LEWIS STRUCTURES

- The valence electrons in an atom are the electrons in the outer most principal shell. Since these are the most important electrons in bonding, they are most focused upon.
- *Lewis structures* use Lewis symbols to show *valence electrons* of main-group elements as dots surrounding the symbol of the atom.
- For example, the electron configuration and Lewis structure of oxygen are shown below:



• The Lewis structures for all main-group elements in the first 3 periods are shown below:

1A							8A
H·	2A	3A	4A	5A	6A	7A	He:
Li	·Be·	۰ġ۰	۰Ċ٠	٠ÿ٠	:ö·	÷Ë·	:Ņe:
Na	·Mg·	·Áŀ	·Ṣi·	·ÿ.	÷Ş∙	:Ċŀ	:Är:

Lewis symbols for the first 3 periods of Main-Group Elements

Examples:

- 1. Which two elements have the most similar Lewis structures:
 - a) C and Si
 - b) O and P
 - c) Li and F
 - d) S and Br

LEWIS STRUCTURES FOR IONIC COMPOUNDS

- *Ionic bonds* are formed by transfer of electrons from a metal to a non-metal. Therefore, the Lewis structure for these compounds is drawn by moving the electrons from metal to non-metal.
- For example, the Lewis structure for potassium chloride is written as shown below:

 $\begin{array}{cccc} K \cdot & : \ddot{C} l \colon & \longrightarrow & K^+ & [: \dot{C} \dot{l} \colon]^- \end{array}$

Note that:

- The transfer of electron gives chlorine an octet and leaves potassium with an octet from the previous principal shell, which is now the valence shell.
- Potassium becomes positively charged because it loses an electron and chlorine becomes negatively charged because it gains an electron.
- The Lewis structure of the anion is usually written within brackets with the charge written outside the brackets. The positive and negative charges attract one another, forming the ionic bond in KCl.

Examples:

- 1. Write the Lewis structure for each compound shown below:
 - a) MgO

b) Li₂S

LEWIS STRUCTURES FOR COVALENT COMPOUNDS

- Covalent compounds are formed by sharing electrons. Therefore, the Lewis structures for these compounds are drawn by allowing neighboring atoms to share some of their valence electrons.
- For example, the Lewis structure for water (H₂O) is shown below:



• The electrons that are shared between the atoms are called *bonding pair* electrons, while those that are only on one atom are called *lone pair* electrons.



• The bonding pair electrons can often represented as dash lines, to emphasize that they are chemical bonds, but the lone pair electrons are always displayed as dots. For example, the Lewis structure of water can also be represented as shown below:

• The Lewis model also explains why halogens are diatomic. Since each Cl atom has only one unpaired electron, 2 chlorine atoms can share the unpaired electron to complete their octet, as shown below:

• The Lewis model also allows atoms to share more than one pair of electrons to achieve octet. For example, when 2 oxygen atoms share only one pair of electrons, they do not achieve octet (diagram on left). However, sharing of 2 pair of electrons (one lone pair and one bonding pair) does achieve octet (diagam on right).

WRITING LEWIS STRUCTURES FOR COVALENT COMPOUNDS

- Lewis structures for covalent molecules can be drawn according to the following steps:
 - 1. Count the total number of valence electrons to be used in the structure. For ions, add one electron for each negative charge, and subtract one electron for each positive charge.
 - 2. Write a skeleton structure, arranging the atoms in the most symmetrical pattern. Remember the number of bonds commonly formed by atoms.
 - 3. Connect each atom by a dashed line representing 2 electrons each.
 - 4. Determine the number of electrons left by subtracting number of electrons used from the total determined in step 1.
 - 5. Distribute the remaining electrons around the atoms in pairs in order to achieve eight electrons around each (*octet rule*). Hydrogen is an exception (doublet).
 - 6. If there are not enough electrons to achieve octet rule for each atom, form double or triple bonds by sharing more than one pair of electrons.

Examples:

Draw Lewis structure for each molecule or ion, using the step-wise procedure outlined above:

1) water (H_2O)

Total number of electrons:

2) carbon dioxide (CO₂)

Total number of electrons:_____

3) chlorite ion (ClO_2^{-})

Total number of electrons:

RESONANCE STRUCTURES

• When writing Lewis structures, it might be possible to write more than one good (valid) structure for some molecules. For example, when writing Lewis structure for SO₂, we can draw the structure below to use all 18 electrons present in the molecule:

:O:S:Ö: (18 of 18 electrons used)

• Since the structure above does not have octet for sulfur, we will need to form a double bond by using a lone pair of electrons on oxygen. Since there are two oxygens in the molecule, the lone pair can be used from either one, leading to 2 equivalent and valid structures shown below:

$$: \overset{\circ}{O} = \overset{\circ}{S} - \overset{\circ}{O}: \longleftrightarrow : \overset{\circ}{O} - \overset{\circ}{S} = \overset{\circ}{O}:$$

• These equivalent structures are called *resonance structures*. The true structure of SO₂ is intermediate between these two structures.

Examples:

1. The Lewis structure for NO₃⁻ includes 3 resonance structures. Draw each of these diagrams.

2. Write Lewis structures for SeO₂. Include resonance structures if necessary.

PREDICTING SHAPES OF MOLECULES

- The Lewis structure of a molecule, in combination with *valence shell electron pair repulsion* (*VSEPR*) *theory*, can be used to predict the shape of a molecule.
- The VSEPR theory is based on the idea that electron groups around the central atom of a molecule repel each other. The repulsion between these electron groups determine the shape of the molecule.
- Electron groups are defined as: lone pairs, single bonds or multiple bonds.
- For example, CO₂, with the Lewis structure shown below, has two electron groups (two double bonds) around the central atom. The repulsion between these groups produce a linear shape for the molecule with bond angle of 180°.





• As another example, the molecule H₂CO, with Lewis structure shown below, has 3 electron groups around the central atom. The repulsion between these groups produce a trigonal planar geometry with a bond angle of 120°.



- A summary of possible shapes and the corresponding bond angles based on the total number of electron groups is listed on the next page.
- Note that the shape produced by the electrons is called *electron geometry*. When one of more lone pairs are around the central atom, the shape of the molecule as it appears to us is different than the electron geometry, and is referred to as *molecular geometry*.

PREDICTING SHAPES OF MOLECULES

TABLE 10.1 Electron and Molecular Geometries

Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Angle between Electron Groups**	Molecular Geometry	Example	
2	2	0	linear	180°	linear	ö=C=ö∶	
3	3	0	trigonal planar	120°	trigonal planar	Ö: ∥ H−С−Н	
3	2	1	trigonal planar	120°	bent	:ö=š−ö:	•
4	4	0	tetrahedral	109.5°	tetrahedral	H H—C—H H	4
4	3	1	tetrahedral	109.5°	trigonal pyramidal	н—й—н ∣ н	~ ? ~>
4	2	2	tetrahedral	109.5°	bent	н— <u>Ö</u> —н	~

* Count only electron groups around the *central* atom. Each of the following is considered one electron group: a lone pair, a single bond, a double bond, and a triple bond.

** Angles listed here are idealized. Actual angles in specific molecules may vary by several degrees. © 2015 Pearson Education, Inc.

Examples:

Predict the electron and molecular geometry and bond angle for each molecule of ion shown below:

1. PCl₃

2. SO₃^{2–}

δ

ELECTRONEGATIVITY & BOND POLARITY

- The ability of an element to attract electrons within a covalent molecule is called electronegativity.
- For example, oxygen is more electronegative than hydrogen. This means that on the average, the shared electrons are more likely to be found near the oxygen atom than near the hydrogen atom.
- As a result, in the O–H bond, the oxygen atom carries a partial negative charge (δ–) while the hydrogen carries a partial positive charge (δ+).



- The result of this uneven sharing of electrons in the O–H bond is the separation of charge in the bond, called *dipole moment*. Covanlent bonds that have dipole moment are called polar *covalent bonds*.
- The dipole moment in a bond is sometimes shown with a vector representation, where the vector points to the direction of the atom with the partial negative charge.

forming the bond and the bond length.

- The *magnitude of the dipole moment*, and therefore the *degree of polarity* of the bond, depend on the *difference in electronegativity* between the two elements
- For a fixed bond length, the greater the electronegativity difference, the greater the dipole moment and the more polar the bond.



ELECTRONEGATIVITY & BOND POLARITY

• The electronegativities of elements in the periodic table is shown below. Note that electronegativity increases across a period and decreases down a group.

н																	He
2.20		-															n.a.
Li	Be											В	С	Ν	0	F	Ne
0.98	1.57											2.04	2.55	3.04	3.44	3.98	n.a.
Na	Mg											Al	Si	Р	s	Cl	Ar
0.93	1.31											1.61	1.90	2.19	2.58	3.16	n.a.
K	Ca	Sc 1.26	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.50	1.54	1.05	1.00	1.55	1.65	1.00	1.91	1.90	1.05	1.01	2.01	2.10	2.55	2.90	3.00
Rb	Sr	Y	Zr	Nb	Mo	Τc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
0.82	0.95	1.22	1.33	1.60	2.16	1.90	2.20	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66	2.60
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
0.79	0.89	1.10	1.30	1.50	2.36	1.90	2.20	2.20	2.28	2.54	2.00	1.62	2.33	2.02	2.00	2.20	n.a.
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	_	Uuq	_	_	_	_
0.70	0.89	1.10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		n.a.				

Examples:

1) Rank the bonds shown below from most polar to least polar:

2) For each molecule shown below, draw a vector representation of the dipole moment present in the molecule. Identify the largest and smallest dipole moments in the group.

a) NO

b) HCl

c) CO

Cl

NON-POLAR & POLAR COVALENT BONDS

- If two elements with *nearly identical electronegativities* form a covalent bond, they share the electron equally, and there is *little or no dipole moment*. These bonds are called *non-polar covalent bonds*. For example, Cl₂ molecule, composed of 2 chlorine atoms (with same electronegativities) form such a bond.
- When two elements with *intermediate electronegativity difference* form a bond, such as two nonmetals, the electrons are shared unequally and there is an *intermediate dipole moment*. These bonds are called *polar covalent*. H and F form such a bond.
- If there is a *large electronegativity difference* between two elements forming a bond, such as a metal and nonmetal, the electron is transferred and a there is a *large dipole moment*. These bonds are called *ionic*. Sodium and chlorine form such a bond.
- The relationship between electronegativity difference and bond polarity and bond type are summarized below:







MOLECULAR POLARITY

- Many molecules with polar bonds become non-polar, because their bond polarities cancel out one another due to their shapes.
- For diatomic molecules, the polarity of the molecule can easily be determined from the polarity of the bond, since the bond forms the molecule. Therefore, diatomic molecules with non-polar bonds are non-polar, and those with polar bonds are polar.
- For molecules with more than two atoms, it is more difficult to distinguish between the polar and non-polar molecules, because two or more polar bonds may cancel each other.
- For example, consider the carbon dioxide molecule: each C=O bond is polar because the difference in electronegativity between oxygen and carbon is 0.89. However, due to the linear shape of the molecule, the dipole moment of each bond is cancelled since they are in opposite directions, leading to a non-polar molecule.



- Water, on the other hand, also has two polar O–H bonds, since the electronegativity difference between hydrogen and oxygen is 1.24. However, the bent shape of the water molecule does not allow the two dipole moments of the bonds to cancel one another. As a result water is a polar molecule.
- Molecules with symmetrical shapes such as linear, trigonal planar and tetrahedral, allow for cancellation of dipole moments and are non-polar when all atoms around the central atom are the same.
- Molecules with unsymmetrical shapes such as bent and pyramidal do not allow for cancellation of dipole moments are always polar.

MOLECULAR POLARITY

- In summary, to determine if a molecule is polar:
 - First determine whether the molecule contains polar bonds. A bond is polar if the two atoms forming the bond have different electronegativities. If no polar bonds exist, the molecule is non-polar.
 - Next determine if the polarity of the bonds cancel one another because of the shape. Use VSEPR model to determine the shape of the molecule and then evaluate if the polarity of the bonds can be cancelled due to the shape.

Examples:

1) Determine whether each molecule shown below is polar or non-polar:

a) PF₃

b) SeO_2

c) SO₃