv \text{C} \) 839 kJ/mol

F. RESONANCE

In many cases, the Lewis structure of a molecule predicts more than one possible placement for double bonds. When more than one possible arrangement exists, we must draw all the resonance structures. In fact, the experimental data indicates that the actual molecule is a "blending" of all the possible resonance structures. **Resonance structures** = Lewis structures with the same arrangement of atoms, but different arrangements of electrons.

Always use square brackets (even when there is no charge) and arrows between all of your resonance structures.
Example 1: Draw the Lewis structure for the carbonate ion.

\[ \text{C} \quad \text{O} \quad \text{e}^- \quad \text{O} \quad \text{e}^- \quad \text{O} \]

\[ \text{carbon needs 2 more } e^- \]

\[ \text{au} \text{O} \text{have a satisfied octet} \]

\[ \text{The double bond could be formed by ANY of the oxygen atoms.} \]

\[ \text{at a time... not au} \]

* The actual structure is a BLEND of 3 resonance structures, 1 Lewis diagram doesn't represent.

Example 2: Which should have the shorter sulfur-oxygen bonds, \( \text{SO}_3 \) or \( \text{SO}_3^{2-} \)?

\( \text{SO}_3 \)

\[ \#e^-: 6 + 3(6) = 24e^- \]

\[ \text{Sulfur needs 2 more } e^- \]

\[ \text{Oxygens } 8e^- \]

\[ \left( \begin{array}{c} \text{O} \\ \text{S} \\ \text{O} \end{array} \right) \quad \left( \begin{array}{c} \text{O} \\ \text{S} \\ \text{O} \end{array} \right) \quad \left( \begin{array}{c} \text{O} \\ \text{S} \\ \text{O} \end{array} \right) \]

\[ \text{L6 bonds are } 1 \frac{1}{3} \]

\[ \text{resonance structure is really a hybrid} \]

\[ \text{any of the unshared } e^- \text{ pairs could have formed the double bond} \]

\( \text{SO}_3^{2-} \)

\[ \#e^-: 6 + 3(6) + 2 = 8\text{e}^- \]

\[ \text{place additional } e^- \text{ to complete octet} \]

\[ \left( \begin{array}{c} \text{O} \\ \text{S} \\ \text{O} \end{array} \right) \quad \left( \begin{array}{c} \text{O} \\ \text{S} \\ \text{O} \end{array} \right) \quad \left( \begin{array}{c} \text{O} \\ \text{S} \\ \text{O} \end{array} \right) \]

\[ \text{L6 bonds are} \]

\[ \text{SO}_3 \text{ has shorter bonds.} \]

\[ \text{(shorter+} \text{stronger)} \]
Assignment #5 can be completed in the space provided below

Chemical Bonding: Exercise Set 1

1. Define the following terms:
   a) Electronegativity –
   b) Open shell –
   c) Covalent bond –
   e) Valence electrons –
   g) Valence –
   h) Ionic bond –
   i) Polar covalent bond –

2. Draw the Lewis Structure for each of the following ionic compounds (see notes for guidance):
   a) \( K_2S \)     b) \( AlN \)     c) \( Rb_3P \)

3. Draw the Lewis Structure for each of the given compounds (show your work):
   a) \( H_2Se \)     b) \( Br_2 \)     c) \( BeF_2 \)
   
   d) \( NO^- \)     e) \( N_2H_4 \)     f) 1-Pentene \( (C_5H_{10})^- \)
4. Which atom is bigger: Pb or Si? Why?

5. Is it easier to break the double bond in $O_2$ or $S_2$? Why?

6. Explain how an ion is formed.

7. Which ionic solid should have the higher melting temperature: AlN (s) or NaF (s)? Why?

8. What number of covalent bonds is each of the following atoms expected to form?
   a) I ____  b) N ____  c) Se ____  d) B ____  e) P ____  f) C ____  g) O ____

9. What is the maximum number of covalent bonds each of the following atoms can form?
   a) N ____  b) O ____  Because each can donate a _________ to _________.
      This is known as a ______________ - ______________ bond.

10. Draw the Lewis structures for the circular molecule benzene, $C_6H_6$. Explain the significance of
    having more than one electron dot structure. What is the name for this phenomenon? Would you
    expect the molecule to have different carbon-carbon bond lengths? Explain.

11. Define the “octet rule” and account for any exceptions to it.
G. MOLECULAR SHAPE AND POLARITY

Let's reconsider covalent molecules in a little more detail:

- When a whole network of atoms are covalently bonded together, we have a special case of covalent bonding: **covalent crystals**. Examples of these substances include diamond, silicon carbide and boron nitride. The covalently bonded atoms form a **crystal lattice** or **network**.

- Note the very high melting temperatures:
  - Boron nitride (BN) ~ 2700°C
  - Silicon carbide (SiC) ~ 2700°C
  - Diamond (C) ~ 3800°C

- What would you conclude about the strength of the covalent bonds in covalent crystals? **Covalent bonds are VERY strong.**

**Q**: Is it surprising that **many** covalent compounds do **not** have very high melting points?

**Examples**:  
- CH₄ ~ -183°C  
- O₂ ~ -219°C  
- F₂ ~ -220°C

What explains this fact? It turns out that there are other types of bonding responsible for the phases of these substances. Consider H₂O which melts at 0°C.

So when ice melts, it is the **much weaker forces of attraction BETWEEN the molecules** break (not the covalent bonds)

The covalent bonds **within** these molecules are strong **but** the bonds **between** molecules are weak and easy to break.
Types of Covalent Bonds:
We have discussed the two extreme cases of bonding: **complete e- transfer** - ionic bonding
And **covalent bonds** with completely **equal sharing of e-**
Between these extremes are covalent bonds which involve **UNEQUAL** electron sharing.

When atoms with **different electronegativities** form covalent bonds, those **ΔEN values** may be minimal or significant.

In math & science, the Greek letter delta is used as a prefix and has two meanings: **Δ** means **change** while **δ** means **partial**

<table>
<thead>
<tr>
<th>ΔEN</th>
<th>Bond Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>non-polar covalent</td>
</tr>
<tr>
<td>&lt; 0.4</td>
<td>mostly covalent</td>
</tr>
<tr>
<td>0.4 - 1.7</td>
<td>polar covalent</td>
</tr>
<tr>
<td>&gt; 1.7</td>
<td>ionic</td>
</tr>
</tbody>
</table>

Table 6.3.3 Relationship of ΔEN and Bond Designation

**Non-Polar Covalent bonds**: If the electronegativity of both atoms in a covalent bond is **identical**, the electrons in the bond will be **equally attracted** to both of them, and form a **non-polar** covalent bond.

This results in a **symmetrical** distribution of e- density around the two atoms.

Bonding in **diatomic molecules** (for example O₂ or Cl₂) is **always non-polar**, because the electronegativity of the atoms in each molecule is **the same**.

**Mostly Covalent bonds**: If **ΔEN** is **< 0.4**, the bonding electrons between the two atoms spend no more of their time nearer one nucleus than the other.

Such bonds are designated as being "**mostly covalent**" because **ΔEN** appears to be **insignificant** (mostly equal sharing of e-).

Another way to characterize this is to say that these bonds have **little ionic character**.

29
Polar Covalent Bonds (aka polar bonds)

**Definition:** A polar covalent bond is one that has one or more electron pairs are *unequally shared.*

- occurs between two atoms when $0.4 < \Delta \chi < 1.7$
- the electron density is *enriched* around the more electronegative element and is *deficient* around the less electronegative element.

Electronegativity and Polar Covalent Bonds

As $\Delta EN$ increases beyond 0.4, the pair of bonding electrons will be *drawn closer* and closer to the nucleus of the atom with the *higher electronegativity*.

This *unequal* distribution of electron density will give that end of the bond a *partially negative* "pole" and the other a *partially positive* "pole."

A bond "dipole" is said to exist and the bond itself is known as a *polar covalent bond*.

**Effect of electronegativity on polarization**

The greater the electronegativity difference between the two atoms in a bond the greater the polarization of the bond.

---

This can be illustrated by looking at the hydrogen halides:

- \( \text{e.g. } H-F \ 4.0-2.2=1.8 \)

### Ionic or covalent?

Rather than saying that ionic and covalent are two distinct types of bonding, it is more accurate to say that they are at the two *extremes on a scale*.

Less polar bonds have more covalent character.

---

More polar bonds have more ionic character.

The more electronegative atom attracts the electrons in the bond enough to ionize the other atom.
Polar & Non-Polar Molecules

A **polar molecule** is one where there is an imbalance in the total sharing of electrons within the molecule.

To be a polar molecule, requires the presence of polar covalent bonds and that those bonds are arranged asymmetrically.

A **non-polar molecule** is one where the total sharing of electrons is balanced.

To be a non-polar molecule, requires either the absence of any polar covalent bonds or that any polar covalent bonds are arranged symmetrically.

**Non-polar molecules**
If the polar bonds are arranged symmetrically, the partial charges cancel out and the molecule is non-polar.

\[
\begin{array}{ccc}
\delta^- & \delta^+ & \delta^- \\
\hline
O & C & O \\
\end{array}
\]

**Polar molecules**
If the polar bonds are arranged asymmetrically, the partial charges do not cancel out and the molecule is polar.

\[
\begin{array}{ccc}
\delta^+ & \delta^- \\
\hline
\delta^- & \delta^+ & \delta^- \\
H & O & H \\
\end{array}
\]

**Key Point:**

**Polar molecules** are those that contain polar covalent bonds and are **ASIMMETRICAL**.

**Non-polar molecules** either

i) have no polar covalent bonds

ii) have polar covalent bonds but the molecule is **SYMmetrical**.

**Example** Verify that the following molecules contain polar covalent bonds:

a) HCl

\[
\begin{array}{c}
\text{Cl} \quad -\quad \text{H} \\
\text{ΔEN: 3.0 - 2.1} \quad = \\
\text{0.9} \quad > \quad \text{0.4} \\
\Rightarrow \text{polar covalent bond}.
\end{array}
\]

b) H$_2$O

\[
\begin{array}{c}
\text{O} \quad -\quad \text{H} \\
\text{ΔEN: 3.5 - 2.1} \quad = \\
\text{1.4} \quad > \quad \text{0.4} \\
\Rightarrow \text{polar covalent bond}.
\end{array}
\]

c) CF$_4$

\[
\begin{array}{c}
\text{C} \quad -\quad \text{F} \\
\text{ΔEN: 4.0 - 2.5} \quad = \\
\text{1.5} \quad > \quad \text{0.4} \\
\Rightarrow \text{polar covalent bond}.
\end{array}
\]

**Example** Classify the molecules in the previous example as polar or non-polar.

a) HCl is a **polar molecule** due to asymmetry.

b) H$_2$O is a **polar molecule** due to asymmetry.

c) CF$_4$ is a **non-polar molecule** due to symmetry.

**Why is this important?**

- the more polar a molecule is, the more attractive it is to other polar molecules.
- the melting and boiling temperatures of all covalent compounds depend on forces of attraction between molecules.

*recall H$_2$O is the "universal solvent"*  
• polar solute will dissolve polar solute  
• non-polar solvent will dissolve non-polar solute

when dissolving: "Like dissolves like"  
ex. polar solvent will dissolve polar solute  
non-polar solvent will dissolve non-polar solute
H. INTERMOLECULAR FORCES OF ATTRACTION

Intramolecular Forces are forces that act within molecules.

- The covalent bonds within a molecule are the most obvious example.
- Disulfide bonds (which cross-link proteins) are another example.

Intermolecular Forces are attractive forces between molecules.

- Due to molecules being permanently, or temporarily, polar (see below...)
- Much weaker than ionic and covalent bonds but can be very significant in large numbers.

Types of intermolecular force

The molecules in simple covalent substances are not entirely isolated from one another. There are forces of attraction between them. These are called INTERmolecular forces, “inter” means “between”, or “Van der Waals forces.”

There are three main types of intermolecular forces:

- **London Forces** — temporary dipolar attractions between neighbouring atoms, for example, between I₂ molecules in iodine crystals.
- **Permanent dipole-dipole forces** for example, found between HCl molecules in hydrogen chloride.
- **Hydrogen bonds** — for example, found between H₂O molecules in water.

Van der Waals forces (animation) (This particular ex. is "London Forces")
**Strength of van der Waals forces**

The strength of van der Waals forces **increases** as molecular size increases.

This is illustrated by the boiling points of group 7 elements. Atomic radius increases down the group, so the outer electrons become further from the nucleus. They are attracted less strongly by the nucleus and so temporary dipoles are easier to induce.

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**The Two Types of Intermolecular Forces (a.k.a. van der Waals Forces)**

1. **London Forces** are weak attractive forces between non-polar molecules (temporary dipoles):
   - are the weakest of all intermolecular forces
   - strength grows with as # of e⁻'s increases.
   - always present, but significant only when no other forces are present.
   - only way to explain why Noble gases (He, Ne, Ar, ...) and non-polar molecules (e.g. H₂, O₂, S₈, CF₄, etc) can form liquids and solids (non-reactive...so we know it isn't intra molecular forces)

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**London Forces are the weakest type of bonding**

The more electrons an atom or molecule has altogether, the stronger the London Forces existing between it and a neighbouring atom or molecule.

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The greater the atomic number of an atom, the stronger the London forces it experiences.
2. **Dipole-dipole Forces** are forces of attraction between polar molecules (permanent dipoles).

- dominant intermolecular force between all polar molecules
- the strongest of these is the Hydrogen Bond.
  - only capable between molecules containing \( H \cdot N, H \cdot O, H \cdot F \)

** why do these three bond types have such strong polarity? N, O, F have very high \( \chi \) values (4+ electrons)

Within any substance containing **polar** molecules, each molecule has a **positive** and a **negative** pole — a **molecular dipole**.

Because of these partial charges, the molecules in the liquid and solid phases will **naturally orient themselves** so that the **positive pole** of one molecule will be next to and **attract** the **negative pole** of an adjacent molecule.

\[ \Delta T < 1.7 \]

If molecules contain bonds with a **permanent dipole**, the molecules may align so there is **electrostatic attraction** between the opposite charges on neighbouring molecules. *(inter molecular \( \Rightarrow \) between molecules)*

**Permanent dipole-dipole forces** (dotted lines) occur in hydrogen chloride (HCl) gas \( \Rightarrow \)(shown below) \( \Rightarrow \)

This network of dipole-dipole forces will result in **higher melting and boiling points** because more energy will be required to **overcome the attractions** between the molecules.

The permanent dipole-dipole forces are approximately \( \frac{1}{100} \) the strength of a covalent bond.

**Examples**

Hydrogen bonds are responsible for water being sticky and its ability to act as a solvent for many things. They are also why it has surface tension and forms raindrops.

Hydrogen bonds are the intermolecular forces that hold the double helix together in DNA.

GC pairings (3 H bonds) provide a stronger force than AT pairings (2 H bonds).

Thermophilic bacteria (naturally live in very hot water) have a lot of GC pairings in their DNA.

This understanding led an oligonucleotide chemist to develop the Polymerase Chain Reaction (PCR) which now allows us to amplify DNA.
**What is hydrogen bonding?**

When hydrogen bonds to nitrogen, oxygen or fluorine, a [larger dipole occurs] than in other polar bonds.

This is because these atoms are [highly electronegative due to their high nuclear charge] and small size.

When these atoms bond to hydrogen, electrons are withdrawn from the H atom, making it $\text{H}^+$ (slightly positive).

The H atom is very small so the positive charge is more concentrated, making it easier to link with other molecules.

*Hydrogen bonds are therefore particularly strong examples of permanent dipole-dipole forces. (i.e: stronger than $\text{L}^+ \text{O}^-$ than dipole-dipole)*

In molecules with OH or NH groups, a [lone pair of $\text{e}^-$ on nitrogen or oxygen] is attracted to the slight positive charge on the hydrogen on a neighbouring molecule.

Hydrogen bonding makes the [melting and boiling points of water] higher than might be expected.

It also means that alcohols (OH groups) have much higher boiling points than alkanes of a similar size.

**Boiling points of the hydrogen halides**

The boiling point of hydrogen fluoride is much higher than that of other hydrogen halides, due to fluorine's [high electronegativity].

The means that [hydrogen bonding] between molecules of hydrogen fluoride is much stronger than the permanent dipole-dipole forces between molecules of other hydrogen halides.

More energy is therefore required to separate the molecules of hydrogen fluoride.

**Summary of intermolecular forces:**

- **Weakest:** London Forces and dipole-dipole forces (no H-bonds)
- **Strongest:** Hydrogen bonds
Chemical Bonding Exercises Set 2

1. What explains the fact that at room temperature F₂ is a gas while I₂ is a solid?

2. Write the number of valence electrons possessed by each of the following species:
   a) Ge  
   b) Y  
   c) W⁴⁺  
   d) Sn²⁺  
   e) Bi  

3. Which substance has a lower melting temperature: CaBr₂ (s) or SrI₂ (s)? Explain why.

4. Write the valence for each:  
   a) S  
   b) B  
   c) Ca  
   d) Xe  
   e) Ga  
   f) Bi  

5. Write the number of open and closed shells for each of the species given below.
   a) At¹⁺  
   b) Ba  
   c) I⁵⁺  
   d) V⁺  

6. Although oxygen and fluorine molecules are roughly the same size, each oxygen atom shares four electrons with its neighbour while each fluorine atom shares only two electrons with its neighbour. Which bond should be stronger? Explain.

7. Which types of bonds or forces increase in strength going down a group in the periodic table? (I only want you to consider bonds/forces between atoms or molecules of the same element)

8. Which types of bonds or forces decrease in strength going down a family in the periodic table? (Again, only in terms of bonds/forces between atoms or molecules of the same element)

9. Provide brief explanations for the following facts:
   a) the melting temperatures of the noble gases increase going down the periodic table.
   b) the reactivity of the alkali metals increases going down the periodic table.
   c) the reactivity of the noble gases increases going down the periodic table.
   d) the melting temperature of the alkali metals decreases going down the periodic table.
   e) the reactivity of the halogens decreases going down the periodic table.
10. Define “allotrope”. Name the allotropes of carbon.

11. *If* a noble gas *could* form a +1 cation, which noble gas would do so most easily? Why?

12. Molecule “M” has closed outer shells as a result of pure covalent bonding within its structure. What type of bond would attract molecules of “M” to each other?

13. Briefly explain the difference between ionic bonding, covalent bonding and metallic bonding.

14. Use your periodic table to classify each of the bonds as covalent, polar covalent, or ionic. Then predict the formula of the compound based on the valence each type of atom.
   
   a) Ba and Br  
   b) Mg and P  
   c) Si and N

   d) As and F  
   e) Ga and Se  
   f) B and Te

15. For each pair of compounds, state which should have the higher boiling points. Why?
   
   a) $\text{BCl}_3$ *vs.* $\text{BCl}_2\text{F}$  
   b) $\text{NH}_3$ *vs.* $\text{SbH}_3$

   c) $\text{CH}_3\text{CH}_2\text{CH}_3$ *vs.* $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  
   d) $\text{CH}_3\text{CH}_2\text{CH}_3$ *vs.* $\text{CH}_3\text{OH}$
I. MOLECULAR SHAPE
Consider the Lewis structure for water:

It is determined by what is going on around each central atom.
Electron groups associated with the central atom are repulsive to each other and move as far away from each other in space as possible (around the central atom).

Converting Lewis Structures into 3D
The process of inferring a three-dimensional shape from a Lewis structure is based on a very simple premise

VSEPR Theory (Valence Shell Electron Pair Repulsion Theory)
- Non-bonding pairs (aka “lone pairs”) = valence e’s on each central atom that are not involved in bonding.
- Bonding pairs (or groups) = valence e’s pairs (or groups) on a central atom that are involved in bonding.
- all non-bonding pairs and bonding pairs (or groups) around the central atom are called

  = the arrangement of around a central atom.

Example 1 Give the for ammonia (NH₃) and formaldehyde (CH₂O).

Molecular Shape = the arrangement of the around a central atom.

Use VSEPR to figure out the SPG, then use that info to determine the actual shape of the molecule.

Example 2 Give the molecular shapes for ammonia & formaldehyde.