

Chapter 4 – Structure and Properties of Substances

Chemical Bond:

- Bonded atoms have lower energy than single, un-combined atoms because they are more stable
- Atoms bond to become like noble gases in electron arrangement. They can achieve a full octet in two ways: 1) ionic bonding 2) covalent bonding

Lewis Structure

A Lewis symbol is a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element. Each dot represents one electron.

e.g.

Hydrogen

Oxygen

Chlorine

Chloride ion

Ionic Bonding

- Definition:
- Occurs between a _____ with _____ electronegativity and a non-metal with _____ electronegativity.
- The units of ionic compounds can not be separated by heating the crystals.
- The solid compounds are arranged in an array of repeating units such as a lattice so that the system has the minimum possible energy. See pg 165 figure 4.1
- Representation of ionic bonding:
 - Lewis Structure
e.g. Magnesium and Fluorine
 - Orbital Diagram
e.g. Magnesium and Fluorine

Properties of Ionic Solids

- Crystalline with smooth shiny surfaces
- Hard but brittle – strong attraction between _____ and _____ ions makes the structure hard
- Non-conductors of electricity and heat because the ions are not free to move to carry an electric current
- Conductors of electricity only when _____
- High melting point
- Soluble in _____.

Do Practice problems 1-4 on page 165

Covalent Bonding

- Covalent bonding is a balance between the forces of _____ and _____ that act between the nuclei and electrons of two or more atoms.
- A covalent bond may be formed when two half-filled atomic orbital's from two atoms overlap to share the same region of space which forms a new orbital
- The new orbital has energy levels lower than those of the original atomic orbital's which makes it more a favourable configuration.

Properties of Molecular Compounds

- _____ melting point and boiling points
- _____ conductors of electricity because _____
- Insoluble in water
- Exist as a _____, _____, _____ at room temperature

Predicting Ionic and Covalent Bonds

- Pauling realized that electron pairs could be shared evenly or unevenly
- Created "electronegativity" to explain and predict the polarity of molecules
- Electronegativity:
- Electronegativity _____ down a group and _____ across a period
- When the electronegativities between two atoms are compared, the greater the Δ EN (electronegativity difference), the _____ the polarity of the chemical bond
- A very polar bond is an _____ bond while a non-polar bond is a covalent bond
- General rule:

Do Practice Problems 5-8 on page 169

Metallic Bonding

- Metals are shiny, silvery, flexible solids with good thermal & electrical conductivity
- All metals have a closely packed structure
- Based on electronegativity differences, metals do not form ionic bonds. They do not form covalent bonds because they do not have sufficient number of valence electrons.
- However, they share their electrons throughout the entire structure of metal

Steps for Drawing a Lewis Structure for Simple Molecules and Ions

1. Sum up the total number of valence electrons for the elements in the molecule. If the molecule is charged, subtract one electron for each positive charge or add one electron for each negative charge.
2. Write the structure for the molecule with a dash between each atom.

Note:

- groups of atoms will usually have the less electronegative atom surrounded by atoms having greater electronegativity.
- Never place a hydrogen atom in the center since it can only form one bond.
- The common valence or number of bonds formed for some common atoms are:

H = 1

O and S = 2

N = 3

C = 4

F, Cl, Br, and I = 1

3. Place electrons around the outer atoms to fill their outer shells.

Note:

- Most atoms require eight electrons ("octet rule") so they will resemble an inert gas.

4. Subtract the number of electrons used so far from the total calculated in step 1 and place these remaining electrons on the central atom or atoms.
5. If the central atom ends up with less than 8 electrons, then it probably forms a multiple bond with an adjacent outer atom.
6. Finally, you should calculate the formal charge on the atoms.

Note:

- the charge on an atom depends on the balance between the negative charges of electrons and the positive charges of protons. Since only the valence electrons can be gained or lost, the following equation can be used to calculate formal charge:

Examples:

- a) HCN
- b) SO_4^{2-}
- c) ClO_4^-
- d) CO_3^{2-}
- e) NCl_3
- f) SO_3^{2-}

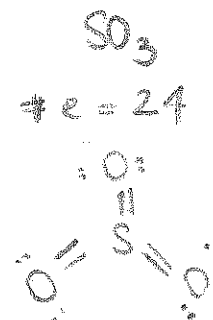
Co-ordinate Covalent Bonds

- In a covalent bond, each atom contributes one electron to the shared pair.
- In some cases, such as H_3O^+ , one atom contributes both of the electrons to the shared pair.
This type of bond is called **co-ordinate covalent bond**.
- It forms when a filled atomic orbital overlaps with an empty atomic orbital.

Exceptions to the Octet Rule (By: 1996 Michael Blaber)

There are three general ways in which the octet rule breaks down:

1. Molecules with an odd number of electrons
2. Molecules in which an atom has less than an octet
3. Molecules in which an atom has more than an octet



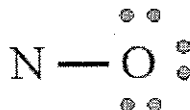
1. Odd number of electrons

Draw the Lewis structure for the molecule nitrous oxide (NO):

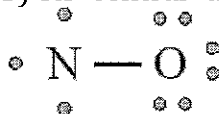
1. Total electrons: $6+5=11$
2. Bonding structure:



3. Octet on "outer" element:



4. Remainder of electrons ($11 - 8 = 3$) on "central" atom:



5. There are currently 5 valence electrons around the nitrogen. A double bond would place 7 around the nitrogen, and a triple bond would place 9 around the nitrogen.

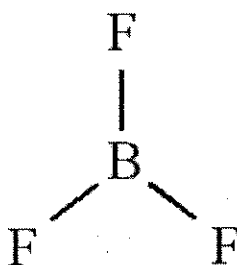
We appear unable to get an octet around each atom

2. Less than an octet (most often encountered with elements of Boron and Beryllium)

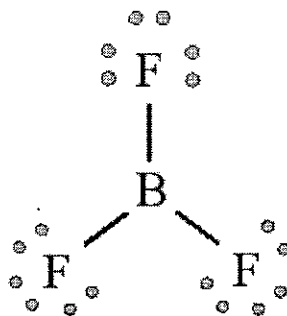
Draw the Lewis structure for boron trifluoride (BF_3):

1. Add electrons (3×7) + 3 = 24

2. Draw connectivities:



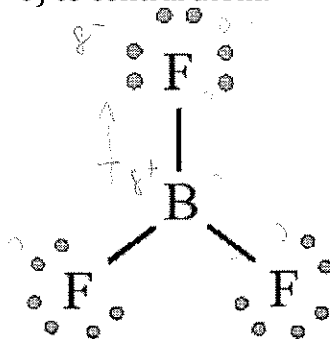
3. Add octets to outer atoms:



4. Add extra electrons ($24 - 24 = 0$) to central atom:

$$\text{B: } 3 - 3 = 0$$

$$\text{F: } 7 - 1 - 6 = 0$$

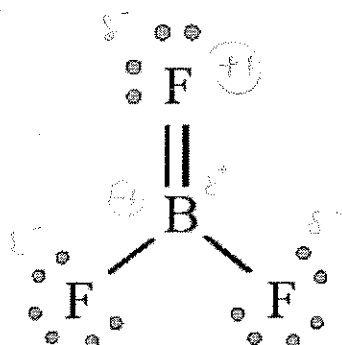


5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

$$F: 7 - 2 - 4 = 1$$

$$B: 3 - 4 = -1$$



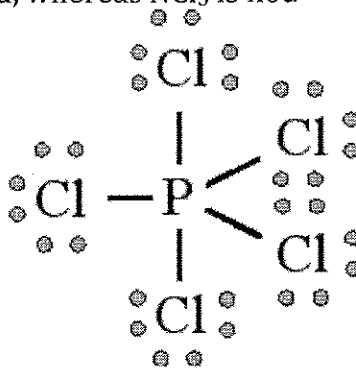
6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3 , with single bonds, and 6 valence electrons around the central boron is the most likely structure***

3. More than an octet (most common example of exceptions to the octet rule)

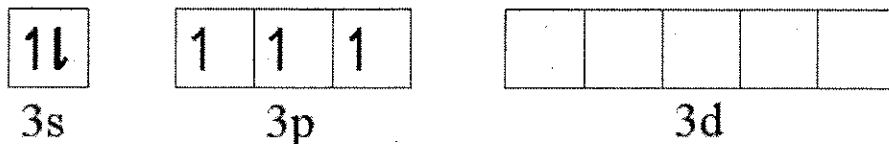
PCl_5 is a legitimate compound, whereas NCl_5 is not.



Expanded valence shells are observed only for elements in period 3 (i.e. $n=3$) and beyond

- The 'octet' rule is based upon available ns and np orbitals for valence electrons (2 electrons in the s orbitals, and 6 in the p orbitals)
- Beginning with the $n=3$ principle quantum number, the d orbitals become available ($l=2$)

The orbital diagram for the valence shell of phosphorous is:



Third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons

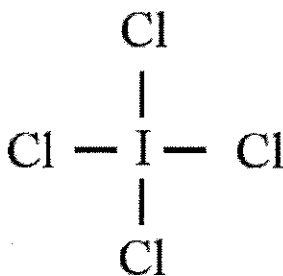
Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

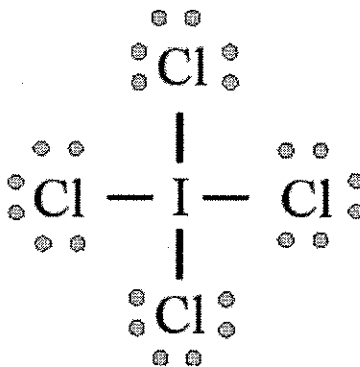
Draw the Lewis structure for ICl_4^-

1. Count up the valence electrons: $7 + (4 \times 7) + 1 = 36$ electrons

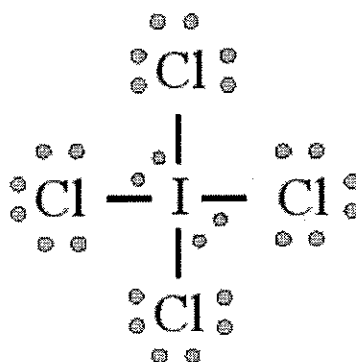
2. Draw the connectivities:



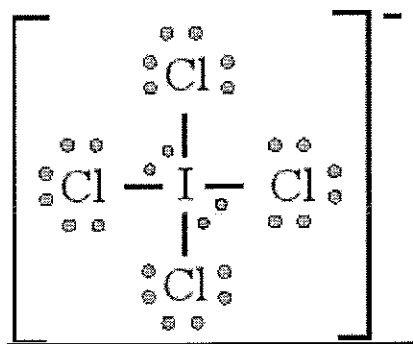
3. Add octet of electrons to outer atoms:



4. Add extra electrons ($36-32=4$) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the $5d$ orbitals)



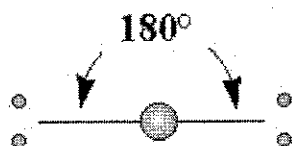
VSEPR Theory

“Valence Shell Electron Pair Repulsion Theory”

- theory based on the electrical repulsion of bonded and un-bonded electron pairs in a molecule or polyatomic ion
- the number of electron pairs are determined by adding the number of bonded atoms plus the number of lone pairs of electrons
 - the 3-D shape can be determined once this number is known by arranging all the pairs of electrons as far apart as possible
- Basic Shapes: (see below)
 1. Linear
 - 2 electron pairs on central atom
 - 180° angle between pairs
 2. Trigonal Planar
 - 3 electron pairs on central atom
 - 120° angles between pairs
 3. Tetrahedral
 - 4 electron pairs on central atom
 - 109.5° angles between pairs
 4. Trigonal Bipyramidal
 - 5 electron pairs on central atom
 5. Octahedral
 - 6 electron pairs on central atom

Number of electron pairs	Arrangement of electron pairs	Electron-pair geometry	Predicted bond angles
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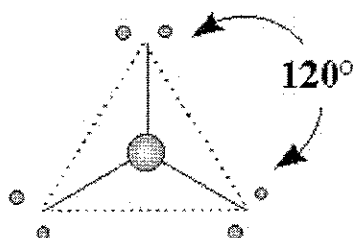
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Linear

180°

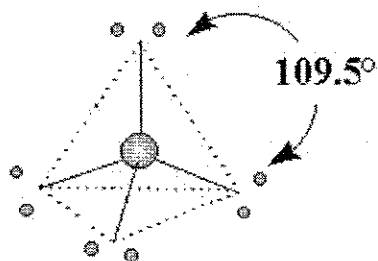
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Trigonal planar

120°

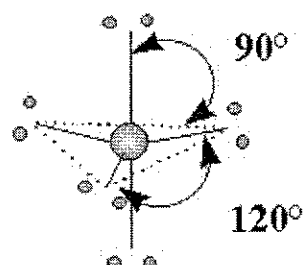
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Tetrahedral

109.5°

5

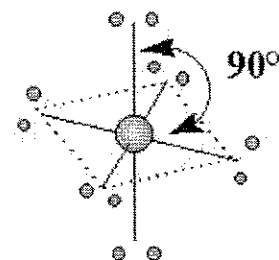


Trigonal bipyramid

90°

120°

6






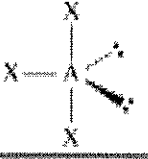
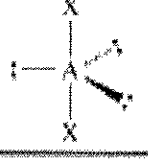


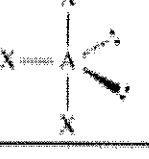
Octahedral

90°

Using VSEPR Theory to Predict Molecular Shape

Note: This is an expansion of the table found on page 245 of the text.

Table 1 Using VSEPR Theory to Predict Molecular Shape

General formula*	Bond pairs	Lone pairs	Total pairs	Molecular shape		Examples
				Geometry**	Shape diagram	
AX_2E	2	1	3	V-shaped (trigonal planar)		$SnCl_2$
AX_5	5	0	5	trigonal bipyramidal (trigonal bipyramidal)		$SbCl_5$
AX_4E	4	1	5	seesaw (trigonal bipyramidal)		SF_4
AX_3E_2	3	2	5	T-shaped (trigonal bipyramidal)		BrF_3
AX_2E_3	2	3	5	linear (trigonal bipyramidal)		XeF_2
AX_6	6	0	6	octahedral (octahedral)		SF_6
AX_5E	5	1	6	square pyramidal (octahedral)		BrF_5
AX_4E_2	4	2	6	square planar (octahedral)		XeF_4

* A is the central atom; X is another atom; E is a lone pair of electrons.

** Electron-pair arrangement in parentheses.

VSEPR THEORY AND SHAPES OF MOLECULES

There is a very simple theory that is remarkably effective in predicting the shapes of molecules formed by the representative elements. The **Valence Shell Electron Pair Repulsion theory (VSEPR Theory)** is based on the idea that valence shell electron pairs stay as far apart as possible from each other to minimize the repulsions between them.

Example	No. Bonding Electron Pairs on Central Atom	No. Lone Pairs of Electrons on Central Atom	VSEPR Shape and Formula	Model, Example and Bond Angles
BeCl_2				
BCl_3				
CN^-				
CH_2Cl_2				
HCHO				
CH_4				
NH_3				
H_2O				

Other VSEPR shapes to know:

Example	No. Bonding Electron Pairs on Central Atom	No. Lone Pairs of Electrons on Central Atom	VSEPR Shape and Formula	Model, Example and Bond Angles
PCl_5				
SF_4				
ClF_3				
SF_6				
BrF_5				
XeF_4				
I_3^{-1}				
HCOO^{-1}				
SO_3^{-2}				
TeF_2				

Polar Molecules

Table 1 Empirical Rules for Polar and Nonpolar Molecules

	Type	Description of molecule	Examples
Polar	AB	diatomic with different atoms	HCl _(g) , CO _(g)
	N _x A _y	containing nitrogen and other atoms	NH _{3(g)} , NF _{3(g)}
	O _x A _y	containing oxygen and other atoms	H ₂ O _(l) , OCl _{2(g)}
	C _x A _y B _z	containing carbon and two other kinds of atoms	CHCl _{3(l)} , C ₂ H ₅ OH _(l)
Nonpolar	A _x	all elements	Cl _{2(g)} , N _{2(g)}
	C _x A _y	containing carbon and only one other kind of atom	CO _{2(g)} , CH _{4(g)}

Do practice problems on pg 188

Intermolecular Forces in Liquids and Solids

Intermolecular Forces

- Intermolecular forces are the forces of interaction that may exist between molecules.
- Intermolecular forces are much weaker than covalent bonds: if covalent bonds are assigned a strength of about 100, then intermolecular forces are generally 0.001 to 15
- Intermolecular forces can be classified as: dipole-dipole forces, London forces, hydrogen bonding

Dipole-Dipole Forces

- molecules may be classified as polar or non-polar: a polar molecule occurs when the net result of the bond dipoles (proportional to the difference in electronegativities of the two atoms involved in the bond) in a molecule are NOT zero
- the dipole-dipole force is an attractive intermolecular force resulting from the tendency of polar molecules to align themselves such that the positive end of one molecule is near the negative end of another
 - the strength of the dipole-dipole force is dependent on the polarity of the molecule

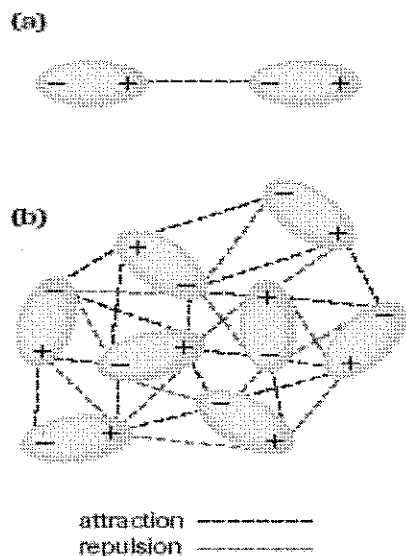


Figure 3

- (a) Oppositely charged ends of polar molecules attract.
- (b) In a liquid, polar molecules can move and rotate to maximize attractions and minimize repulsions. The net effect is a simultaneous attraction of dipoles.

London (Dispersion) Forces

- Fritz London (1930) accounted for the weak attraction between any two molecules (specifically non-polar molecules) by recognizing that electrons orbiting the nucleus of an atom may be on any one side at any point in time
 - as a result there may be a small, instantaneous dipole, with one side having a partial negative charge and the other side having a partial positive charge
 - if another atom is present nearby, the partial negative charge of the first atom will repel the electrons of the second atom creating a partial positive charge of the second atom; the partial negative charge and the partial positive charge of each atom will result in an attractive force between the two atoms
 - this weak attraction occurs instantaneously because the electrons are in constant motion; nonetheless the motion of the electrons in one atom will influence the motion of the electrons of the other atom
- London forces (or dispersion forces) are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about the nuclei
- London forces increase as the molecular weight increases due to:
 - the increased number of electrons in motion
 - the increased size of the molecule, which permits electrons to move further from the nucleus – more polarizable

London force the simultaneous attraction of an electron by nuclei within a molecule and by nuclei in adjacent molecules

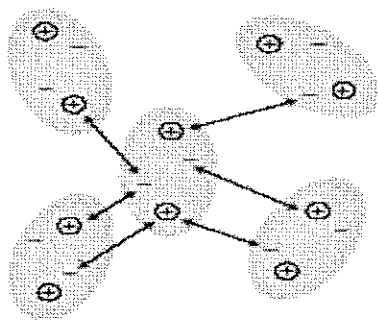
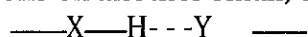


Figure 4
London force is an intermolecular attraction between all molecules. In this figure, only the attractions are shown.

Hydrogen Bonding

- comparison of fluoromethane (CH_3F) and methanol (CH_3OH) will show that their boiling points are significantly differently
 - fluoromethane: -78°C (gas under normal conditions)
 - methanol: 65°C (liquid under normal conditions)
 - both molecules have the same molecular weight and polarity (dipole)
 - suggests that another intermolecular force is at work
 - chemical structure shows that fluoromethane has a C-F bond and methanol has a C-OH bond (similar to water H-OH) – the $-\text{OH}$ group creates additional attractive forces between molecules

- Hydrogen Bonding is a strong attractive force that exists between a hydrogen atom covalently bonded to a very electronegative atom, X, and a lone pair of electrons on another small, electronegative atom, Y



- generally X and Y are the atoms F, O or N
- compare boiling points of hydrides with Group 16 (VIA) elements: H_2O (100°C), H_2S (-60°C), H_2Se (-40°C), H_2Te (0°C)
 - if London forces were the intermolecular forces present one would expect the boiling points to increase from H_2O to H_2Te , based on molecular weight – obviously not the only factor as H_2O has a much higher boiling point
 - consistent with the view that hydrogen bonding exists in H_2O , but is virtually non-existent in the others
 - observe hydrogen bonding in H_2O – relates to partial charges on O and H

hydrogen bonding the attraction of hydrogen atoms bonded to N, O, or F atoms to a lone pair of electrons of N, O, or F atoms in adjacent molecules

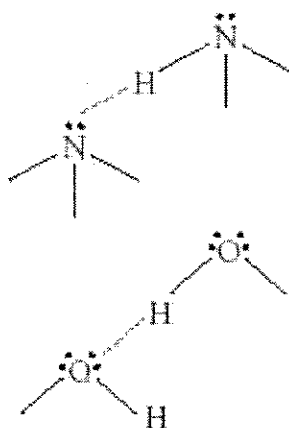


Figure 5

A hydrogen bond (---) occurs when a hydrogen atom bonded to a strongly electronegative atom is attracted to a lone pair of electrons in an adjacent molecule.

- can also see the same pattern when looking at other hydrides of:
 - group 17: HF , HCl , HBr , HI
 - group 15: NH_3 , PH_3 , AsH_3 , SbH_3
 - however, pattern is not evident with group 14 hydrides: CH_4 , SiH_4 , GeH_4 , SnH_4

