Chemistry 3A

Introductory General Chemistry

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- Lewis Structures: The Octet Rule
- Showing Lewis Structures in Covalent Molecules
- The Shapes of Molecules
- Electronegativity & Polarity
- Interacting Forces Between Molecules: Dispersion, Dipole-Dipole, Hydrogen Bonding

Review of Periodic Table Patterns

- The periods of the Periodic Table show a pattern of 2 elements in 1st period, then 8 elements in the 2nd and 3rd periods. (The 4th & 5th have 18 each, then the 6th & 7th have 32 each)
- But it's the elements of the 2nd & 3rd periods, particularly the 2nd, that strongly interest us.
- On the left side of PT, the metal elements want to lose electrons to become POSITIVELY ionized (as cations). They have only 1, 2, maybe 3 electrons in their valence (outermost) shell that they give up in a true ionization of the atom.

Review of Periodic Table Patterns

- The electrons given up readily by the metal elements in the Groups 1 and 2 are taken by the Group 16 and 17 non-metal elements on the other (right) side of the Table, which want those electrons to become negatively charged ions (anions)

- This is all about stability, achieving the lowest energy state. It is about atoms ordering electrons in their orbits in an effort to become like the noble gas Group 18 elements

Review of Periodic Table Patterns

- For Period 2 elements
  - Li and Be will lose 1 and 2 electrons, respectively, to become Li^{+} and $Be^{2}+$, adopting a closed shell configuration looking like He, with its "duet" (2-electron) valence shell
  - On right side of table, F and O will acquire 1 or 2 electrons, respectively, to become F^{-} and O^{2-}, adopting a closed shell configuration looking like Ne, with its "octet" (8-electron) valence shell
- For Period 3 elements
  - Na and Mg will lose 1 and 2 electrons, respectively, to become Na^{+} and $Mg^{2}+$, adopting a closed shell configuration looking like Ne, and "octet" valence shell
  - On right side of table, Cl and S will acquire 1 or 2 electrons, respectively, to become Cl^{-} and S^{2-}, adopting a closed shell configuration looking like Ar, with its "octet" valence shell

The Octet Rule (Ions)

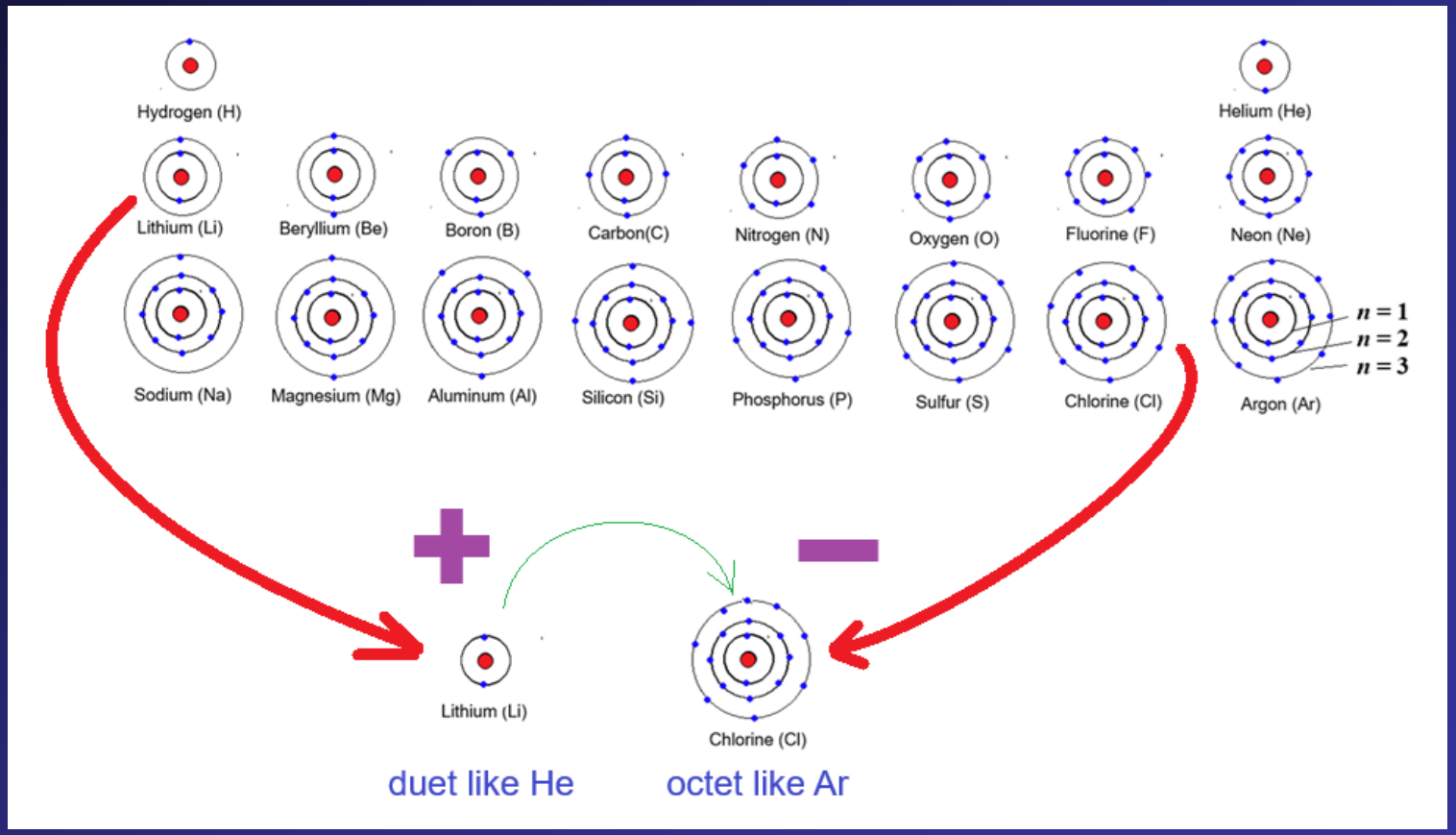
- The octet name refers to particularly to atoms wanting to have a valence shell of 8 electrons that makes them look like the closest noble gas element
- For elements on the left side of table, they will lose electrons to be like the noble gas element of the previous period. They will become positively ionized (1+, 2+, …) in the process
- For elements on the right side of table, they will gain electrons to be like the noble gas element of the current period. They will become negatively ionized (1-, 2-, …) in the process
- This is the case for metals and non-metals which will form ions and become ionic compounds

The Octet Rule (Molecules)

- But when non-metal atoms form bonds with each other, they do NOT gain or lose electrons in the way metal and non-metal atoms do in ionization
- Instead, the non-metal atoms will create a valence shell of 8 electrons around them, but these 8 electrons are shared between the atoms

Wanting To Be Like Noble Gas Elements

Forming the octet (or duet) by ionization, to be an ionic compound



Wanting To Be Like Noble Gas Elements

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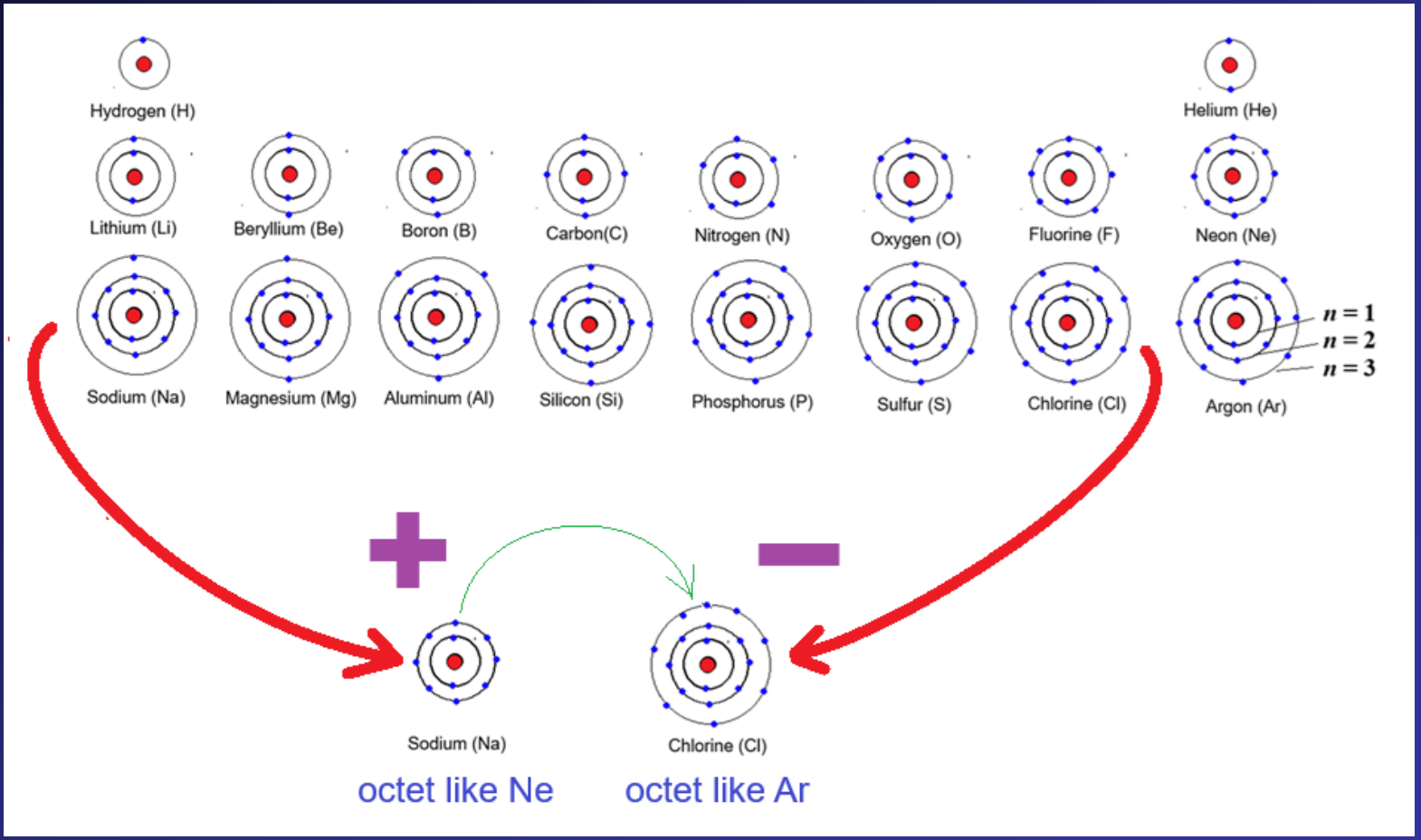
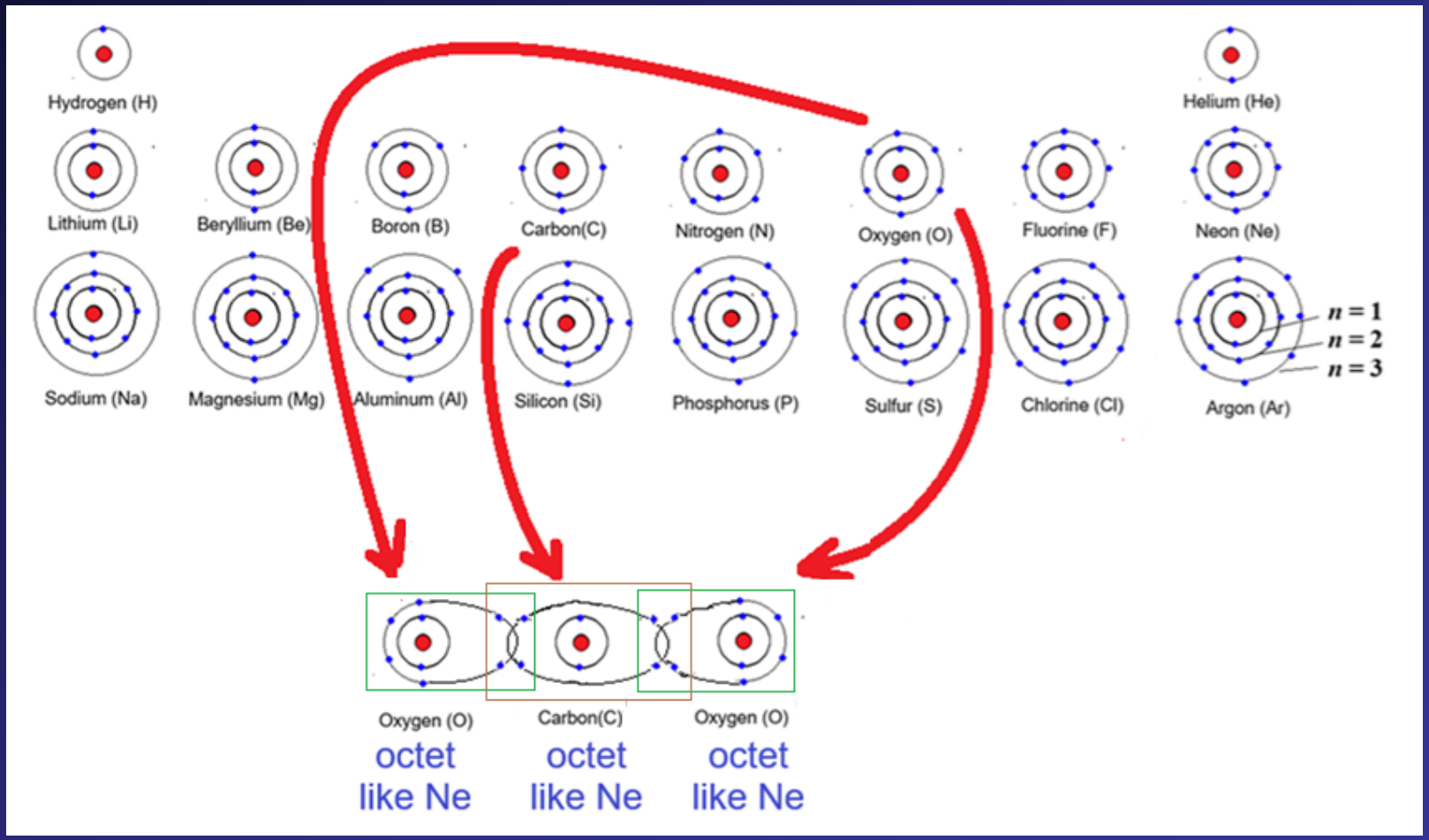


Wanting To Be Like Noble Gas Elements

Forming the octet through covalent bonding, or sharing.

The boxes count 8 electrons in valence (outermost) shells

Count them!



Wanting To Be Like Noble Gas Elements

Forming the octet through covalent bonding, or sharing.

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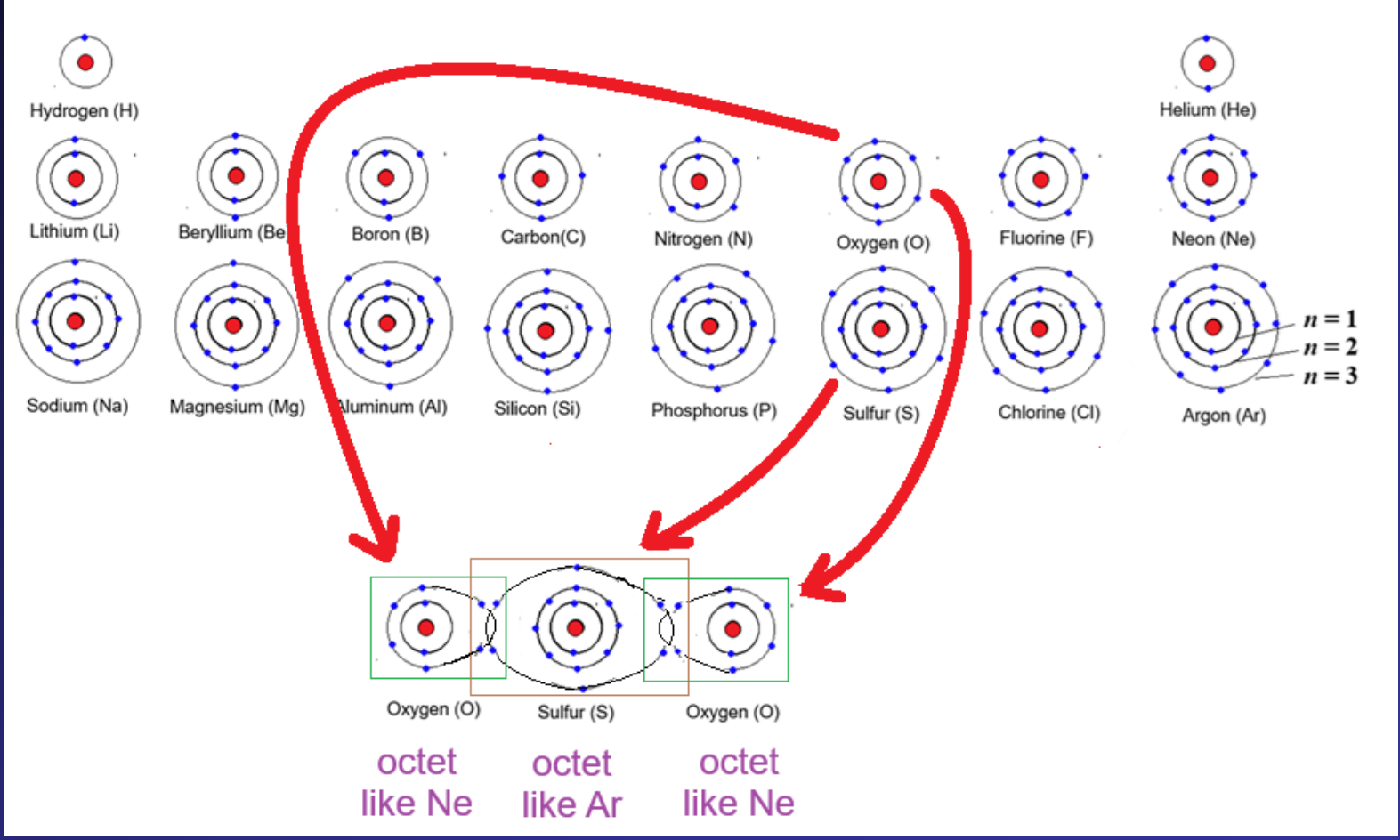
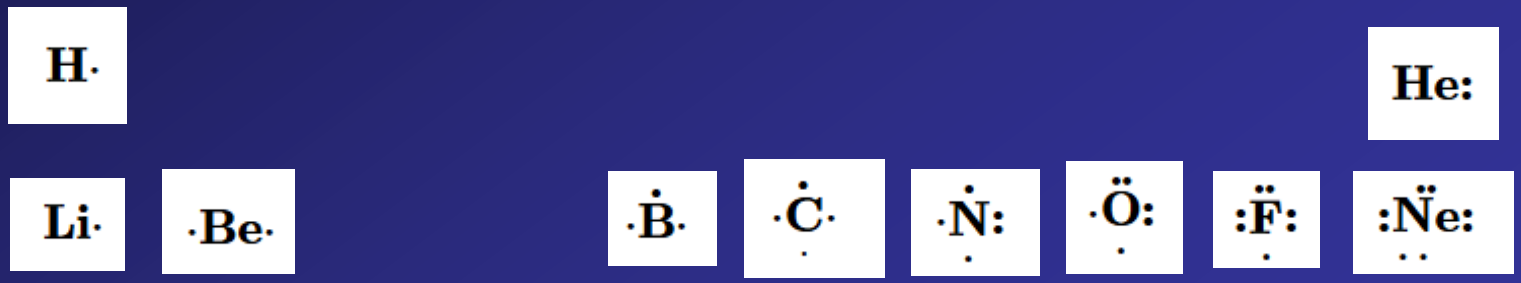


Electron Dot Diagramming

- **Lewis structures** are the presentation of atoms with their **valence** (outermost shell of) **electrons** represented as **dots**
- The dots can be placed around the element symbol top, right, bottom, left

The purpose of these diagrams are as an aid to chemists in showing the electrons available for BONDING of atoms to each other

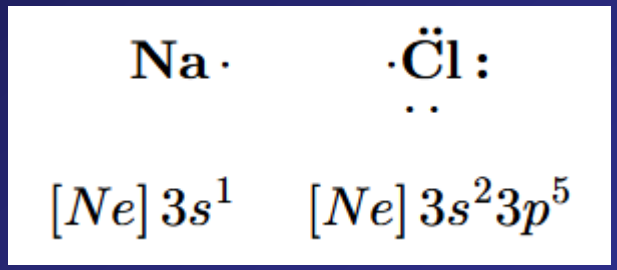


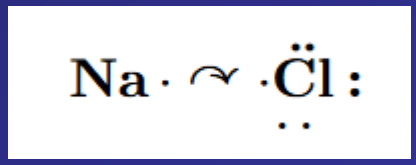
Formation of Ionic Compounds

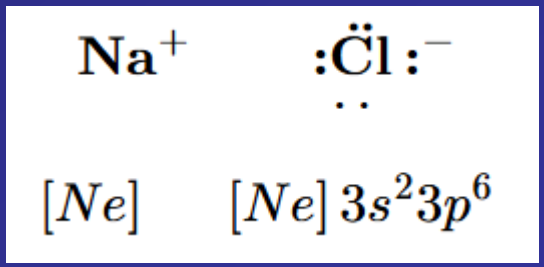
- Sodium (Na) in Group 1 has 1 valence (outermost shell) electron. Getting rid of it will make it have the octet of the noble gas element of the previous period, neon (Ne). This provides an energy stability to sodium. It will become a +1 positive ion, so will be attracted to -1 negative ions.
- Chlorine (Cl) in Group 17 has 7 valence electrons. If it just adds one more electron to that valence shell, it will have the octet of the noble gas element of its period, argon (Ar), providing energy stability to chlorine. It will become a -1 negative ion, so will be attracted to +1 positive ions
- Sodium and chlorine thus form ionic compounds with each other
- Ionic compounds are formed by bonds that are based on positive and negative electric charge points

Lewis Structures of Ionic Compounds

- Initially the Lewis structures show the atoms with their natural number of valence electrons, having zero charge
- For sodium (Na), there is 1 valence electron (dot). For chlorine (Cl), there are 7 electrons (dots)
- Note the electron configurations: Na^0 has its valence shell at ***n*** = 3. Cl^0 in same period has its valence shell at ***n*** = 3 too. (the ***n*** value is just a coincidence)
- An electron moves from Na to Cl → Na^+ and Cl^- form
- Na^+ has electron configuration of Ne now. [Ne] is also $[He]2s^22p^6$, and Cl^- has configuration of [Ar], which is actually $[Ne]3s^23p^6$.

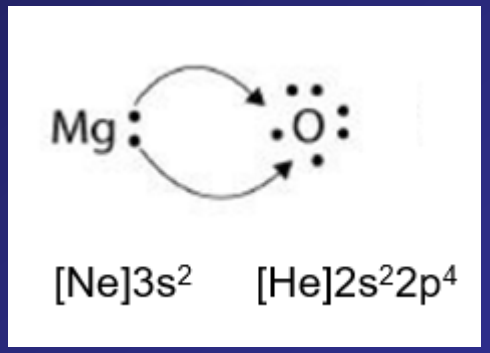


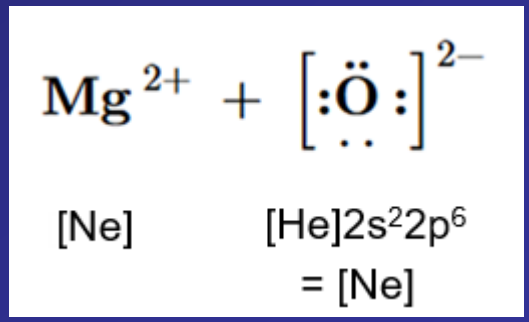




Two Electrons Moved

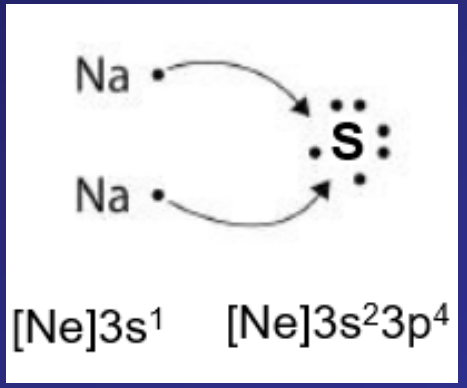
- Group 2 element magnesium (Mg) has two electrons in its valence shell. Note the Lewis structure and the electron configuration of Mg^0
- Group 16 element oxygen (O) has six electrons in its valence shell. See its Lewis structure and electron configuration of O^0
- Mg willingly gives its two electrons, which O willingly takes
- The Mg^{2+} ion now has the octet structure of the previous period noble gas, and O^{2-} has the structure of the noble gas element of its period

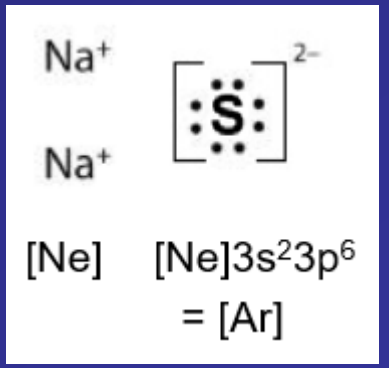




Two Electrons Moved, But FROM Two Atoms

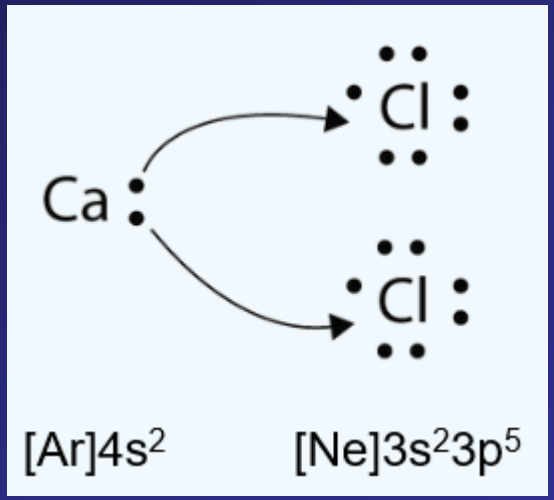
- Sulfur, in same Group 16 as oxygen, but one period down, is ready to take two electrons into its valence shell with 6 electrons, to complete the octet
- It is not required that it be from a Group 2 element with two electrons. Instead it can be two Group 1 elements, like potassium (K) or lithium (Li), but in this case sodium (Na) again
- Note the resulting electron configurations and Lewis structures

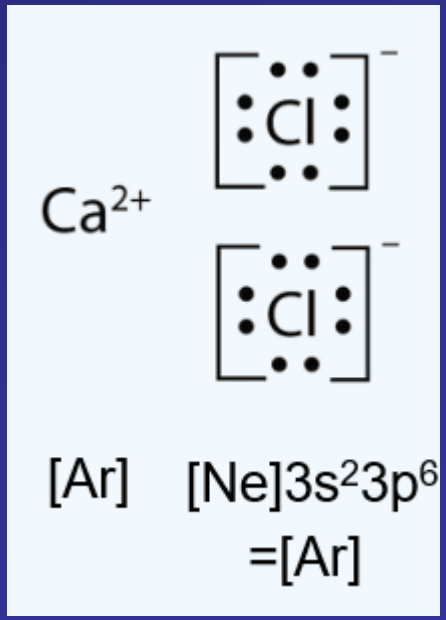




Two Electrons Moved, But TO Two Atoms

- This diagramming just demonstrates how the two valence shell electrons of calcium (Ca) in Ca^0 where one each is used to add one electron to each of two chlorine (Cl) atoms in the Cl^0 state
- The result is a Ca^{2+} ion, two Cl^- ions, and these will be the formula unit of ionic compound solid/crystal that is the compound
- Note how the electron configurations of the ions in the compound show how they form the octet of a noble gas element



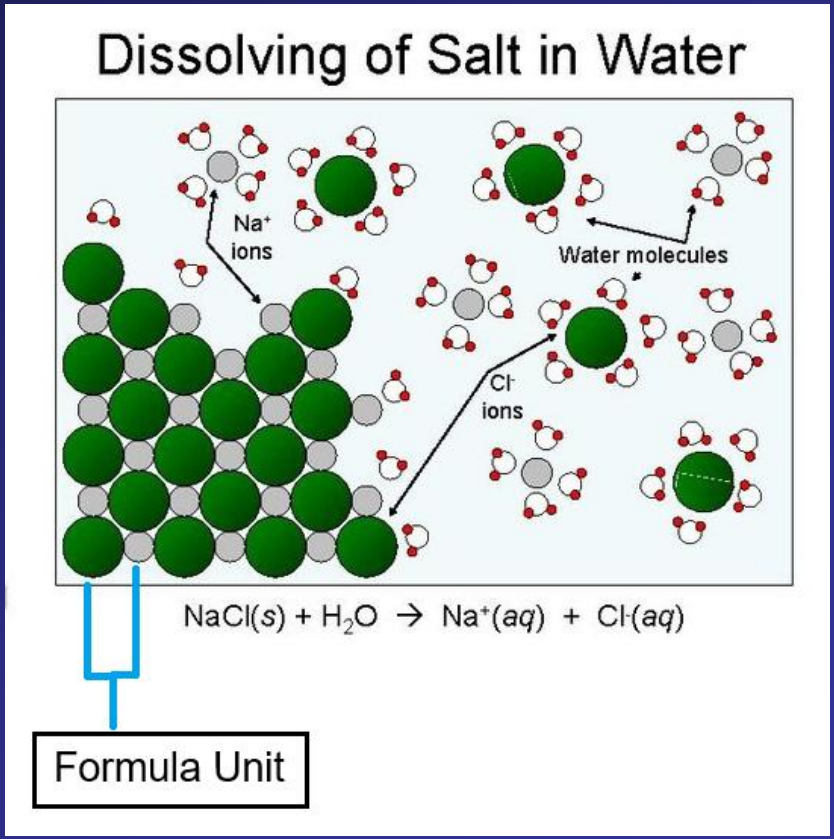


Summarizing Ionic Compound Lewis Structures

- Lewis structures are dot diagrams of atoms where the dots around the atom represent the valence (outermost) shell of electrons
- Electrons are involved in bonding. Bonding of the ionic type is where one atom fully takes the electron(s) of another atom, and the resulting electric (positive and negative) charges are what creates the bond (attraction), a strong force keeping the atoms close to each other
- Start with a Lewis structure of the neutral (zero-charge, non-ionized) atom with its proper number of electrons; then move the dots (electrons) as they interact with other atoms

More Detail on **Formula Unit**

- The formula unit describes an ionic compound (salt) in the solid phase
- It is the smallest, electrically neutral ratio of ions in a 3-dimensional crystal lattice
- Unlike a molecule, it is **NOT** a distinct independent particle
- The formula unit does **NOT** describe solvated ions (ions in the aqueous phase)



Lewis Structures of Covalent Compounds

- Ionic compounds represent one end of a spectrum of chemical bonding
- Covalent compounds—where atoms bond by the sharing of electron pairs—electron pairs make up bonds—represent another end of that chemical bonding spectrum
- It must be re-emphasized that these covalent compounds will typically point to the bonds between nonmetal elements
- Determination of Lewis structures will follow a specific set of rules to be detailed on slides that follow

Lewis Structures of Covalent Compounds

1. Determine total number of valence shell electrons in the molecule/ion
   - Add the electrons from each atom

     OF_2: 6 e^- from O atom, 7 e^- from F

     $6 + 2 \times 7 = 20\ e^-$
   - If species is polyatomic ION, be sure to add or subtract electrons that give the ion its charge

     CO_3^{2-}: 4 e^- from C atom, 6 e^- from O, 2 e^- from charge

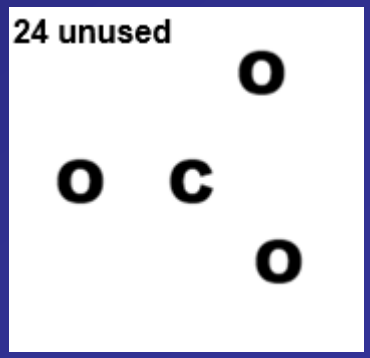
     $4 + 3 \times 6 + 2 = 24\ e^-$

Lewis Structures of Covalent Compounds

2. Arrange atoms to show their specific bonding
   - There is usually one atom in a polyatomic compound that is a central atom, or the atom to which other atoms are bonded to

For example, in CO_3^{2-} or CCl_4, this will be the carbon (C) atom

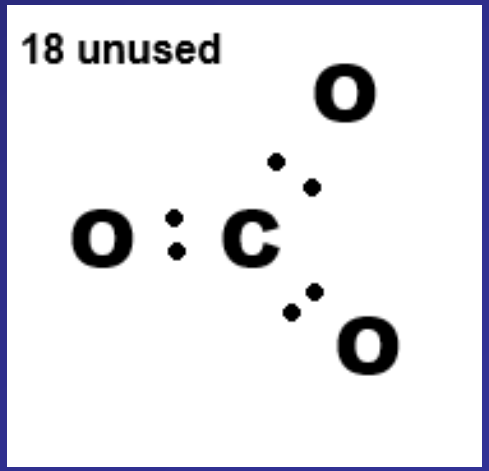
For an atom like hydrogen (H), it would never be a central atom (instead it is a terminal atom, at the terminus of a bonding series)



Lewis Structures of Covalent Compounds

3. Put a bonding pair of electrons between all the atoms

- A single bond between atoms uses two electrons (orbital pair)
- For atoms in a molecule/polyatomic ion to be connected or bonded to each other, there must be at minimum a single bond between them



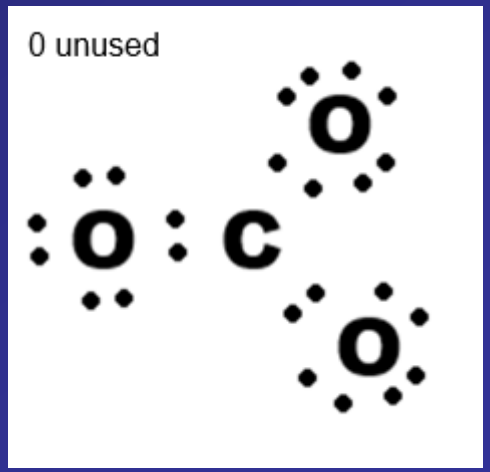
Lewis Structures of Covalent Compounds

4. For the terminal atoms (like oxygen, O), use the remaining electrons to create a total of 8 electrons (the octet) surrounding the atom

Arrange the electrons so they have a paired look!

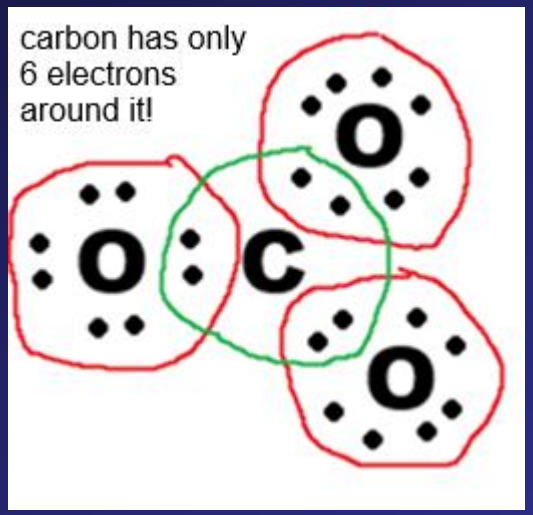
Note the nonbonded **LONE PAIRS** in the atoms!

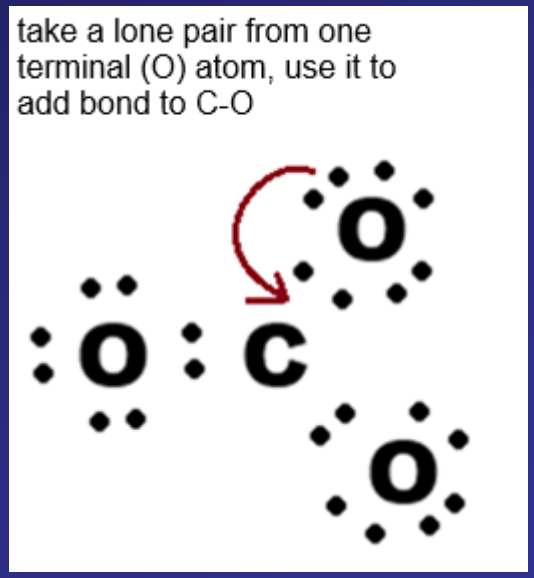
Do not put an octet for hydrogen (H): it only has a duet for its valence shell

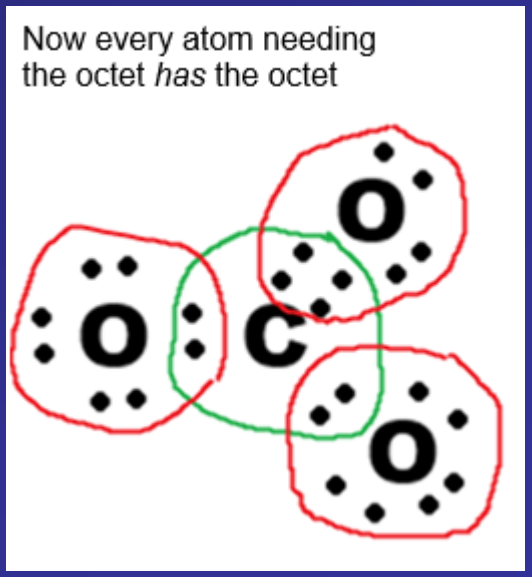


Lewis Structures of Covalent Compounds

5. Leftover electrons are placed on the central atom
6. Now check the central atom: does it have an octet of electrons around it? If NOT, then move lone pairs from other atoms to form double- and triple-bonds between central and terminal atoms to make an octet







Let's Do It Again: Water

1. # valence electrons =
   2 H x 1 e^-/H + 1 O x 6 e^-/O = 8 e^-

2. Arrange the atoms for central and terminus:

H atoms must always be atoms at a terminus

H O H

3. Now put at least one bonding pair between the atoms

H:O:H

bonding electron pairs can be represented by single lines

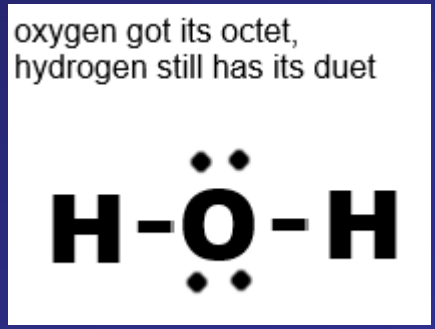
H-O-H

Electrons used were 4; still have 4 left

Let's Do It Again: Water

4. Start with terminal atoms, add electrons to form an octet (only a duet for hydrogen [H])

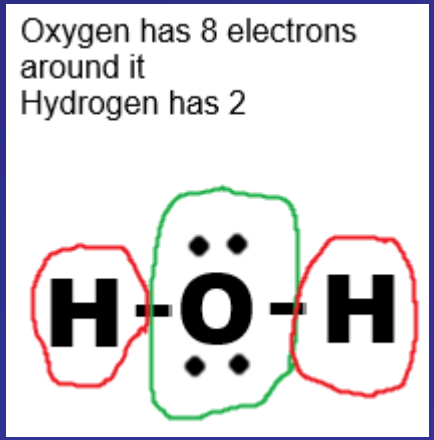
   There are only H atoms at termini, so these will have the duet



5. Leftover electrons get added to central atom

   Oxygen (O) is central atom, and already has its electrons

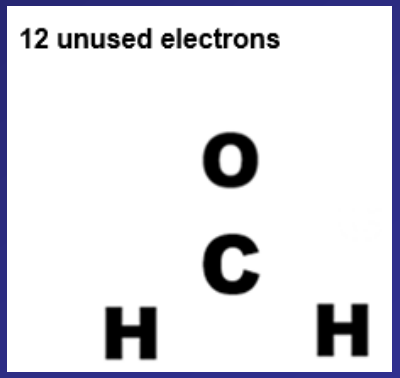
6. The central atom should get its octet of electrons if it doesn't have them, even to form double- or triple-bonds



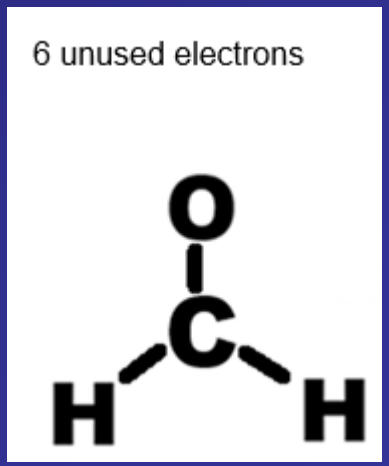
One more time: Formaldehyde (CH_2O)

1. # valence electrons =
   2 H x 1 e^-/H + 1 O x 6 e^-/O + 1 C x 4e^-/C = 12 e^-

2. Arrange the atoms for central and terminus. Carbon (C) typically forms a central atom as in this case



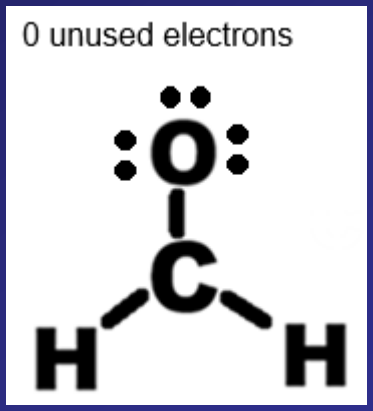
3. Now show the single bond (electron pair) connections



One more time: Formaldehyde (CH_2O)

4. Start with terminal atoms, add electrons to form an octet (only a duet for hydrogen [H])

   There are two H atoms, one O atom

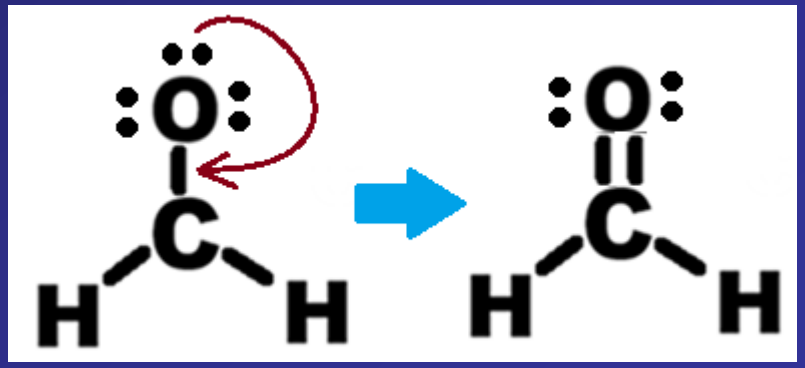


5. Leftover electrons get added to central atom

   No leftover electrons for central C atom

6. The central atom should get its octet of electrons if it doesn't have them, even to form double- or triple-bonds

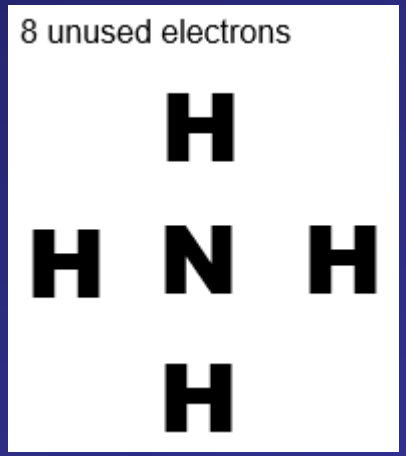
   Carbon (C) did not have its octet & needed a double bond



Polyatomic Ion Lewis Structure (NH_4^+)

1. # valence electrons & charge state =
   4 H x 1 e^-/H + 1 N x 5 e^-/O – 1 e^- [+1 state] = 8 e^-

2. Arrange the atoms for central and terminus. In this case nitrogen (N) forms a central atom



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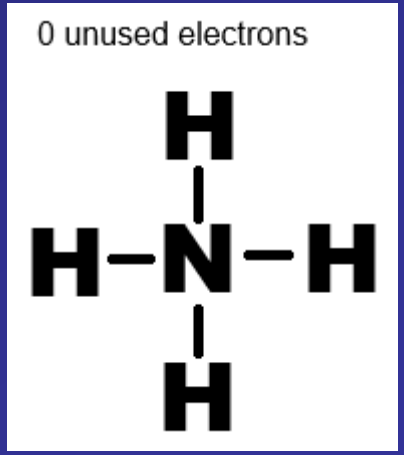


Polyatomic Ion Lewis Structure (NH_4^+)

4. Start with terminal atoms, add electrons to form an octet (only a duet for hydrogen [H])

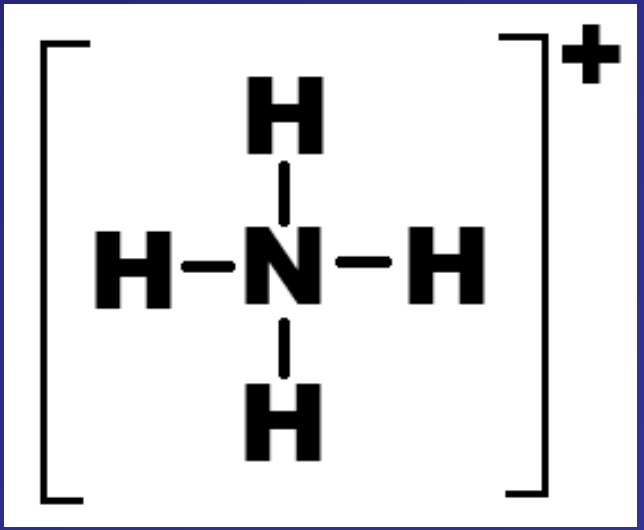
   There are four H atoms, one N atom

5. Leftover electrons get added to central atom

   No leftover electrons for central N atom

6. The central atom should get its octet of electrons if it doesn't have them, even to form double- or triple-bonds

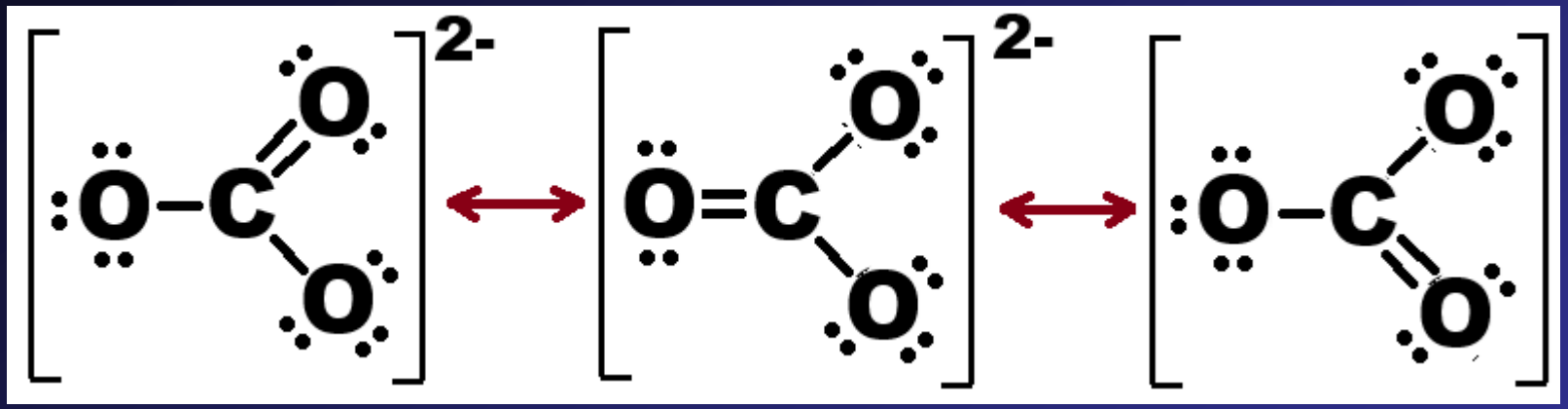
   Not needed



Resonance

- Go back to the slide on carbonate ion (CO_3^{2-})
- It has **3** oxygen (**O**) atoms bonded to the central carbon (**C**) atom
- In completing a proper Lewis structure, **one** of the oxygen atoms was selected to form a double bond while the **other two** oxygen atoms had no change to the bonding arrangement they had with carbon
- So why weren't the other oxygen atoms selected? Why couldn't they be selected?

Resonance



- In fact, any of the oxygens could be the one with the double bond to carbon
- More importantly, it is thought that the double bond can "rotate" around the carbon atom and form and "unform" rapidly with all three oxygen atoms

Resonance

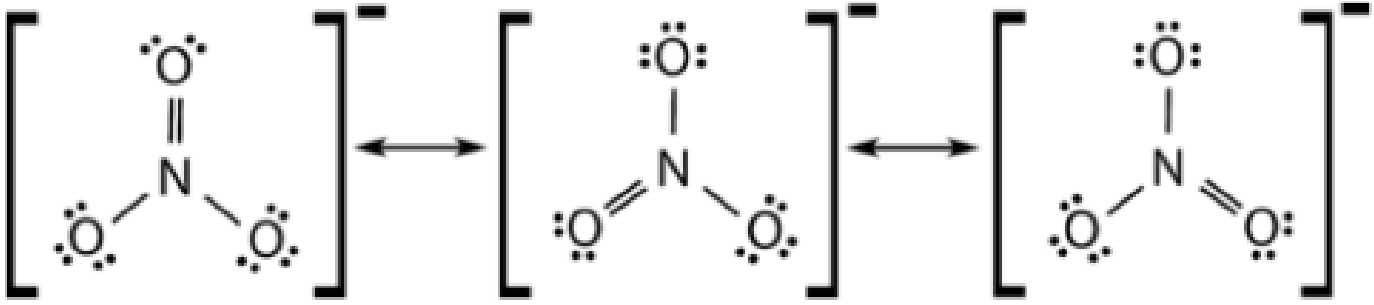


Figure 6.2.1.3: Resonance structure of nitrate anion.

- Look at the structure of nitrate (NO_3^-), and how similar it is to carbonate (CO_3^{2-}), but with N as the central atom to three terminal O atoms
- The double bond forms and "unforms" around all three O atoms
- (Also note that the charge for NO_3 is -1 and for CO_3 it is -2: count the Lewis structure electrons to understand why)

Resonance

- Ozone (O_3) is three oxygen atoms bonded to each other
- In building the Lewis structure for this, there are **18** total valence electrons: **6** each from the three oxygen atoms
- When the rules are followed, a double bond will be formed between two of the O atoms, but not the third
- Because two structures are possible, ozone shows **resonance**

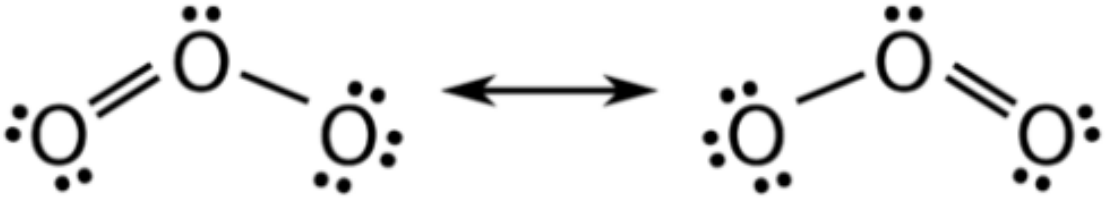
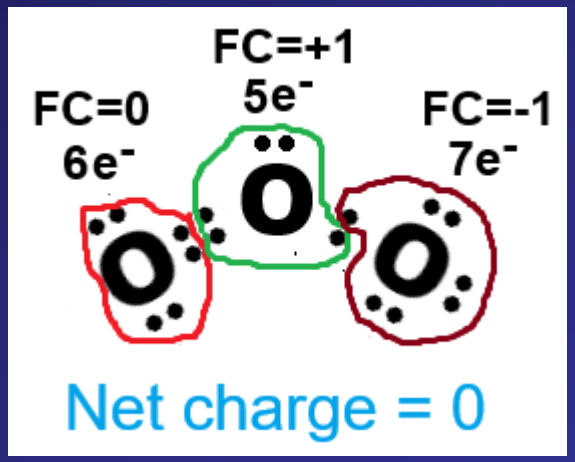


Figure 6.2.1.1: Resonance forms of ozone. Note the use of the double-headed arrow.

Formal Charge

- We interrupt the resonance message to talk about another concept
- In chemistry, formal charge is a hypothetical charge assigned to an atom in a molecule, assuming that the electrons in all chemical bonds are shared equally between the bonded atoms, regardless of their actual electronegativity*

1. Half of the electrons involved in bonds (single, double, triple) belong to one atom, the other half the other atom
2. All nonbonding ("lone pair") electrons belong to one atom



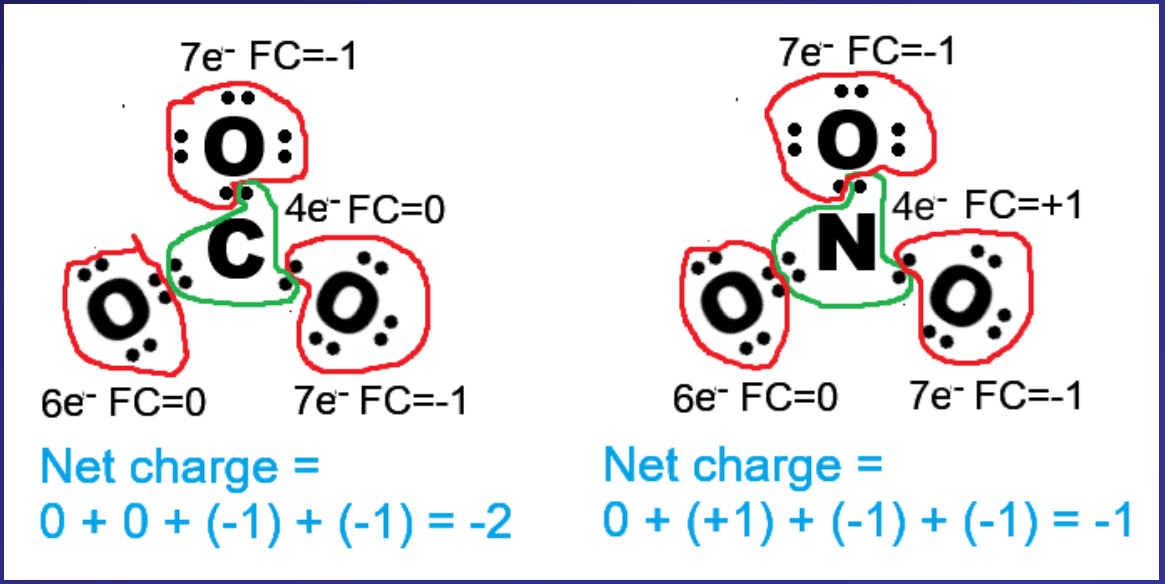
Net charge
= 0 + (+1) + (-1)
= 0

Formal Charge

- You first need to understand how many valence electrons around an atom gives it ZERO charge

  Carbon = 4, Nitrogen = 5, Oxygen = 6

- If nitrogen has **4** electrons belonging to it, it is one short of **5**, so its formal charge is **+1**
- If oxygen has **7** electrons belonging to it, that is one more than **6**, so its formal charge is **-1**
- Add up all atom formal charges to get the NET charge on molecule



Resonance Observation

- Let's get back to resonance. Ozone can have one of two (Lewis) structures
- Bonds between atoms have lengths. It is fact that double bonds create a shorter length (shorter distance between atoms) than single bonds and chemists have ways of determining bond length
- So chemists should see the central O atom shorter in a terminal O atom than the other
- But this is not found. The bond lengths are equal
- Let's go from observation → hypothesis → experiment → theory

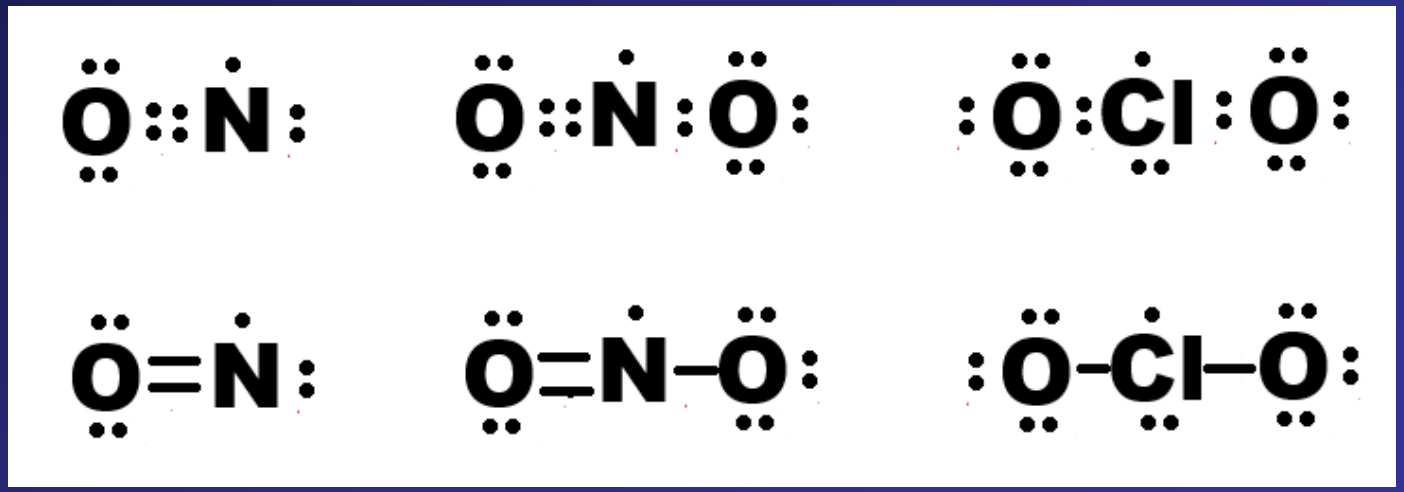
Resonance Theory

- If terminal O atoms are equal distance from central O atom, then the two electrons that create the double bond must be **delocalized** across the whole molecule. (Localized means the bonding electrons would not be "spread out" across the molecule but confined between two atoms)
- This is called a **half-bond** model in explaining resonance

Figure 6.2.1.2: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure 6.2.1.1.

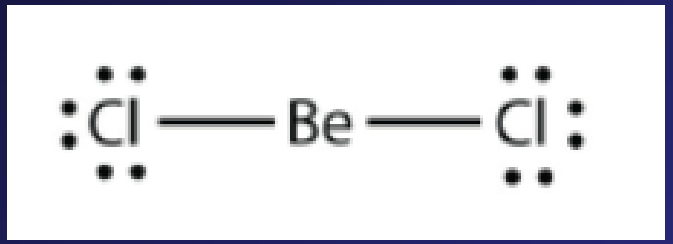
Octet Rule Exceptions

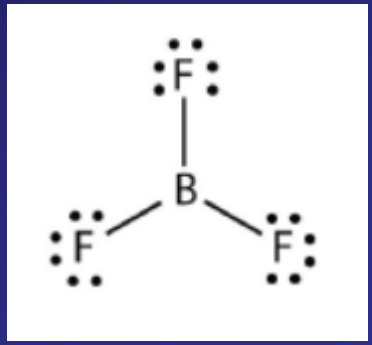
- Usually electrons want to exist as pairs in orbitals
- This is their more stable configuration
- But there are molecules that are semi-stable with an odd number of electrons: **NO, NO_2, ClO_2**



Octet Rule Exceptions

- Electron-deficient molecules are another exception
- **Beryllium** can have just a quartet (4 electrons) and **boron** can have just a sextet (6 electrons)





- Another exception are atoms with MORE than octet: these are expanded valence shell but these are not covered in this course

Molecular Shape Prediction

- All molecules have shapes, geometric characteristics
- Electrons around atoms exist
  - in bonding pairs—connection between atoms
  - in nonbonding pairs (lone pairs)
- Electrons are all negatively charged and want to repel from each other
- This repulsion is what defines/contributes to bonded atoms creating space with each other in shaping the molecule

VSEPR

- Two components to **Valence Shell Electron Pair Repulsion**
  1. **Electron Group Geometry**: this about how groups of electrons arrange from each other
     - **Bonding electron pairs** whether single, double, triple bonds are one group
     - **Nonbonding pairs** are another group
  2. **Molecular Geometry**: this looks at how atoms arrange in a molecule

Two-Terminal Group Molecules

- Molecules with two terminal electron groups will be **linear**

  Electron groups can be atoms or groups of atoms

- The linear shape reflects groups wanting to maximize space

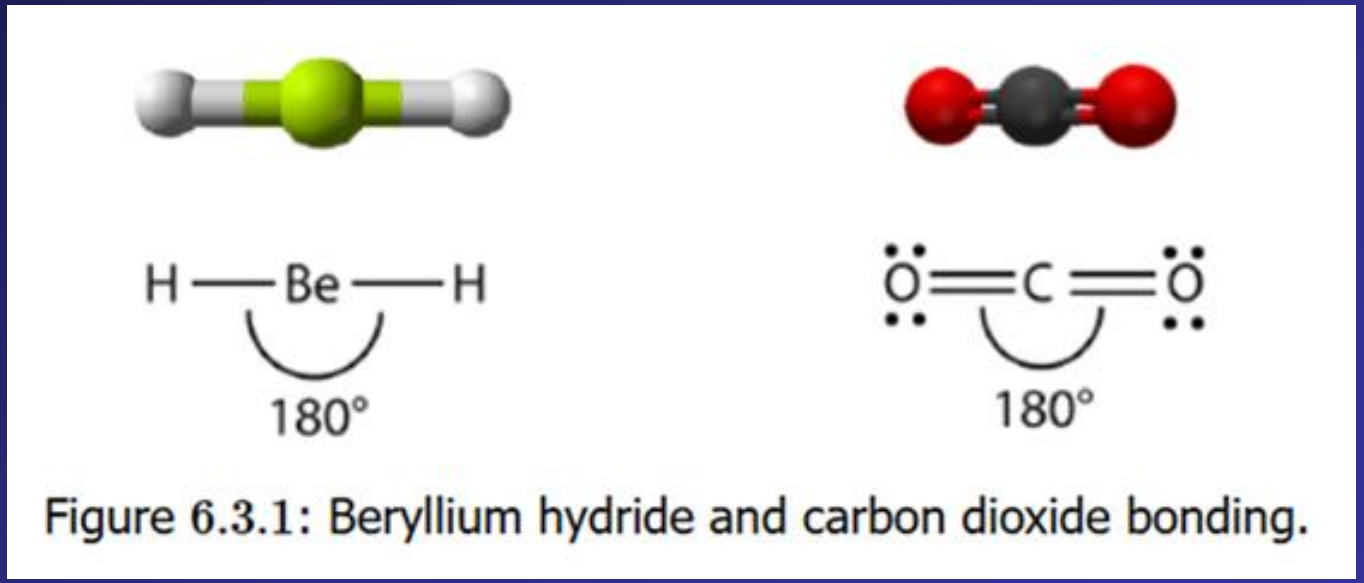
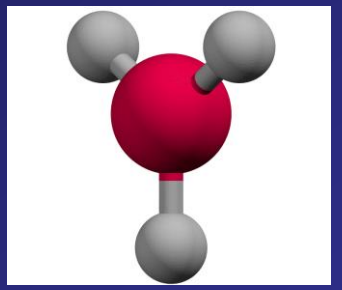


Figure 6.3.1: Beryllium hydride and carbon dioxide bonding.

Three-Terminal Group Molecules



- A trigonal molecule will usually be a **FOUR**-atom molecule, with a central atom and three terminal atoms or groups of atoms
- The bond angles between the terminal atoms to the central atom will be a predictable 120° angle
- All atoms are in ONE PLANE ("**trigonal planar**")

Example: **boron trifluoride -- BF_3**

Note with central atom BORON as an exception to the octet rule, it has only 6 valence electrons (3 bonded pairs) and NO LONE (NONBONDING) electron pair, making this geometry possible

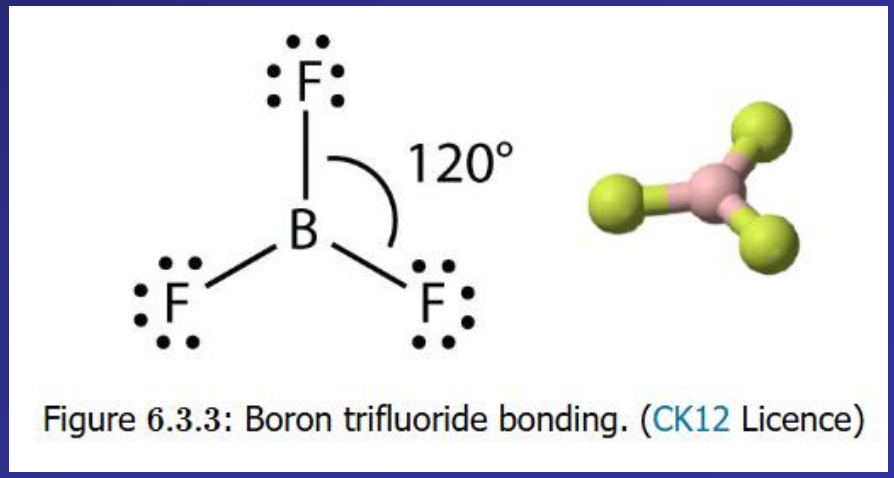


Figure 6.3.3: Boron trifluoride bonding. (CK12 Licence)

Three-Terminal Group Molecules

- A trigonal molecule can be **THREE** atoms/electron groups: a nonbonding (lone) pair can create the trigonal geometry with the lone pair pushing by repulsion (VSEPR) the other two terminal atoms
- The lone pair repulsion creates a "bent" or "angular" shape in the molecule

germanium difluoride -- GeF_2

Note the lone (nonbonding) pair on central germanium atom

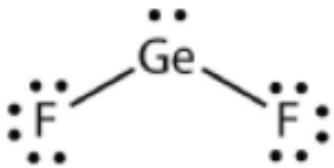
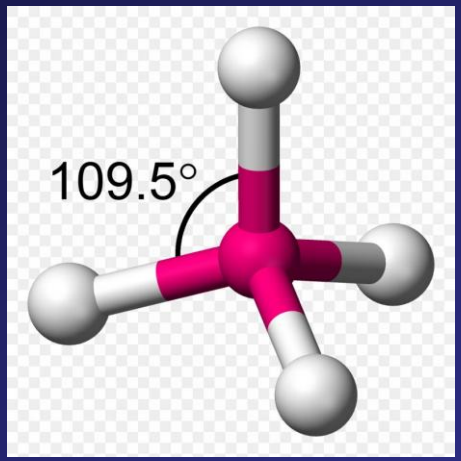
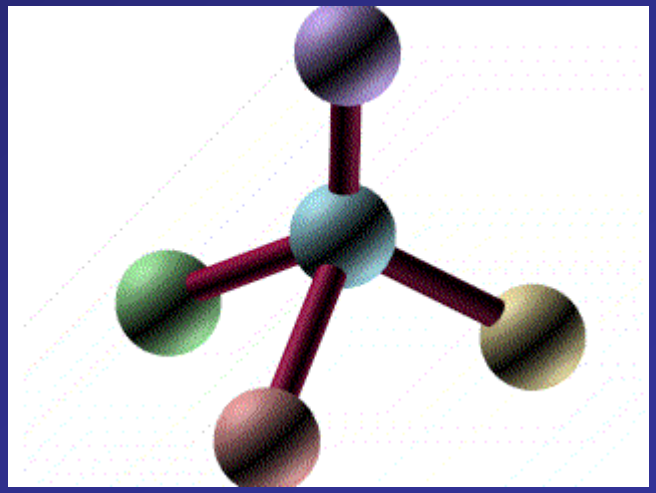


Figure 6.3.4: Germanium difluoride bonding.

Four-Terminal Group Molecules

- A tetrahedral molecule will typically have **FIVE** atoms/electron groups with four terminal atom/electron groups around a central atom
- This is a 3-dimensional geometry with the spacing between the bonds all angles being **109.5°**





Four-Terminal Group Molecules

Examples of three types of 4-terminal electron groups shown below

1. Methane (CH_4) has four **H** atoms around a central **C** atom in tetrahedral arrangement
2. Ammonia ($:NH_3$) has three **H** atoms around a central **N** atom in trigonal pyramidal arrangement because of one lone pair
3. Water ($H_2O::$) has two **H** atoms around a central **O** atom in a bent arrangement because of two lone pairs

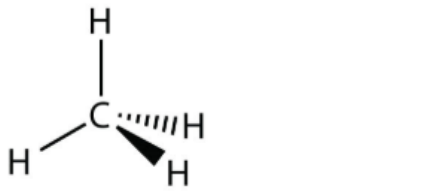


Figure 6.3.6: Methane bonding. (CK12 Licence)

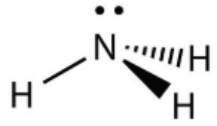


Figure 6.3.7: Ammonia bonding. (CK12 Licence)

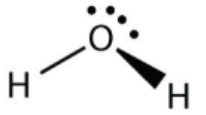


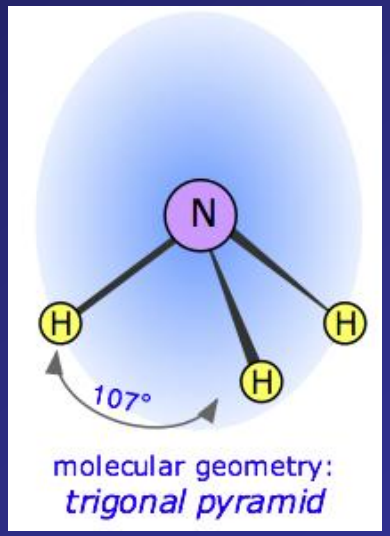
Figure 6.3.8: Water bonding.

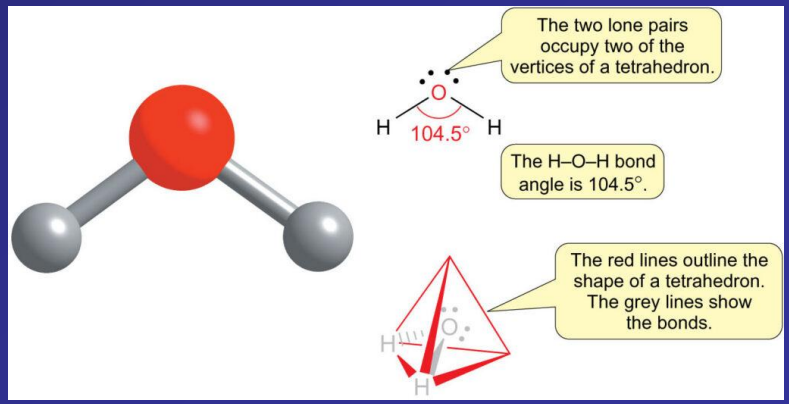
Four-Terminal Group Molecules

- In Valence Shell Electron Pair Repulsion (VSEPR) theory nonbonding (lone) pairs appear to have a greater repulsive force than bonding pairs
- Why?

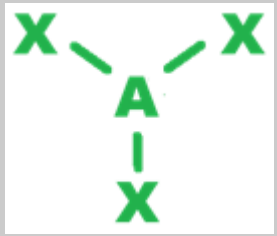
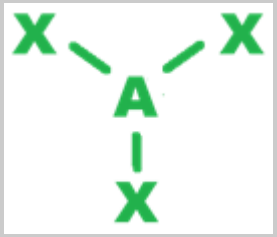
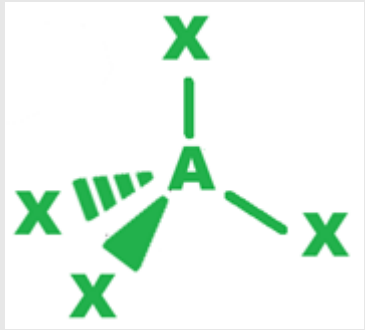
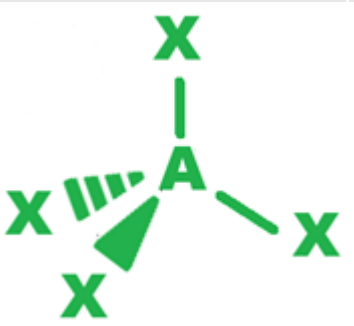
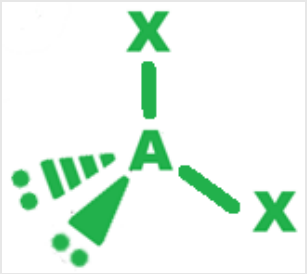
Due to their greater electron density and proximity to the central atom's nucleus, nonbonding (lone) pairs repel other electron groups more strongly than bonding pairs. 😤 This stronger repulsion causes the bond angles between bonded pairs to compress and become smaller than the ideal angles predicted by VSEPR theory.

Lone Pairs	Bond Angle
0	109.5°
1	107°
2	104.5°





Shape Summary

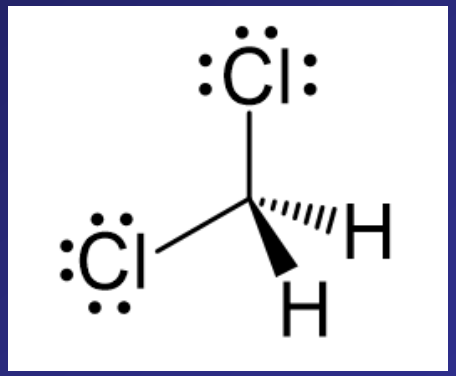
# of Electron Groups	Electron Group Symmetry	Ideal Bond Angle	Molecular Geometry		
			0 lone pairs	1 lone pair	2 lone pairs
2	Linear 	180°	Linear 		
3	Trigonal Planar 	120°	Trigonal Planar 	Bent 	
4	Tetrahedral 	109.5°	Tetrahedral 	Trigonal Pyramidal 	Bent 

What's the Shape?

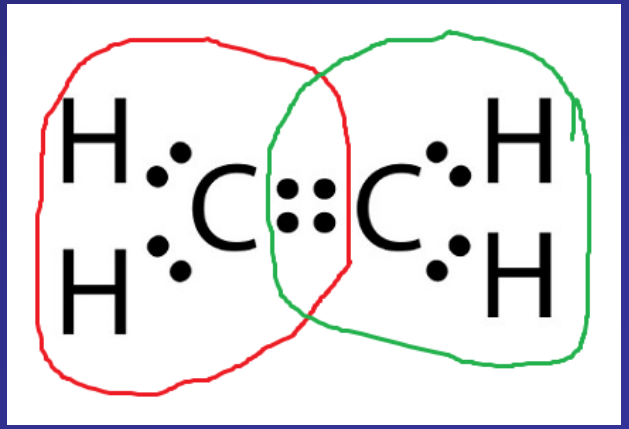
- What is shape of PCl_3? (phosphorus trichloride)
  - Draw Lewis structure
    Cl will have 3 lone pairs each (not contributing to shape)
  - P atom will have 3 terminal Cl atoms
  - One lone pair is on P atom
  - Shape: trigonal pyramidal
- What is shape of NOF? (nitrosyl fluoride)
  - Central atom is N, terminal atoms are O and F
  - Lewis structure: N double bond O, N single bond F, two lone pairs on O atom, 3 lone pairs on F
    1 lone on central N atoms → bent

What's the Shape?

- What is shape of CH_2Cl_2? (dichloromethane)
  - Lewis structure has central C atoms with four terminal atoms: two H atoms, two Cl atoms
  - No lone pairs on C or H, three lone pairs on Cl atoms which do not contribute to shape
  - Shape: tetrahedral



- What is shape of C_2H_4? (ethylene)
  - Two central atoms of C
  - Terminal atoms of each are: two H atoms and one C atom (the other C)
  - Lewis structure: C single bond to both H atoms, double bond other C, no lone pairs
  - Shape: trigonal planar each C



Bond Polarity

- On one side: **ionic**, other side: **covalent**
- In the middle: partial sharing

  better term: **polar covalent**

Despite sharing in covalent bonding of the nonmetal atoms, some of the atoms of nonmetal elements want electrons more than the other atoms of the nonmetal elements.

The atoms of elements forming bonds with electron pairs between them will likely differ in how much they are willing to share all pairs of electrons in the bonds they form between the atoms.

Electronegativity

- **Electronegativity** is a property of every element in the Periodic Table
- **Electronegativity** describes the potential of an atom to attract electrons when it is in a bond. The difference in electronegativity values between two atoms is what predicts the type of bond (ionic, polar covalent, covalent) that will form between them.
- An element will have a HIGHER electronegativity if it wants the electrons (electron pairs) more
- Metal elements on left side of Table will have LOWER electronegativities than nonmetal elements on right side
- **Flourine** at upper right of Table has the highest electronegativity of any element

Electronegativity Values

Values show how much the atoms of element want to hold on to the electrons (electron pairs) in a bond

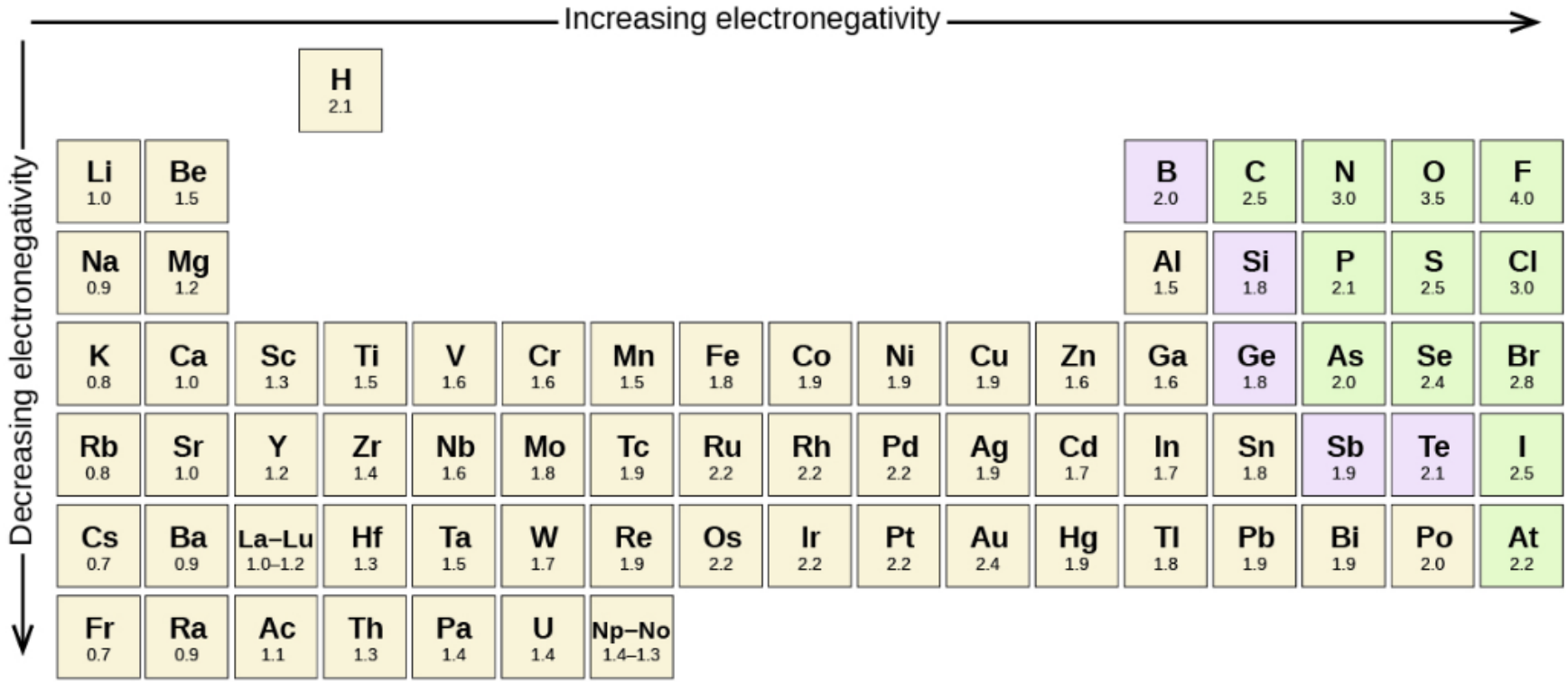


Figure 6.4.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

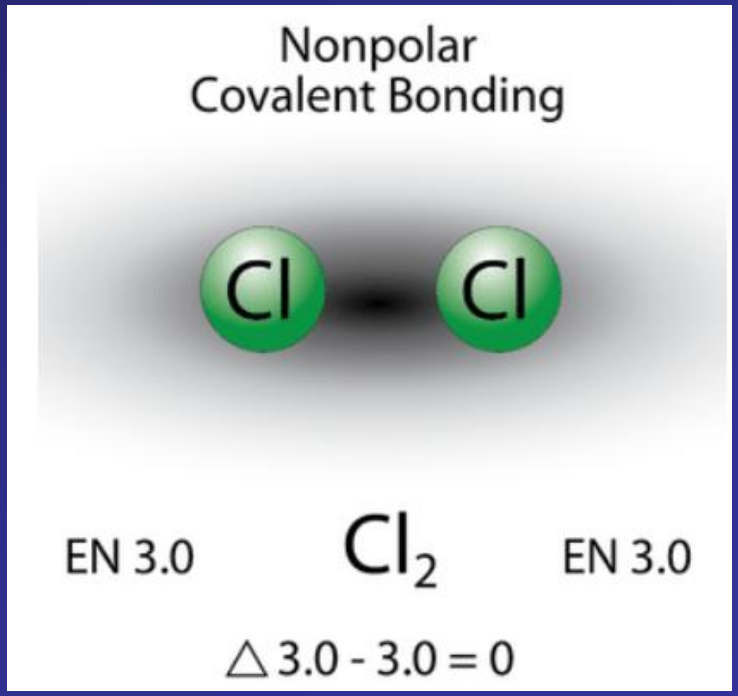
Standard for Bonding Polarity

- For two bonded atoms, compute the difference in their electronegativity values → ΔEN
- If the difference falls within the ranges in the table below, you can class the bond as nonpolar covalent, polar covalent, or ionic

ΔEN	Bond Type
ΔEN **< 0.5**	**Nonpolar covalent**
0.5 ≤ ΔEN **≤2.0**	**Polar covalent**
ΔEN **> 2.0**	**Ionic**

Nonpolar Covalent Bonds

- Chlorine molecule (a gas), has structure Cl_2 (Cl-Cl)
- The Cl atom electronegativity value is **3.0**. The computed difference is ΔEN = **0.** Thus it is a completely nonpolar covalent bond.
- This makes sense that diatomic molecules would have no polar or ionic nature in bonds between them since atoms of identical type would have "equal pull" (attraction) for the electrons in any bond



Polar Covalent Bonds

Hydrofluoric acid (older name hydrogen fluoride) (HF) is a hydrogen (H) atom bonded with the most electronegative element, fluorine (F)

Electronegativities: **H = 2.1, F = 4.0**
ΔEN = 1.9 Polar covalent from the table.
Chemists use delta+ (δ**+**) or delta- (δ**-**) or a *dipole moment* or *dipole vector* (the crossed arrow)

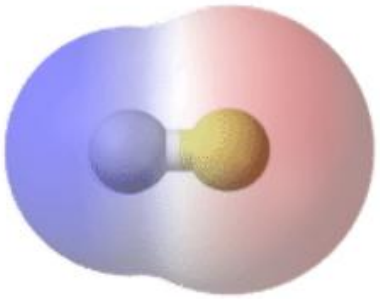


Figure 6.4.3: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

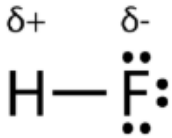


Figure 6.4.4: Use of δ to indicate partial charge.

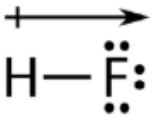


Figure 6.4.5: Use of crossed arrow to indicate polarity.

Understanding Bond Polarity

You understand bond polarity by using the element's/atom's electronegativity values

What is the polarity of the carbon-hydrogen bond (C—H)?

This may the most important chemical bond of all. It is fundamental bond in organic chemistry.

Electronegativities:
C=2.5, H=2.1, **ΔEN = 0.4, nonpolar covalent**

What is the polarity of
the oxygen-hydrogen bond (O—H)?

Another most important bond!

Electronegativities:
O=3.5, H=2.1, **ΔEN = 1.4, polar covalent**

More Bond Polarity

What is the polarity of the rubidium-fluoride bond (RbF)?

Electronegativities:

Na=0.9, Cl=3.0, **ΔEN = 2.1, ionic**

What is the polarity of the rubidium-fluoride bond (RbF)?

Electronegativities:

Rb=0.8, F=4.0, **ΔEN = 3.2,** very **ionic**

What is polarity of the phosphorus-chloride bond (PCl)?

Electronegativities:

P=2.1, Cl=3.0, **ΔEN = 0.9, polar covalent**

Molecular Polarity

- In previous slides we talked about **bond polarity**
- Here we talk about **molecular polarity**: is a molecule itself polar or nonpolar?
- Nonpolar molecules/compounds
  - Usually symmetric: all sides around central atom identical
  - No unshared bonding electron pairs (extreme polarity)
- Polar molecules/compounds
  - Usually asymmetric
  - Central atom has nonbonding (lone) pairs
  - Bonded atoms with high electronegativity differences
- Must understand Lewis structures and VSEPR theory to make this assessment

Molecular Polarity

- A molecule will be polar if it can be shown to have a dipole, where the electron density has an unequal distribution (see image)
- The **H-F** molecule has a polar covalent bond, and this also made this molecule **polar**

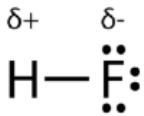


Figure 6.4.4: Use of δ to indicate partial charge.

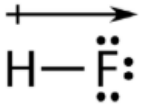


Figure 6.4.5: Use of crossed arrow to indicate polarity.

- Polarity in a molecule is indicated/suggested/symbolized by use of a lowercase delta (δ) with $\delta+$ or $\delta-$ along molecule axis
- It is also symbolized by a crossed-arrow, the cross point representing the positive charge end and arrow pointing to negative charge

Molecular Polarity

- Start with Lewis structures to assess molecular polarity
- Nonpolar compounds
  - Symmetric: sides around central atom identical
  - No unshared pair of electrons
- Polar compounds
  - Asymmetric
  - Bonds in atoms have large differences in electronegativities
  - Presence of nonbonding lone pairs

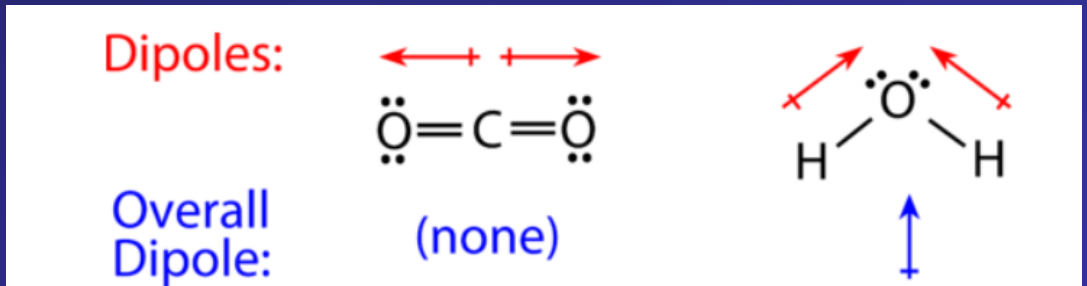


Figure 6.4.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Molecular Polarity

- Overall molecular polarity will be a combination of the **dipole moments** of all the bonds between atoms in the molecule
- Dipole moments (as vectors) will have a **magnitude** that reflects the electronegativity differences in each of the two atoms bonded, AND also the **direction** of the dipole moment, which is determined by molecular geometry or shape.
- Note how nonpolar boron trifluoride and carbon tetrachloride have significant individual ***bond*** dipoles, but the direction of the bond dipole moments have the net molecular dipole moment of zero, so the molecule has no polarity overall.

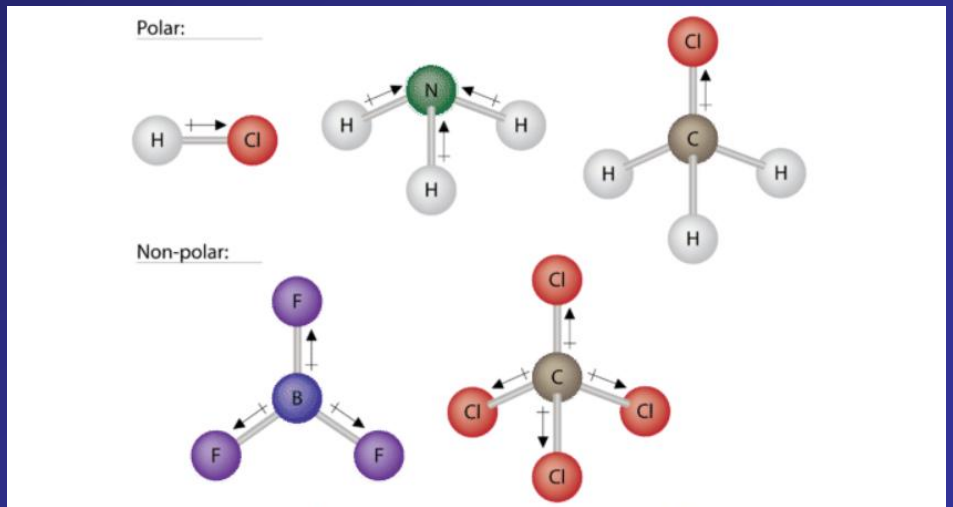


Figure 6.4.8: Some examples of polar and nonpolar molecules based on molecular geometry.

Molecular Polarity Evaluation

Steps to Identify Polar Molecules

1. Draw the Lewis structure.
2. Figure out the molecular shape/geometry (using VSEPR theory).
3. Look up the electronegativity values of each element.
4. If it meets both of the above criteria (polar bond and unbalanced shape), it is polar.
5. If not, it is non-polar.

- With Lewis structures, you are especially looking for nonbonding (lone) pairs!
- The electronegativity differences between atoms shows you BOND polarity (dipole moment) magnitudes
- The shape/geometry will indicate individual bond polarity (dipole moment) directions, which can be "summed" to give overall molecular polarity (dipole moment) direction

Polar Molecule Properties

There are several properties that can be used to distinguish polar from nonpolar molecules

- In an external electric (high voltage) field, polar molecules (image) will align directionally, and this might be observable in an instrument
- Higher melting points for solids
- Higher boiling points in liquids
- Polar substances more soluble in water
- Polar substances have lower vapor pressures (they resist going into gas phase, want to remain liquids)
- All these show strong intermolecular attractive forces

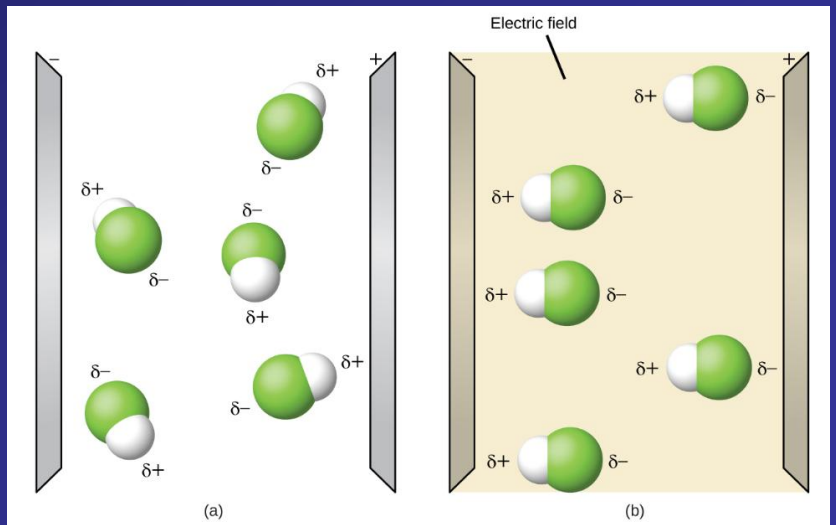
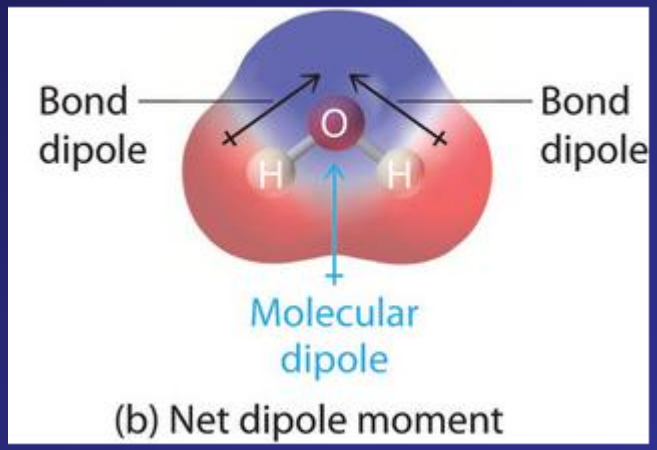


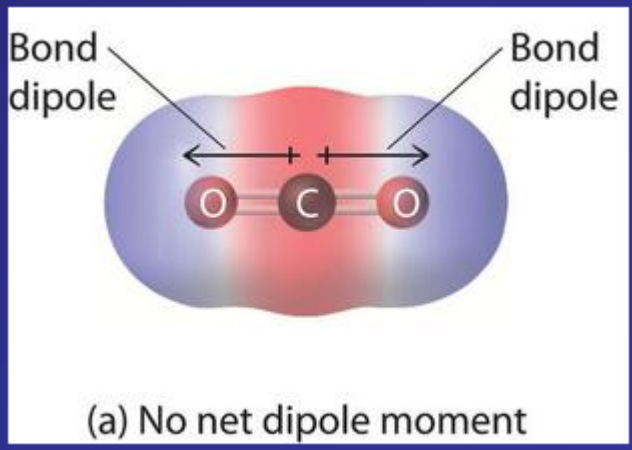
Figure 6.4.9: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

Polar or Nonpolar?

Water: any molecule like H_2O with nonbonding (lone) pairs on the **central** atom (oxygen will be **polar**. Each O–H shows bond polarity, the overall direction of polarity of the angled bond showing a **net dipole**

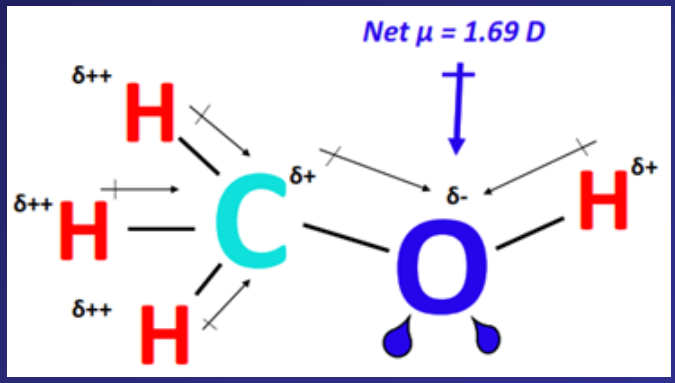


Carbon dioxide: each C–O bond shows bond polarity (the O atom more electronegative), but because O=C=O is linear with the bond dipoles OPPOSING in direction, the molecule shows a **net dipole** of zero (**nonpolar**)

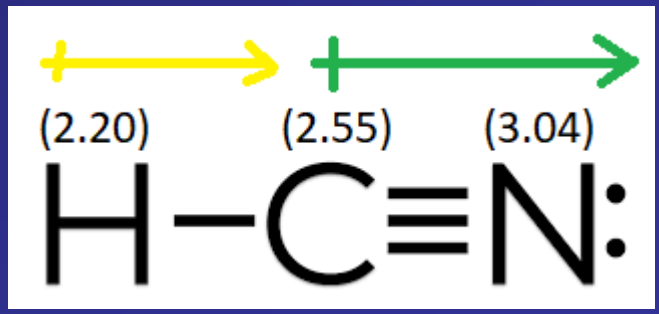


Polar or Nonpolar?

Methanol: the –OH group on central carbon creates an asymmetry in the molecule. The more electronegative O atom creates a net dipole toward the atom's two nonbonding (lone) pairs. Molecule is **polar**.

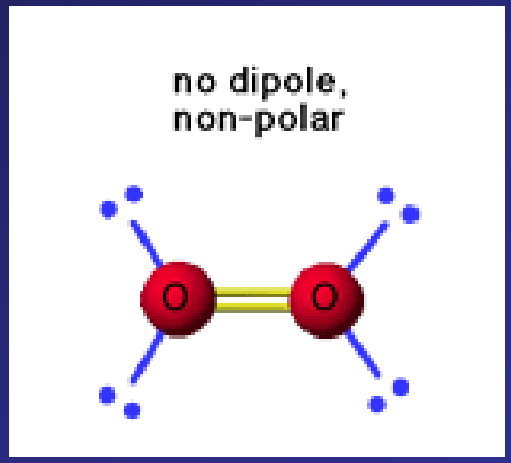


Hydrogen cyanide: H–C bond polarity is toward more electronegative carbon, and there is an additive bond polarity in C–N bond toward nitrogen: **polar**

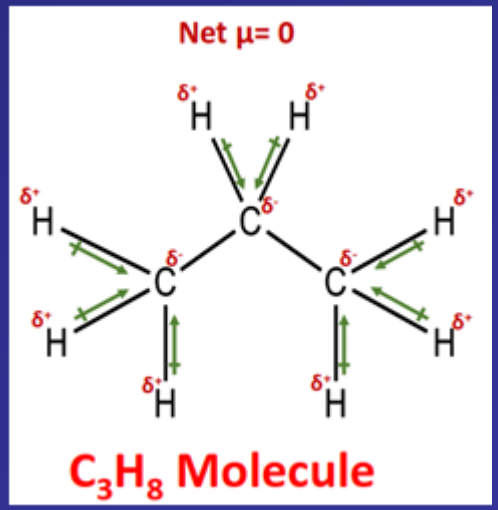


Polar or Nonpolar?

Diatomic oxygen: **O_2** is not different than **Cl_2** or any other ***symmetric*** diatomic molecule with respect showing no bond polarity at all, so the molecule likewise is **nonpolar**.

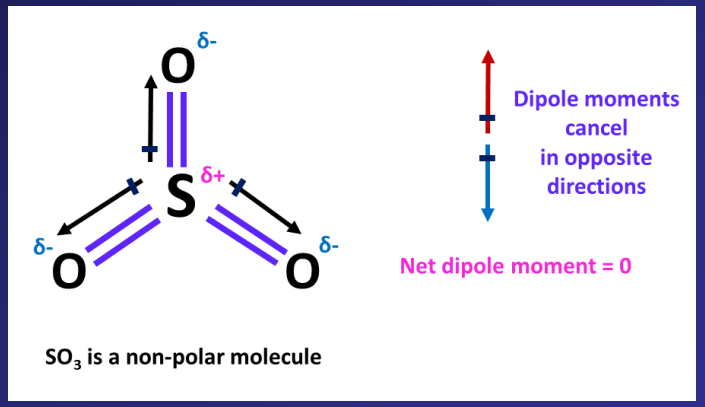


Propane: The molecule shows structural symmetry. While there is bond polarity for all the H–C bonds, the sum of the bond dipole vectors adds up to a net molecule dipole moment (which is vector quantity) of zero. Molecule is **nonpolar**

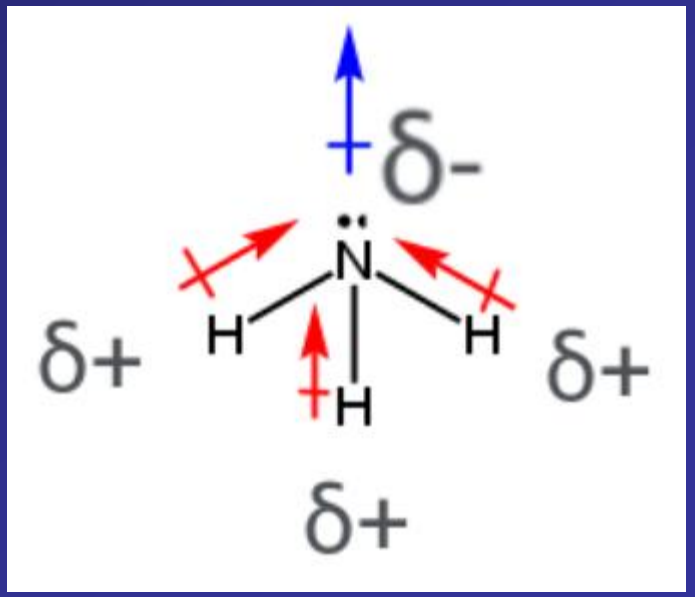


Polar or Nonpolar?

Sulfur trioxide: The three S–O bonds in **SO_3** show bond polarity, but because the molecule as a whole shows trigonal planar ***symmetry*** The net dipole moment is zero, so the molecule is **nonpolar**



Ammonia: The three N–H bonds show significant bond polarity. And the nitrogen with its lone pair provides significant molecular polarity. Molecule is **polar**



Intermolecular Forces

- Intramolecular ("within molecule") forces generally describe the bonds that connect atoms inside a compound/molecule. The energies affecting these bond are considerable: **927 kJ** to break O–H bonds per mol H_2O.
- **Intermolecular** ("between molecule") forces describe the forces or "bonds/bonding" that affect molecules with other molecules, but are much weaker than intramolecular. Energy to put H_2O molecules from liquid to vapor phase is **41 kJ** per mol at 100°C. Covalent bonds are not broken in this process
- Note that while liquids resemble solids more than gases

Intermolecular Forces

- Observable properties of intermolecular forces include melting points of solids, boiling points of liquids
- The nature of intermolecular forces is **electrostatic**: meaning positive and negative charges create attractive interactions
- But these forces weaken at larger distances between molecules
  - So the forces are stronger in solids and liquids, less so with gases
  - But when gases become dense (liquid-like), these forces increase

Dipole-Dipole Interactions

- In polar covalent bonds, there is a dipole because of electronegativity differences between the bonded atoms
- If all the bond dipoles in a molecule do not cancel each other, the molecule becomes **polar** by having a net dipole moment
- All these molecules actually **align** according to their dipole, positive end to negative end

The alignment possibilities are showing in the image

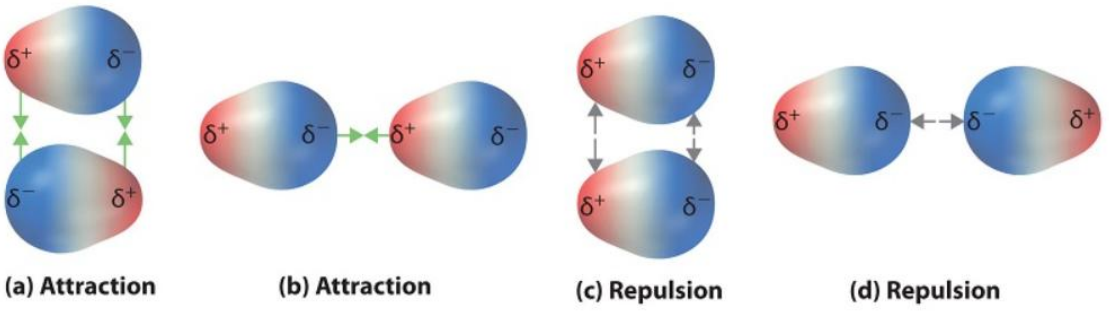


Figure 6.5.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

Dipole-Dipole Interactions

- In liquids, because molecules move freely and continuously, there is a simultaneous occurrence of dipole-dipole interactions, and **Attractive interactions will dominate** as opposed to **repulsive** interactions
- Dipole-dipole interactions are much weaker than ionic interactions
- Dipole-dipole interactions fall off at a distance more rapidly

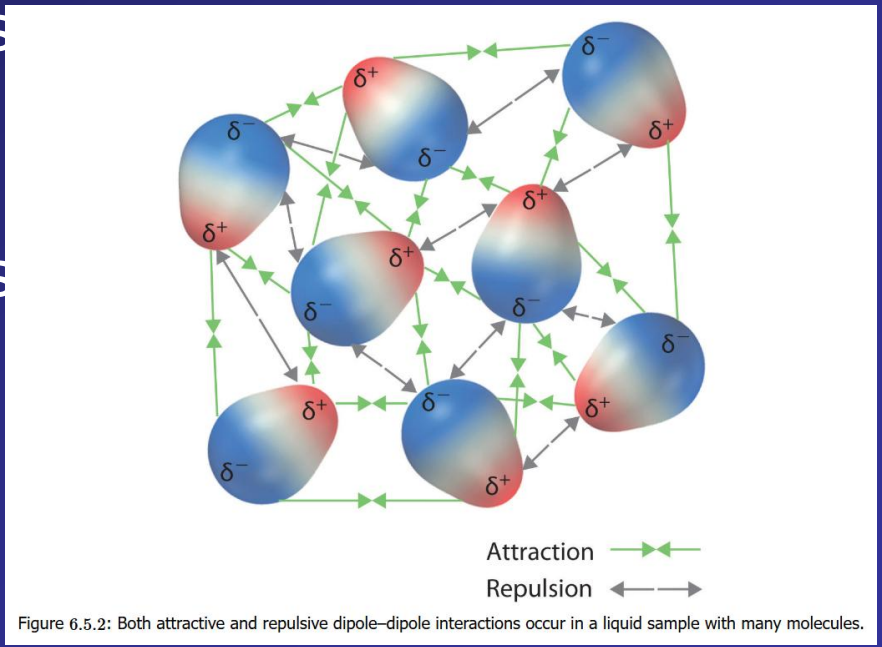
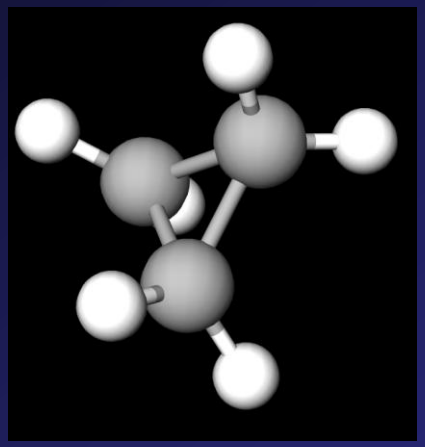
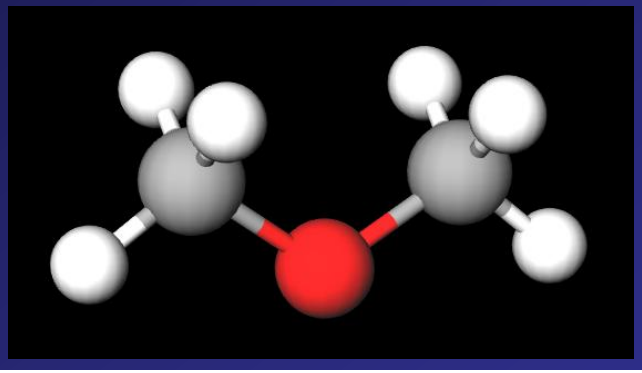


Figure 6.5.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules.

Dipole-Dipole Interactions

- Notice how molecular polarity (dipole moments in molecules) create stronger intermolecular interactions that stabilize the liquid state, raising boiling points





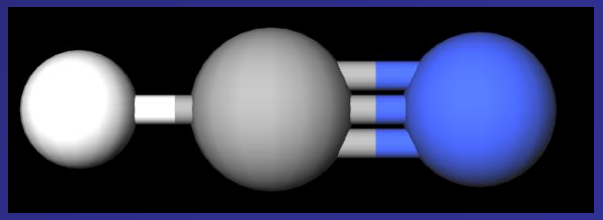


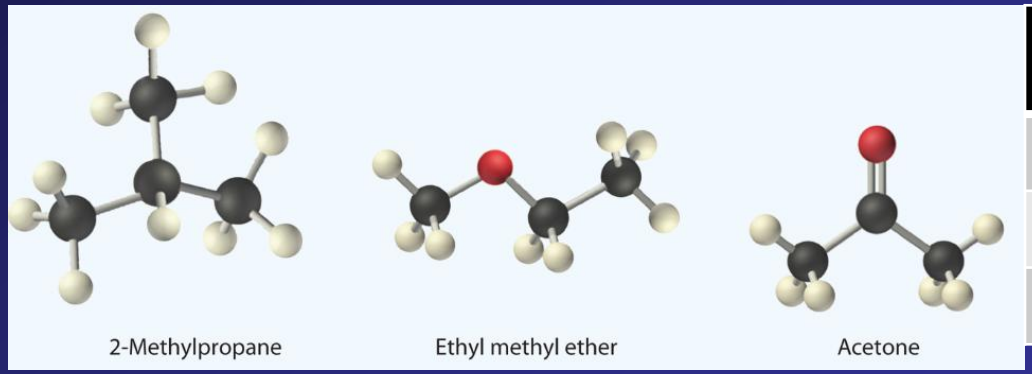
Table 6.5.1: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

Dipole-Dipole Interactions

Can you guess which molecules below would have the higher boiling point temperatures?

- In 2-methylpropane, the C–H bond polarity is not significant and the molecule quite symmetrical and is nonpolar. Boiling point should be low
- For ethyl methyl ether, the two C–O bonds are quite polar among the nonpolar C-H bonds and atomic groups, with some molecular polarity. Boiling point should be higher.
- For acetone, the one C=O bond provides the overall dipole for the very polar molecule, with boiling point at highest



molecule	b.p.	dipole moment
2-methyl propane	–11.7°	0.13 D
methyl ethyl ether	7.4°	1.17 D
acetone	56.1°	2.88 D

London Dispersion Forces

- What explains how nonpolar molecules (bromine [Br_2], benzene [C_6H_6], hexane [C_6H_{12}]) can be liquids at room temperature (instead of gases)
- Why are iodine [I_2] and naphthalene solids?

- 1930: London proposes theory that electron distributions in atoms and nonpolar molecules result in short-lived instantaneous dipole moments, creating **momentary attractive forces** in nonpolar molecules

Table 6.5.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

London Dispersion Forces

- These forces occur because the electric charge points are constantly in motion, shifting or moving in space in way that creates a time-based (instant) polarity, a dipole moment
- This can cause an **induced dipole** in an adjacent (nearby located) atom or molecule, creating an attraction or repulsion
- And this can propagate to another atom or molecule in these instantaneous ways

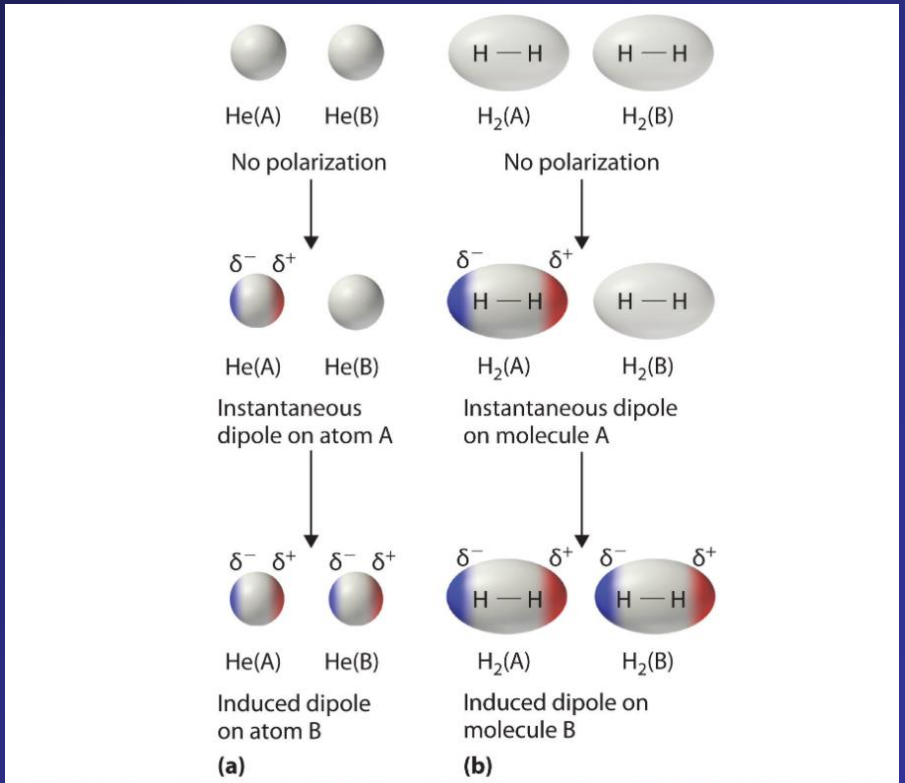


Figure 6.5.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

London Dispersion Forces

- Support for the theory of these forces can be seen in the noble gases
- The element xenon (Xe) boils at –108.1°C and helium (He) boils at –269°C
- **He** is a very small atom with a $1s^2$ two-electron configuration. In sharp contrast, **Xe** is much larger with 54 electrons: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6$
- With all the electrons of Xe especially some distance from the nucleus, it is possible to create induced or instantaneous dipoles in Xe atoms which can cause an attraction to other Xe atoms, and these attractions pull Xe atoms to each other, taking it from a gas to a liquid, compared to He. This is called **polarizability**
- London dispersion forces increase with atomic and molecular size.

Mass and Surface Area

- It should be noted how **mass** of molecules increases the tendency to stay as a liquid as opposed to a gas (affects boiling point)
- Also molecules as shapes have a **surface area**: more linear molecules will have a higher boiling point because they have more potential for dipole interactions (attractions) along the length of a molecule compared to molecules with a more spherical shape having fewer points of contact (attractions)

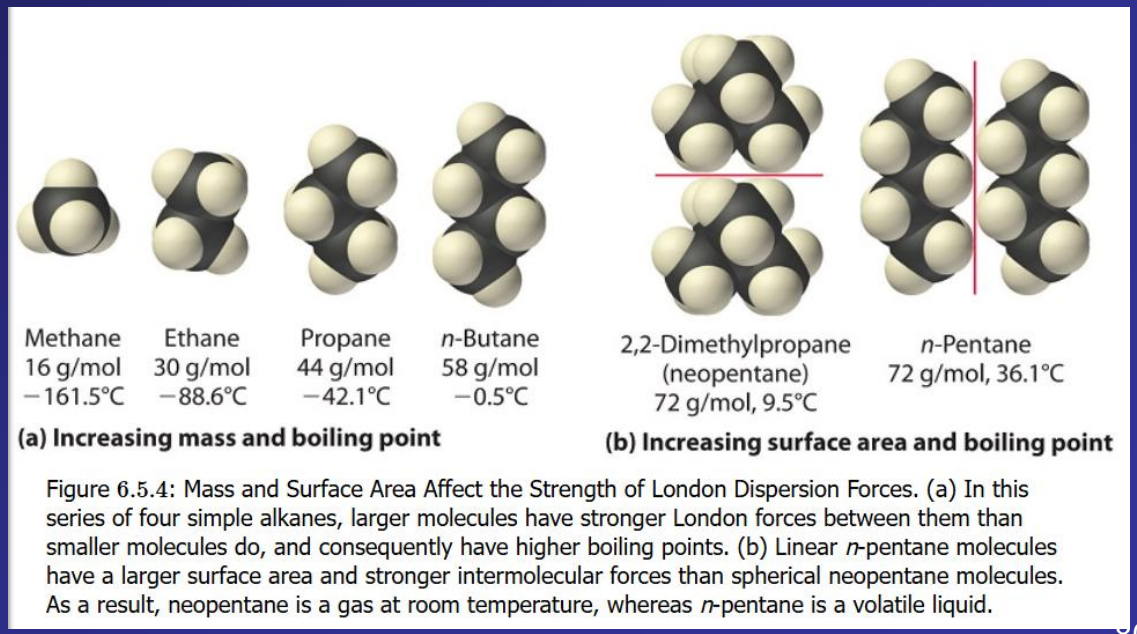


Figure 6.5.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

Summary

- Polar molecules with their dipole moments created by polar bonds between atoms due to electronegativity differences within the molecule will have strong intermolecular interactions that can be observed by many physical properties from gas to liquid to solid states, with melting and boiling point patterns among other properties
- But even nonpolar molecules with nonpolar atom-atom bonds can show instantaneous induced dipoles because electrons within atoms can be perturbed, and these perturbations and propagate to nearby molecules/atoms, creating intermolecular interactions
- Suggested viewing this YT video: https://www.youtube.com/watch?v=RCRTcIEQ-Hk

Hydrogen Bonding

- The **hydrogen bond** is one of the most significant intermolecular bonds in chemistry
- It occurs when the hydrogen (H) is bonded to the more electronegative atoms of the 2nd period: oxygen (O), nitrogen (N), fluorine (F), and to a smaller degree with atoms of the 3rd period: sulfur (S) and chlorine (Cl)
- Hydrogen bonding is much stronger than London dispersion forces
- This is seen in boiling points being higher for NH_3, HF, and H_2O which breaks the pattern or trend of increasing boiling points as atoms get bigger with the period.

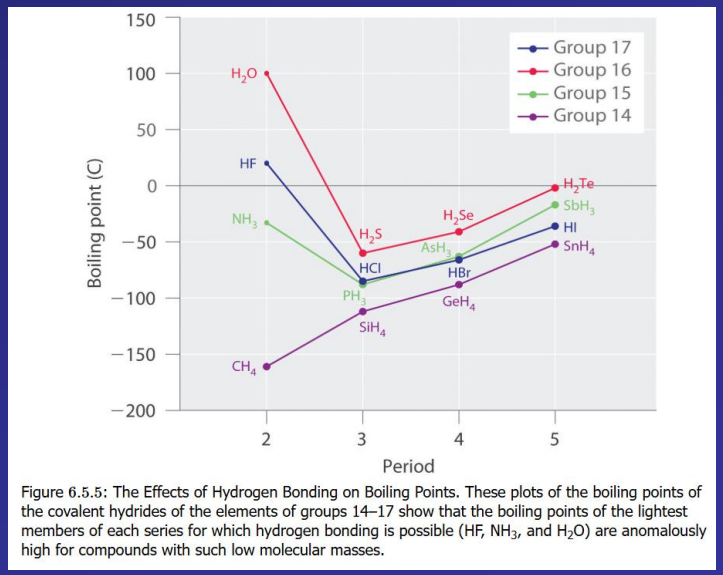
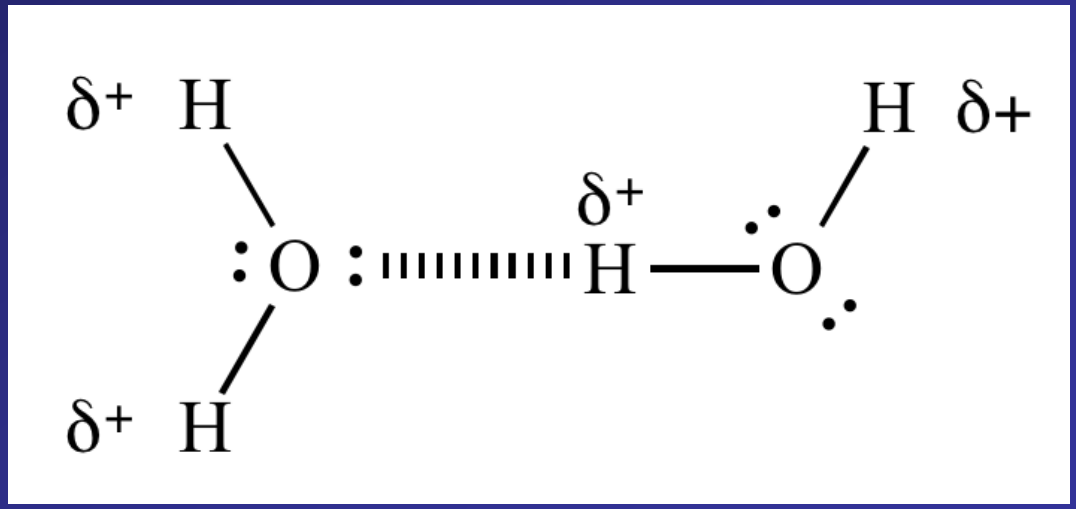


Figure 6.5.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

The Hydrogen Bond

- H_2O forms a liquid (water) and solid (ice) principally because of the hydrogen bond
- The high electronegativity of the O atom forms the strongly polar covalent O–H bond, and the positive charge concentration in the H atom can create an attraction of the H atom particularly to the nonbonding (lone) pair electrons in an O atom of an adjacent H_2O molecule
- Note the series of stacked short vertical lines to symbolize the hydrogen bond



H-Bond Terms

- The dotted line (or stacked lines) are used to symbolize the hydrogen bond (H-bond)
- It will be a bond between the H atom covalently bonded to an atom with electronegativity higher than the H atom (O, N, F, S, Cl) --**hydrogen bond donor**-- and a lone non-bonding pair of electrons on a similar more-electronegative atom (O, N, F, S, Cl) --**hydrogen bond acceptor**-- of an adjacent molecule

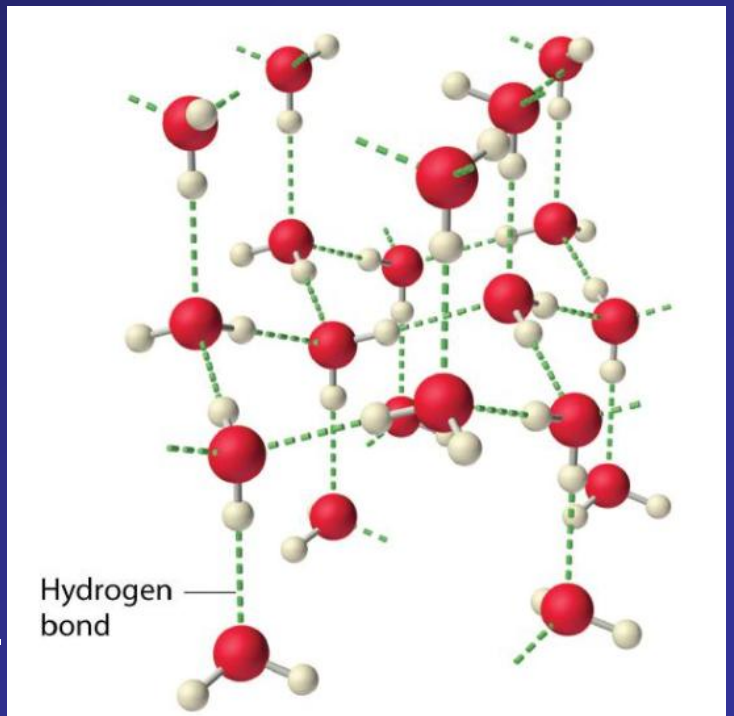


Figure 6.5.6: The Hydrogen-Bonded Structure of Ice