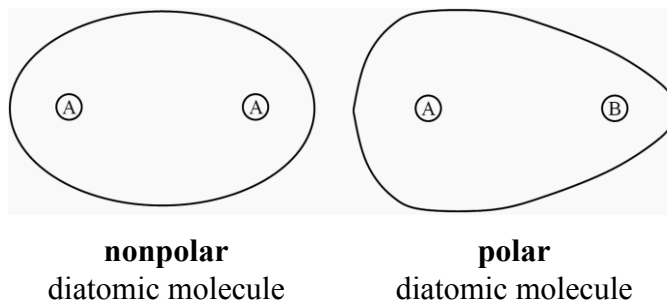


ALE 13. Polarity of Molecules(Reference: Sections 9.5 and 10.3- Silberberg 5th edition)**How does a molecule's shape determine whether or not it is polar?****The Model: Electronegativity (Ref. Sec. 9.5)**

A covalent bond is a shared pair of electrons between two atoms.

Consider the hypothetical **homonuclear** substance, "A—A". The region describing where the bond electron density is likely to be found looks like what is shown to the right. (The size of the nuclei is exaggerated.)



The figure above and on the right represents a **heteronuclear** compound "A—B", in which the atom "A" is more **electronegative** than the atom "B".

The **electronegativity** (EN) of an element measures its attraction for the electrons *in a chemical bond*. The higher the electronegativity, the greater the atom's attraction for bonding electrons. One scale of electronegativity was developed by the American chemist Linus Pauling. On this scale, fluorine, the most electronegative element, has an electronegativity of 4.0. Figure 1 shows the electronegativities of the elements with which we deal most often—see your textbook for a table of electronegativities for all of the elements. In general, electronegativity increases from bottom to top in a column and from left to right across a period.

Increasing electronegativity →

1	1												3	4	5	6	7			
1	H												B	C	N	O	F			
2	Li	Be											Al	Si	P	S	Cl			
3	Na	Mg	Transition elements										Ga	Ge	As	Se	Br			
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn	Sb	Te	I			
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Hg	Tl	Pb	Bi	Po			
6	Cs	Ba											Pt	Au	Hg	Tl	Pb	Bi	Po	
	0.79	0.9											2.3	2.5	2.0	2.0	2.3	2.0	—	
	2.1												1.5	1.8	2.0	2.2	2.5	3.0	3.5	4.0
	1.0	1.5											1.5	1.8	2.1	2.5	3.0			
	0.9	1.2											1.8	2.0	2.2	2.6	2.8			
	0.8	1.0	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	2.0	1.6	1.8	2.0	2.2	2.6	2.8			
	0.8	1.0	1.2	1.3	1.6	2.2	—	2.2	2.3	2.2	1.9	1.7	1.8	1.8	2.0	2.1	2.5			
	0.79	0.9											2.3	2.5	2.0	2.0	2.3	2.0	—	

↑ Increasing electronegativity

Figure 1. Electronegativities of some elements (Pauling scale).

When two atoms combine, the nature of the bond between them is determined by the difference between their electronegativities (denoted ΔEN). If the atoms forming the bond differ in electronegativity by more than 1.7 units, the bond will be at least 50% ionic (referred to as percent ionic character); we treat such a bond as wholly ionic. If the values differ by less than 0.4 units, we consider the bond to be wholly nonpolar. If the difference is between 0.4 and 1.7 electronegativity units, the bond is considered to be polar covalent. Remember that *electronegativities have been calculated from fairly imprecise data* for particular bonding situations. *Electronegativity is useful in predicting the nature of a bond and for*

comparing bond types, but the prediction is only an approximation. Remember too that no sharp distinction exists between ionic, polar covalent, and nonpolar bonds; rather, they form a continuum. Even the most ionic bond (between cesium and fluorine) has some covalent character, and only bonds between atoms of the same element have no ionic character.

In these bonds, the atom with the higher electronegativity will be the negative end of the bond and, in extreme situations, will become the negative ion. To show these partial charges on a polar covalent bond, we mark the positive end of the bond with a δ^+ and the negative end of the bond with a δ^- . Table 1 summarizes these data.

Table 1. Guidelines for predicting bond type from electronegativity data

Difference in electronegativity (ΔEN)	Type of predominant bond	Example	EN	ΔEN	Element with a more positive charge
> 1.7	ionic	NaCl	Na = 0.9 Cl = 3.1	2.2	sodium
$> 0.4 - 1.7$	polar covalent	C-Cl	C = 2.5 Cl = 3.0	0.5	carbon
≤ 0.4	nonpolar covalent	H-H	H = 2.1 H = 2.1	0.0	neither
		C - H	C = 2.5 H = 2.1	0.4	neither

Key Questions

- Electrons in a bond: (circle the correct response)
 - spend more time around the more electronegative atom.
 - spend more time around the less electronegative (*i.e.*, the more **electropositive**) atom.
 - spend equal amounts of time around both atoms, regardless of their relative electronegativities.
- Suppose both A and B contributed one electron to the covalent bond between them. If the two electrons spend 60% of their time around A, then which of the following is true? (Circle the correct response.)
 - A will have a fully negative charge and B will have a fully positive charge.
 - A will have a partial negative charge and B will have a partial positive charge.
 - Both A and B will be neutral with respect to charge.
 - A will have a partial positive charge and B will have a partial negative charge.
 - A will have a fully positive charge and B will have a fully negative charge.

3. What is the difference between electronegativity and electron affinity? Are they the same thing?
4. Noble gases have measured values for electron affinity, but are not assigned electronegativity values. Why do you think electronegativity values are not assigned to the Noble gases?

The Model: Dipole Moment (Ref. Sec. 10.3)

Dipole moment, μ , is a measure of the polarity of a polar covalent bond. Dipole moment is defined as the product of the magnitude of charge on the atoms and the distance between the two bonded atom. Dipole moment, μ , is commonly measured using the unit **debye (D)**.

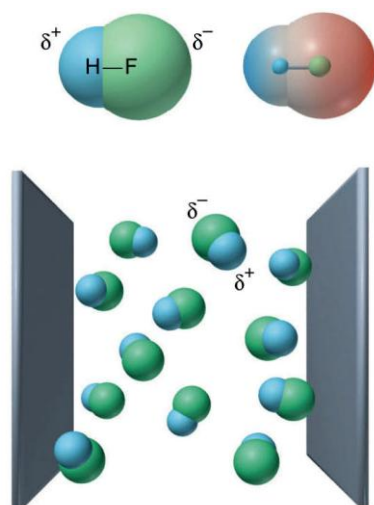
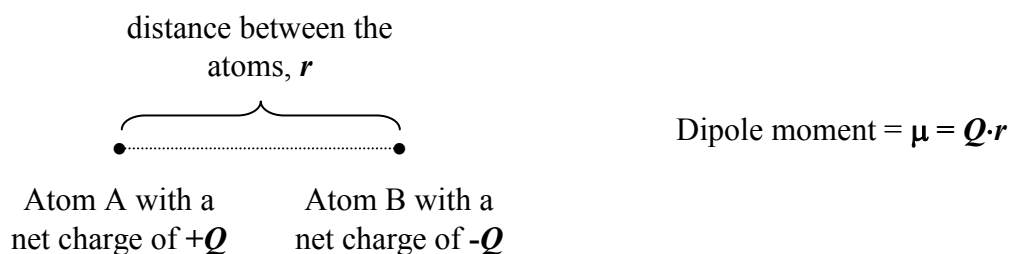


Figure 2a. Orientation of HF molecules in the absence of an external electric field.

The orientation of polar molecules in an electric field.

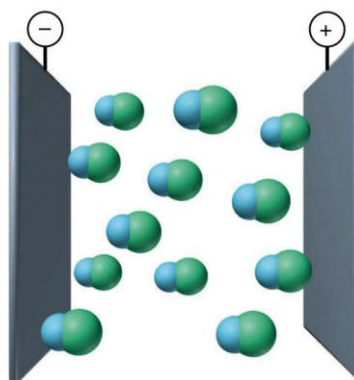


Figure 2b. Orientation of HF molecules in the presence of an external electric field.

Key Questions

5. What happens to the value of the dipole moment when:
- the magnitude of $+Q$ (and, by necessity, $-Q$) increases?
 - the distance between the charges decreases?
- 6a. Describe the orientation of the HF molecules in figure 2a.
- b. Describe the orientation of the HF molecules in figure 2b.
- c. Explain why the molecules in figures 2a and 2b have different orientations.
7. Complete the following table by (1) filling in absolute differences in the electronegativities (ΔEN) of the two elements that make up each diatomic—show your work in the table below, and (2) classifying whether the compound is nonpolar covalent, polar covalent or ionic.
- | Gaseous Compound | μ (D) | $ \Delta EN $
(Show work in space below) | Classification of Compound |
|-------------------------|-----------|---|-----------------------------------|
| NO | 0.15 | | |
| HI | 0.44 | | |
| ClF | 0.88 | | |
| SO | 1.55 | | |
| HF | 1.82 | | |
| AgCl | 5.73 | | |
| LiF | 6.33 | | |
8. What is the general trend in the relationship between the magnitude in the difference of electronegativities of the two bound atoms and the magnitude of the dipole moment of the gas-phase diatomic molecule of the elements? “As ΔEN _____, the the dipole moment of the gas-phase diatomic molecule tends to _____.”

9. An often-used “rule of thumb” employed in order to classify a bond as covalent or ionic is:

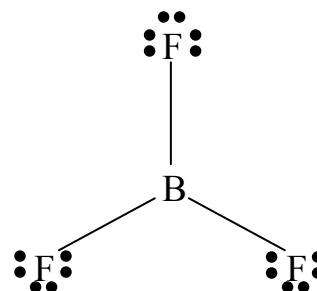
If $\Delta EN \gtrsim 1.7$, then the bond is 50%+ ionic.

(It follows that the greater ΔEN is beyond 1.7, the more ionic the bond is.) Using HF and AgCl as examples from the table in [Question 7](#), explains why the above must be just a “rule of thumb” and is not always valid.

The Model: Polarity of Polyatomic Molecules (Ref. Sec. 10.3)

While individual bonds may be polar, we need to look at the overall shape of a molecule to determine if there is a *molecular* dipole moment. In general, we need to ask the simple question: “Does the molecule have spherical (or circular) symmetry?” If the answer to that question is “Yes!”, then the molecule is nonpolar (*i.e.*, $\mu = 0$). If the answer is “No!”, then the molecule is polar (*i.e.*, $\mu > 0$).

As an example of “circular symmetry”, consider BF_3 . To be sure, the individual B—F bonds *are* polar. But because the three B—F bonds are distributed 120° apart from each other in a plane, the three bond dipoles have circular symmetry. In essence, the “pulls” of electron density toward the three fluorine atoms are equal in magnitude and opposite in direction, so they cancel each other out. Thus the “center of mass” of the protons is coincident with the center of mass of the electrons (*i.e.*, at the boron atom, the center of the molecule). Since $r = 0$, this makes $\mu = 0$, and the BF_3 molecule is nonpolar.

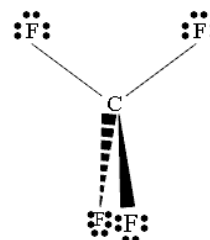


Key Questions

- 10a. An example of “spherical symmetry” is demonstrated with phosphorous pentafluoride. Draw the Lewis structure of PF_5 . Next, use VSEPR Theory to predict the shape of PF_5 . Rewrite the Lewis structure as a 3-D figure using bold wedges and dashed wedges.

- b. We can separate a compound into “halves”, investigate the halves for regional polarity, and then recombine the halves to determine the overall molecular polarity. Investigate the “equatorial plane” of the PF₅ molecule for polarity in that “half”. Investigate the “poles” (North Pole and South Pole at the same time) as the second “half”. Explain in a couple of sentences why $\mu = 0$ for PF₅.

11. When considering a tetrahedral molecule, it is probably most effective to orient it on the page as the 3-D representation of CF₄ is to the right.



- a. Are the two F's above the C equivalent to the two F's below the C? (Circle the correct response.)

Yes or No

- b. Think now about a plane including the C and the two F's that are going in and out of the plane of the paper. (This plane is perpendicular to the plane of the paper.) Is what is on the left-hand side of that plane equivalent to what is on the right-hand side of the plane?

Yes or No

- c. Now consider the plane of the paper, which includes the C and the two F's that are connected to the C by thin solid line segments. Is what is above that plane equivalent to what is below the plane?

Yes or No

- d. Is CF₄ polar or nonpolar? (Circle the correct response.)

12. A student who is learning about molecular polarity wonders if SiH₂Cl₂ is polar or nonpolar. What do you think, is it polar or nonpolar? Answer this question by drawing the Lewis structure of SiH₂Cl₂ using thick and dashed wedges in order to see the three dimensionality of the molecule and then explain if it's a polar or nonpolar molecule.

13. [Problem 10.53](#): How can a *molecule* with polar covalent bonds fail to be a polar molecule? Give an example to support your explanation.
14. [Problem 10.58](#): Which molecule in each pair has the greater dipole moment? *Circle your choice* and *be able* to give a reason for your choice.
- a.) ClO₂ or SO₂ b.) HBr or HCl c.) BeCl₂ or SCl₂ d.) AsF₃ or AsF₅

How can Lewis Structures and Bond Energies be used to Calculate Heats of Reaction?

Model (ref. Sec 9.4)

Energy must be *added* to a compound to break a chemical bond—i.e. *bond breaking is endothermic*—energy is needed to separate the atoms that are chemically bonded. Conversely, *chemical bond formation is exothermic*—i.e. energy is released to the surroundings when chemical bonds form.

For a chemical reaction to occur...

- Bonds within the reactants must be broken (an endothermic process, ΔH is positive)
- Bonds within the products must be made (an exothermic process, ΔH is negative)

Bond Energy = the energy required to break a bond. If the Lewis structure of the reactants and the products is known, Bond energies can be used to determine the ΔH of a reaction.

$$\Delta H_{\text{rxn}} = \Sigma \text{BE}_{\text{reactant bonds broken}} - \Sigma \text{BE}_{\text{product bonds formed}}$$

Exercises

15. Use bond energies from [Table 9.2 \(page 353\)](#) to calculate the heat of reaction of the following reaction, an important reaction that occurs in the livers of all vertebrates as a means of detoxifying highly toxic ammonia, NH₃, (produced when cells breakdown amino acids) to produce much less toxic urea, (H₂N)₂CO, which is then secreted in the urine:



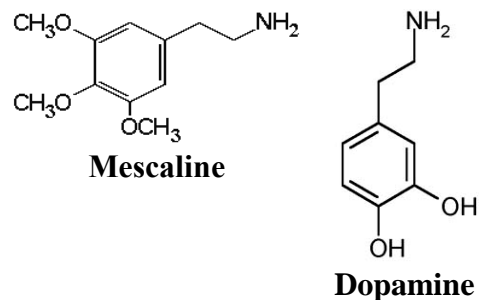
Although you should be able to use Lewis structures to determine the kind of bonds in each compound, above, see [problem 9.49 on page 374](#) for their structures.

16. Acetylene gas, C_2H_2 , burns with oxygen in oxyacetylene torches to produce carbon dioxide, water vapor, and the great heat needed for welding metals. Use the heat of combustion of acetylene, 1259 kJ/mol, and the bond energies from [Table 9.2 \(page 353\)](#) to calculate an estimate of the $C\equiv C$ bond energy in kJ/mol and compare your calculated value with that in [Table 9.2](#).

Comprehensive Questions

17. [Problem 10.97](#)

The structures of mescaline, a hallucinogenic compound in peyote cactus, and dopamine, a neurotransmitter in the mammalian brain appear to the right. Suggest a reason for mescaline's ability to disrupt nervous communication within the mammalian brain.



18. [Problem 10.80 \(modified\)](#): A gaseous compound has a composition by mass of 24.8% C, 2.08% H, and 73.1% Chlorine. The gas has a density of 4.3 g/L at STP. Determine the empirical and molecular formula of the compound and draw the 3-D structures of all possible isomers, indicating all bond angles in each isomer.