

7.1 Introduction to chemical bonding: The octet rule

The electron configurations of atoms can help us understand how atoms combine to form compounds. We shall focus only on compounds formed from “main group” elements.

Our first concern is: What type of bond will two atoms form?

Recall:

metals from groups 1, 2:

atoms from groups 14, 15:

atoms from groups 16, 17:

Therefore, we expect:

Other questions to consider:

- What are the stable ions an atom will form?
- How many bonds will an atom form?
- How strong will the bond between two ions or atoms be?
- How will the bonds in a molecule be oriented in space?

A simple, yet very useful, rule of thumb is the **octet rule**:

An atom tries to attain a noble gas configuration either by sharing or transferring electrons.

When electrons are transferred from one atom to another, we form monatomic ions. The ions are attracted to each other and form an ionic bond.

When electron pairs are shared between a pair of atoms, the nuclei of the two atoms are drawn towards each other and form a covalent bond

General rule of thumb:

When metals from the s block combine with atoms from the p block to form a binary compound, we usually get ionic bonds.

When atoms from the p block combine with each other to form a compound, we usually get covalent bonds.

Example: The ground-state electron configurations of H, C, O, Na and Cl are shown in the box on the right. Use this information, together with the octet rule to predict

- (i) the stable ions formed by Na, O, Cl
- (ii) the nature of the bond formed between Na and O
- (iii) the nature of the bond formed between Na and Cl
- (iv) the nature of the bond formed between H and C
- (v) the nature of the bond formed between H and Cl

H,	$1s^1$
C,	$[\text{He}] 2s^2 2p^2$
O,	$[\text{He}] 2s^2 2p^4$
Na,	$[\text{Ne}] 3s^1$
Cl,	$[\text{Ne}] 3s^2 3p^5$

7.2 Lewis Symbols and Lewis Structures

Lewis symbols for the atoms of the second period are:

A Lewis structure is comprised of Lewis symbols and it shows how the ions or atoms are bonded together.

Lewis structures for Ionic Compounds

Lewis structures for Covalent Compounds

- Use group #'s to determine the # of valence e^- 's
- Put a pair of e^- 's between each pair of bonded atoms
- Distribute remaining valence e^- 's around atoms but keep in mind the following:
 - (i) an H atom **never** has more than 2 e^- 's
 - (ii) second row atoms **never** have more than 8 e^- 's
 - (iii) atoms from the third period (and beyond) might have an "expanded" octet (i.e. more than 8 e^- 's)

Sometimes, it is possible to draw more than one acceptable Lewis structure. For such cases,

- the "true" structure is assumed to be a hybrid (or a weighted average) of the *resonance* structures
- the most important structure is the one with the smallest formal charges

formal charge =

Example: Draw Lewis structures for the following. When appropriate, draw resonance structures and assign formal charges.

(i) HOCN

(ii) C₂H₄

(iii) O₃

(iv) $\text{H}\underline{\text{N}}\text{O}_3$ (H is bonded to O)

(v) $\underline{\text{B}}\text{F}_3$

(vi) $\underline{\text{Br}}\text{F}_3$

7.3 The strength of an ionic bond

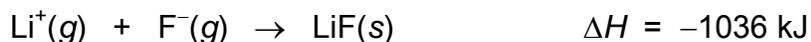
The potential energy associated with the interaction of two charges is proportional to the product of the charges and inversely proportional to the distance between the charges:

$$PE = \frac{q_1 q_2}{4 \pi \epsilon r}$$

The attractive force between “+” and “-” is quite strong so ionic compounds are typically solids with very high melting points. The relative stability of ionic compounds can be measured by comparing their lattice energies:

Lattice
energy =

Lattice energies can be estimated from other thermochemical data using Hess' Law & the Born-Haber cycle (CHEM 123).



7.4 The strength of a covalent bond

The strength of a covalent bond depends upon

- the sizes of the atoms
- the bond-order
- whether the bond is polar or non-polar

Tabulated bond energies show how the bond strength is affected by the sizes of the atoms, the bond-order, and the polarity of the bond.

See Tables 11.2 and 11.3.

Bond
energy

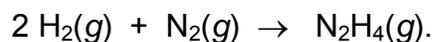
General observations:

- (1) small atoms tend to form strong, compact bonds

- (2) bond length decreases and bond strength increases as the bond order increases

Bond energies are approximate (because they are “average” values obtained by considering a variety of different compounds) but they are useful because they can be used to estimate ΔH° for a **gas-phase reaction**.

Example: Use bond energies to estimate ΔH° for the reaction



7.5 Electronegativity values and Polar Covalent Bonds

Electronegativity values (see Figure 11.6) can help us determine whether two atoms will share a pair of electrons equally.

Bond polarities are important because they affect

- acid strength of hydrogen-containing molecules (CHEM 123)
- how a molecule interacts with light (CHEM 129)

Electronegativity ↔

Some electronegativity values:

1										18							
H 2.1											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	He Ne	
Li 1.0	Be 1.5											Al 1.5	Si 2.1	P 2.1	S 2.5	Cl 3.0	Ar
Na 0.9	Mg 1.2	3	4	5	6	7	8	9	10	11	12	Ga 1.6	Ge	As 2.0	Se 2.4	Br 2.8	Kr
K 0.8	Ca 1.0	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn	Sb	Te 2.1	I 2.5	Xe
Rb 0.8	Sr 1.0	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Tl	Pb	Bi	Po 2.0	At 2.2	Rn
Cs 0.8	Ba	(57-71) La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
Fr 0.7	Ra	(89-103) Ac-Lr	104 Rf	Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut					

Note:

- F, O, Cl and N are the most electronegative elements
- s block metals (not H!) have $EN \approx 1$
- d block metals have $EN \approx 1-2$ (values not shown)
- p block: $EN > 1$ and increase left to right

Digging Deeper: The most commonly used electronegativity scale is the "Pauling scale". If the EN of atom X is known, then the EN of atom Y is obtained using the equation

$$EN(X) - EN(Y) = a \sqrt{D_{XY} - \bar{D}}$$

where a is a constant, D_{XY} is the bond dissociation energy of XY and

$$\bar{D} = \sqrt{D_{X_2} D_{Y_2}}$$

is the "geometric mean" of the bond dissociation energies for X_2 and Y_2 .

Fluorine is assigned an EN value of 4.0. The EN for H could then be obtained from $EN(F)$ together with the bond dissociation energies of H_2 , F_2 and HF.

Electronegativity values can help us decide whether the bond formed between two atoms is primarily ionic or primarily covalent.

General rule of thumb:

$$\Delta EN > 1.7 \Rightarrow$$

$$0 < \Delta EN < 1.7 \Rightarrow$$

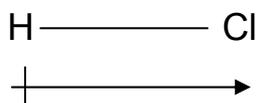
When electron pairs are not shared equally, the bond will have a dipole moment (μ) because one end of the bond will be slightly “+” and the other will be slightly “-”:

$$\mu = |\delta| r$$

Significance?

Polar covalent bonds have “ionic character” plus “covalent character” \Rightarrow polar covalent bonds are often much stronger than pure covalent bonds

Example: Experimental measurements indicate that the HCl molecule has bond length of 127.4 pm and a dipole moment of 1.03 debye. (1 debye = 3.34×10^{-30} C m). What is the % ionic character of the HCl bond?



If the HCl bond was 100% ionic, i.e. H^+Cl^- , then we would have

$$\begin{aligned}\mu_{\text{ionic}} &= (1.602 \times 10^{-19} \text{ C})(127.4 \times 10^{-12} \text{ m}) = 2.041 \times 10^{-29} \text{ C m} \\ &= 6.11 \text{ debye}\end{aligned}$$

The observed dipole is only 1.03 debye. Therefore:

$$\% \text{ ionic} = \frac{\mu}{\mu_{\text{ionic}}} \times 100 = 17$$

Therefore, the H-Cl bond has 17% ionic character.

VSEPR Theory

VSEPR = Valence Shell Electron Pair Repulsion

The basic premise of VSEPR theory is:

Did you know?

R. J. Gillespie, a professor of chemistry at McMaster University in Hamilton, Ontario, is widely regarded to be the “father” of VSEPR theory.

VSEPR theory can be used as a guide to predict the geometry around an “internal” atom of a molecule. It is imperative that you **memorize the ideal VSEPR geometries and ideal molecular geometries!**

Keep in mind the following points:

- VSEPR is a model. It is not perfect.
- VSEPR theory is most appropriate for predicting geometries associated with atoms of the *p*-block.

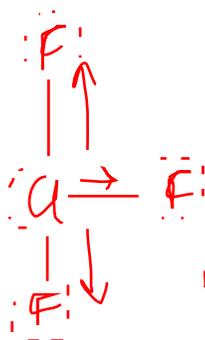
Example: Use VSEPR theory to predict the geometries of H_2O , ClF_3 , SO_3 and H_2CO . Which of these molecules possesses a permanent dipole moment?

Underlined is the central atom.

H_2O valence $e^- = 2(1) + 6 = 8$



ClF_3 : # of valence electrons = $7 + 3(2) = 28$



5 groups

net dipole \rightarrow

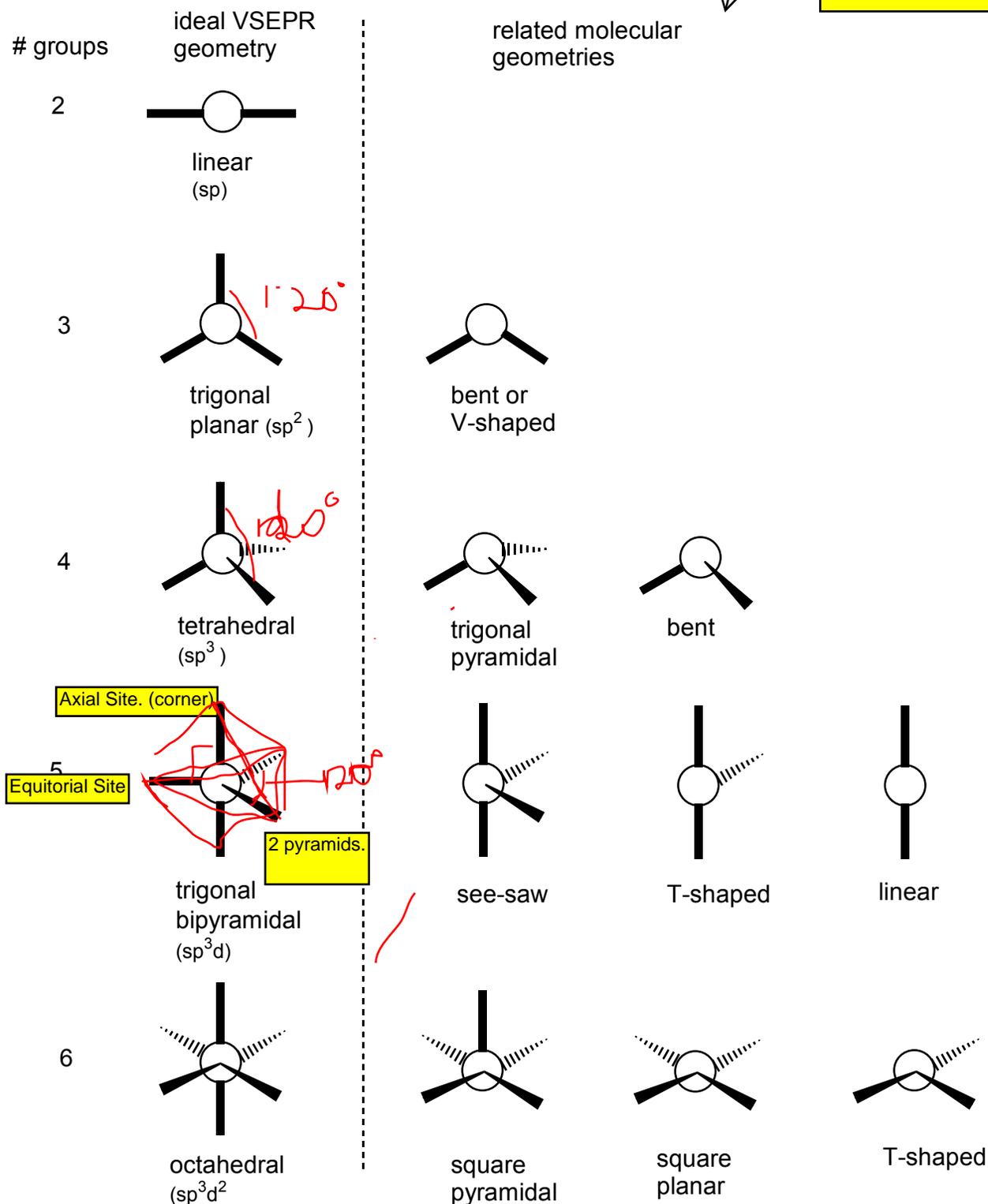
around Cl \Rightarrow trig. bipyramidal arrgmt. of grps.

2 LP's \Rightarrow Molecular Geometry is T-Shaped

ClF_3 is polar molecule.

Means that: if 1 or more of the bonds are really "lone pairs". Lone pairs are ignored while looking at geometry, thus the difference

VSEPR geometries and related molecular geometries



Note: we can get the same geometry from different "parent" geometry. The # of 'lone pairs' will depend on the parent geometry too, and that will be the only difference.