Unit 1, Lesson 07: Introduction to Covalent Bonding and the Octet Rule

- non-metals (except Noble gases) have high electronegativity and high ionization energy. They have a strong "pull" on new electrons
- if two non-metals are combined, each non-metal will try to pull one or more valence electron away from the other. Because both non-metals are simultaneously pulling on each other's valence electrons, this pulls the atoms together and they end up sharing valence electrons, forming a covalent bond.

A **covalent bond** is a shared pair of electrons, usually between atoms of the same or similar, high electronegativities. Covalent bonding is most common between non-metal atoms.

By sharing valence electrons, both non-metals complete a stable octet electron arrangement, and become more stable (lower energy).

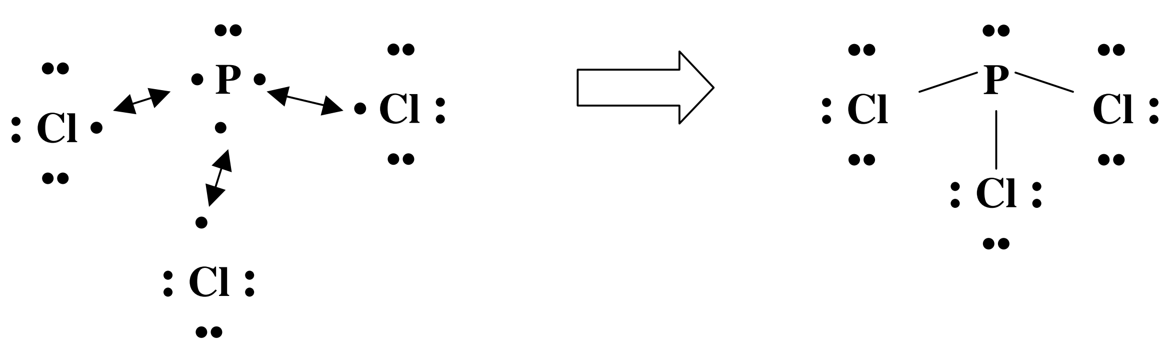
Octet Rule: atoms tend to form bonds until they are surrounded by eight (8) valence electrons, with the exception of hydrogen which will have two (2) valence electrons.

We can show the formation of covalent compounds using electron dot (Lewis dot) diagrams.
Follow these steps:

1. The chemical formula for the compound indicates the number of each type of atom in the molecule
2. The first element in the compound usually has the lowest EN and goes in the centre of the molecule
3. If hydrogen is the first element, it can not go in the middle of a molecule because it can only form one bond. Instead, put whichever element will form the most bonds in the middle
4. Draw the electron dot diagrams for all of the atoms, drawing the appropriate atom in the middle
5. Play the "dating game" to pair up the unshared electrons in such a way that hydrogen will form one bond and all other atoms will achieve a stable octet. You may need to draw double or triple bonds.
6. Draw the structural formula for the compound using a small line (−) to represent the covalent bonds
7. Draw in all lone pairs

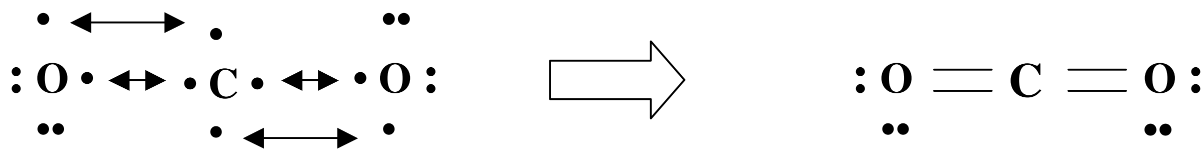
eg. PCl_3

- the chemical formula tells us that the molecule contains one phosphorus atom combined with three chlorine atoms
- draw the electron dot diagrams for these atoms. Phosphorus comes first and has the lowest electronegativity, so it goes in the middle
- play the "dating game"- match up the single electrons until they all have partners
- draw the structural formula using a small line to represent the covalent bonds and include all lone pairs



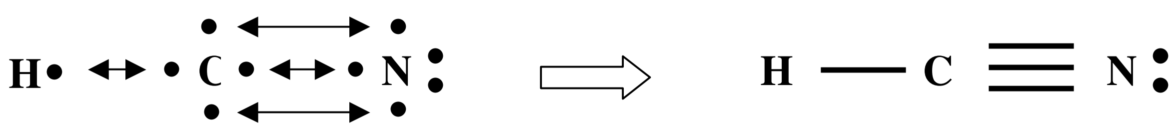
eg. CO_2

- this molecule is made of one carbon atom and two oxygen atoms
- carbon comes first and has the lowest electronegativity, so it goes in the middle
- when you play the "dating game" you will see that each oxygen will form ***two*** bonds with the central carbon atom. These are called **<u>double bonds</u>**. Double bonds are shorter and stronger than single bonds.



eg. HCN (hydrogen cyanide)

- there is one atom of each carbon, hydrogen and nitrogen
- hydrogen is first but it only forms one bond so it can not go in the middle. Carbon forms 4 bonds and has a lower electronegativity than nitrogen, so carbon is the central atom

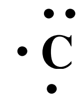


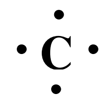
- nitrogen and carbon are sharing three pairs of electrons; this is called a **<u>triple bond</u>**. Triple bonds are shorter and stronger than double bonds.

Hybridization of Valence Electrons

The orbital diagram for carbon is:

↑↓	↑↓	↑	↑	
$1s^2$	$2s^2$	$2p^2$		

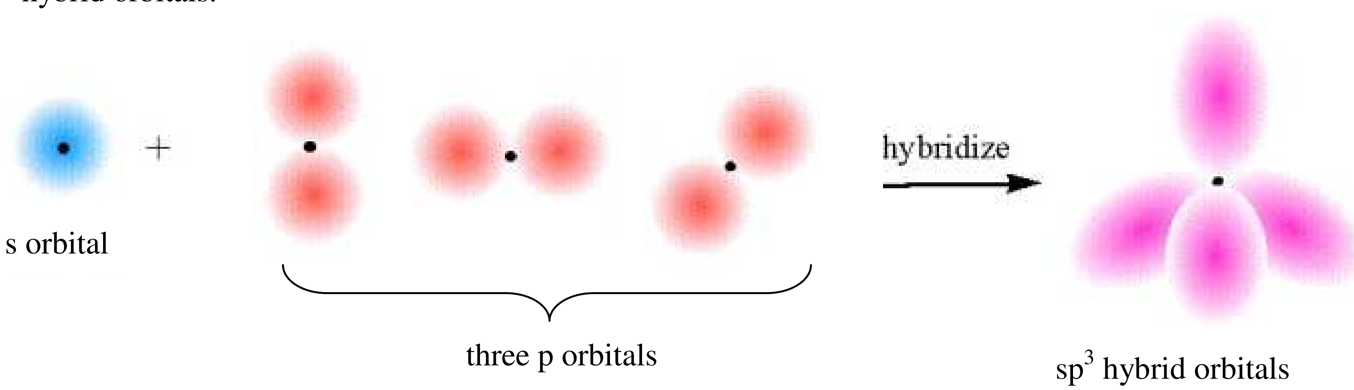
According to this electron configuration, in its valence shell, carbon has one lone pair and two half-filled orbitals (two unshared electrons), so its electron dot diagram should be drawn: 

However, you have been taught to draw carbon's electron dot diagram as: 

Which is correct?

Experimentally, carbon forms four bonds. It is usually unpaired electrons that participate in bonding, so the second electron dot diagram is correct.

It turns out that carbon's four valence electrons "hybridize". That is, they spread out equally around the nucleus with one electron in each of four equivalent orbitals. This is a lower energy arrangement. Because the four "new" orbitals are a blending of one "s" and three "p" orbitals, they are called "sp^3" hybrid orbitals.



Carbon now has four half-filled sp^3 hybrid orbitals available for bonding. Its actual orbital diagram should be drawn:

↑↓	↑	↑	↑	↑
$1s^2$	$2sp^3$			

Carbon and silicon (the Group IV) elements all show sp^3 hybridization and form 4 bonds.

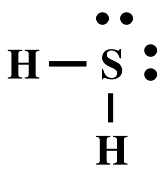
Polarity in Bonding

All covalent bonds involve shared electrons, but the electrons are not always shared *equally* between the atoms. The difference in electronegativity (ΔEN) between the bonding atoms determines how equally the electrons will be shared.

ΔEN < 0.50 defines a pure (non-polar) covalent bond

- a covalent bond between two atoms of the same element is a truly non-polar bond because the difference in electronegativity (ΔEN) between the atoms is zero. The bonding atoms share the electrons exactly equally between them.
- as long as ΔEN < 0.50, the bonding electrons are shared equally enough that the bond behaves like a non-polar bond

eg.



$\Delta EN_{S-H} = 2.55 - 2.20$

$= 0.35$

0.35 is less than 0.50 so the bond is classified as a pure covalent bond

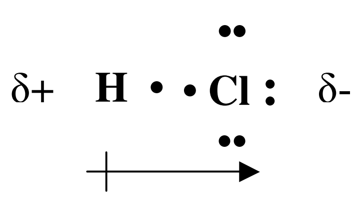
*The electronegativity differences that are used to define pure and non-polar bonds varies between textbooks. Our text defines a pure covalent bond as ΔEN <0.40; other texts use 0.70 as the cut-off. At GCI, the teachers have agreed to use 0.50 so that we agree between chemistry and biology. Remember, these numbers are somewhat arbitrary- the idea is to try and define bond types so that they explain the observed chemical and physical properties of compounds.

ΔEN between 0.50 and 1.70 defines a polar covalent bond

- when ΔEN is between 0.50 and 1.70, the electrons will be attracted much more strongly toward the atom with higher electronegativity and pulled away from the less electronegative atom
- because the bonded electrons are shifted toward the more electronegative atom, it obtains a slight partial negative charge (δ-). The electrons are shifted away from the less electronegative element, so it obtains a partial positive charge (δ+)
- δ is the small Greek letter delta, it means "a small difference"

eg. HCl (H---Cl)

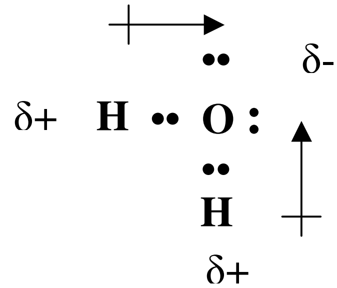
- the electronegativity of chlorine is 3.16; the electronegativity of hydrogen is 2.20
- ΔEN = (3.16 - 2.20) or 0.96
- this value is between 0.50 and 1.70, so the bond between H and Cl is polar
- the bonding electrons will be more strongly attracted to the chlorine (it is more electronegative)
- because the bonding electrons will spend more time closer to the chlorine atom, it will have a slight negative charge (δ-)
- because the electrons will be shifted away from the hydrogen atom, it will have a slight positive charge (δ+)
- HCl is a covalent compound, but it is a polar covalent compound



The polarity of the bond can be indicated one of two ways:

1. by drawing in the δ- and δ+ to show which parts of the bond are partially charged, or
2. with a vector (arrow). The end of the arrow with the "+" sign shows the δ+ end of the bond. The arrow points to the δ- end of the bond.

eg. $\mathbf{H_2O}$ (Look at just one H--- O bond at a time).



- the electronegativity of oxygen is 3.44
- the electronegativity of hydrogen is 2.20
- $\Delta EN = (3.44 - 2.20)$ or 1.24
- ΔEN is between 0.50 and 1.70 so the H --- O bond is polar
- the bonding electrons will be more strongly attracted to the oxygen (it is more electronegative)
- because the bonding electrons will spend more time with the oxygen atom, it will have a slight negative charge (δ-)
- because the electrons will be shifted away from the hydrogen atoms, they will each have a slight positive charge (δ+)
- H_2O is a polar covalent compound

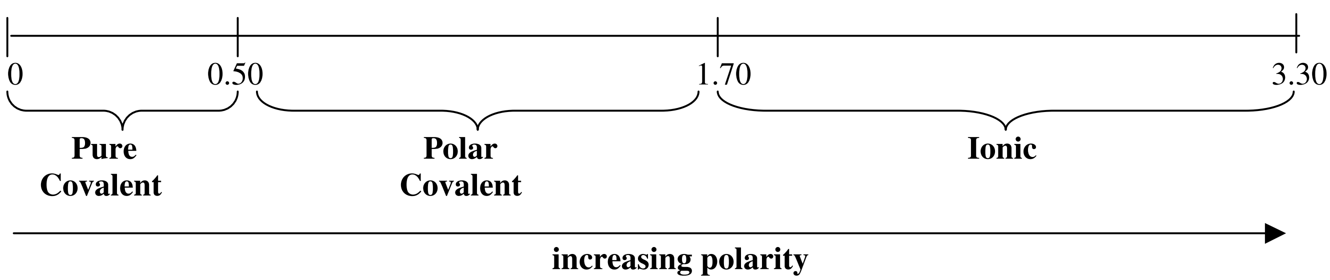
ΔEN greater than 1.70 defines an ionic bond

- the electrons are essentially transferred from the atom with the lowest electronegativity (usually a metal) to the atom with the highest electronegativity (usually a non-metal)
- the metal loses electron(s) to form a fully charged positive ion
- the non-metal gains electron(s) to form a fully charged negative ion
- the electrostatic attraction between the ions forms an ionic bond

While we classify bonds as pure covalent, polar covalent or ionic according to their ΔEN, in reality, there is a range of values (a continuum) of electronegativity differences in bonds. The greater the ΔEN, the more the electrons are shifted, and the more polar the bond:

- a truly pure covalent bond between two identical atoms, electronegativity difference is 0.00
- to the most ionic bond between cesium and fluorine, electronegativity difference is 3.30

We can show this range of values on a **"Bonding Continuum"** :



Summary: If the difference in electronegativity between the bonding atoms is:

< 0.50	pure covalent (the electrons are essentially equally shared between the bonding atoms)
0.50 to 1.70	polar covalent (the electrons are shifted toward the more electronegative atom, creating small or partial charges, δ- and δ+)
> 1.70	ionic (the electrons are actually removed from the metal and shifted to the non-metal)

In general, as ΔEN increases:

- the strength of inter-molecular attraction (attraction between molecules) increases
- the melting and boiling points of the compounds increases
- odour (generally) decreases

Percent Ionic Character

Another way of expressing the amount of polarity of a bond is called "% ionic character". The more polar a bond is, the higher its percent ionic character.

To calculate % ionic character:
1. determine the difference in electronegativity (ΔEN) of the bonding atoms
2. use the ΔEN to look up the % ionic character on the small chart on the back of your periodic table (if the ΔEN is in between two of the reported numbers, guestimate what the % ionic character would be)

eg. the ΔEN for a P – F bond is $(3.98 - 2.19) = 1.79$
- from the chart on the back of the periodic table, this corresponds to about 55% ionic character

Using the chart "in reverse", if a bond has more than 50% ionic character, this relates to a ΔEN of about 1.70 so the bond is considered to be an ionic bond. If a bond has less than 50% ionic character, then it is considered to be a covalent bond. There is no such thing as a bond with 100% ionic character. All bonds involve "sharing" electrons at least a little bit. There are bonds with 0% ionic character- these are bonds between two atoms of the same element eg. H_2, F_2 or O_2.

Covalent Compounds: Their Properties

Covalent compounds are made of uncharged or only partially charged atoms so there is relatively small low inter-molecular attraction between the particles in covalent compounds.

Because of the weak inter-molecular attraction in covalent compounds, they have the following physical properties:
1. may be gases, liquids or soft solids at room conditions (SATP)
2. low melting and boiling points
3. often have distinctive odours (because pieces of molecules break off easily to travel through the air and land in our noses for us to smell)
4. are non-conductors of electricity in their pure form (the electrons are bonded between atoms and not free to move from atom to atom)