

# Bonding

History: In 55 BC, the Roman poet and philosopher Lucretius stated that a force of some kind holds atoms together. He wrote that certain atoms when they collide, “do not recoil far, being driven into a closer union and held there by the entanglement of their own interlocking shapes.” This was an early attempt to define the chemical bond.

Historically, the most difficult problem was in understanding the nature of the force of attraction between atoms in chemical compounds. To solve this problem, it was necessary to discover how electrons are arranged in atoms of different elements.

It is now known that chemical bonds tend to form and chemical reactions tend to take place so that substances are more stable than the original substances.

Chemical bonding between atoms involves the interaction of the electrons in the valence shells of the atoms.

There are **three fundamental types of chemical bond**:

1. ionic
2. covalent
3. metallic,

although there are examples of bonds intermediate between these.

The bond type depends on the attraction for electrons of the atoms involved, i.e. their electronegativity. If the elements have *very different electronegativities* then ionic bonding results.

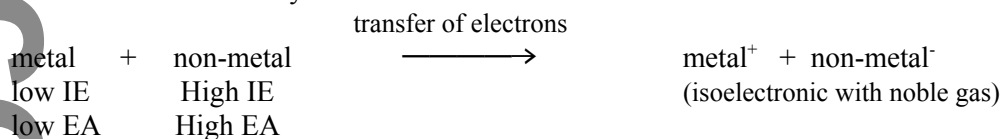
If both of the elements have quite *high electronegativities* then the bonding will be covalent, whereas if they both have *low electronegativities* they form a metallic bond.

*Each type of bonding gives rise to distinctive physical properties for the substances formed.*

## IONIC BONDS

How do these work?

Metals have large atomic radii, low ionisation energies, therefore give up their valence electrons, non-metals with their small atomic radii and high electron affinities gain electrons easily, thus combine with metals readily.



An ion is a charged sphere surrounded by a uniform electric field and therefore attracts oppositely charged spheres in all directions – no particular orientation is favoured, thus ionic bonding is considered **non-directional**, i.e. the forces of attraction are non-directional.

Ions, ∴ tend to cling together in large clusters known as **ionic crystal lattices (ionic giant structures, ionic crystals)**.

Ionic lattices are made up of a regular array of positively and negatively charged ions, held together by electrostatic attraction.

The lattice extends in **three dimensions**. The particular arrangement of ions depends on the relative charges and sizes of the ions.

- The formation of an ionic compound can be considered as the sum of a number of individual processes:
1. converting the elements into gaseous atoms (atomisation, sublimation, bond-dissociation energy)
  2. losing and gaining electrons to form the cations and anions, ( ionisation energy, electron affinity)
  3. finally the coming together of these ions to form a solid compound (enthalpy of formation, lattice energy)

Let us try this for the formation of sodium chloride: NaCl

### See Notes on The Born – Haber Cycle: Thermodynamics

**Lattice Energy:** is the standard enthalpy change when one mole of an ionic substance is formed from its gaseous ions.

The magnitude of the lattice energy depends upon the nature of the ions involved:

1. the charge on the ions: the greater the charge, the greater the electrostatic attraction and hence the lattice energy
2. the size of the ions: the larger the ions, then the charge to surface area density is lower, greater the separation of the charges and the lower the lattice energy.

Example: Which compound in each pair has the higher lattice energy, justify your answer.

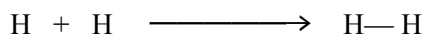
- a. LiCl, NaCl                      b. NaF, NaI                      c. MgO, BaO

## COVALENT BONDING

How do these work?

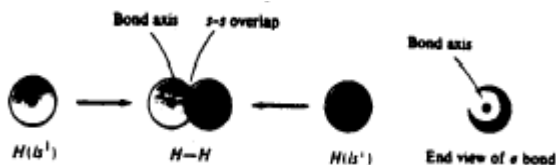
Covalent bonding occurs between atoms that have quite *high electronegativities*, i.e. between two non-metals.

Example: The simplest example of bond formation by atomic orbital overlap is given by the H<sub>2</sub> molecule.



The single electron associated with each hydrogen atom occupies a spherical 1s orbital.

Overlap of the two 1s orbitals allows pairing of the electron spins and the formation of a single covalent bond.



In covalent bonding the two atoms involved share some of their valence electrons.

The attraction of the two nuclei for these shared electrons results in the atoms being bonded together.

The electrons in the bond spend enough time in the space between the two atoms to provide the “glue” that holds the atoms together.

Each nucleus is attracted toward the region of high electron density between them.

The bonded atoms come together for their electron clouds to overlap.

Only one pair of electrons with their spins paired can be shared by two overlapping orbitals.

The region of high electron density represented by the overlap indicates the covalent bond.

The possibility for bond formation exists when two atoms can approach each other in such a way that occupied orbitals with similar energies are able to come into contact or overlap.

The greater the amount of overlap, the stronger the bond, lower the energy of the atoms (more stable the bonds).

**See: Potential Energy Curve for the formation of H<sub>2</sub>**

### The Octet Rule

When forming covalent bonds, the atoms involved, other than hydrogen, tend to form bonds until they are surrounded by eight valence electrons. Therefore: # bonds = 8 — # valence electrons

Examples:

Carbon:

Oxygen:

Nitrogen:

Two covalent bonds between atoms constitutes a double bond, e.g. O=O

Three covalent bonds between atoms constitutes a triple bond, e.g. N<sub>2</sub>

### **Relationship between bond length, bond strength and type of bond:**

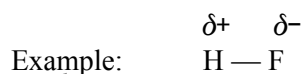
	C—C,	C=C,	C≡C
Bond Length (pm)	154	134	121
Bond Strength (kJ mol <sup>-1</sup> )	346	598	837

As the number of bonds increases bond length \_\_\_\_\_, but bond strength \_\_\_\_\_.

## Polar Covalent Bonds

When two atoms bonded together covalently are the same element, the sharing of those electrons is equal and the bond is said to be a pure covalent bond.

Compounds made of different elements, with different electronegativities will form a polar bond. The electrons will be attracted to the atom with the higher electronegativity, more of the time.



## Coordinate Covalent Bond (Dative Bonds)

Up until now we have always assumed that each element found in a covalent bond was responsible for providing one electron each to the bond.

In a coordinate covalent bond, both electrons are contributed by one atom, e.g.



A coordinate bond differs from a covalent bond in only one respect. What is this?

A coordinate bond is formed between a Lewis acid and a Lewis Base:

Lewis Acid:

Lewis Base:

## Resonance Structures

Single bonds are longer than double bonds. Double bonds are longer than triple.  
(Look up the bond lengths in your Data Book)

Consider the Lewis structure for  $\text{SO}_3$ :

All of the above structures are equivalent, each has a double bond and two single bonds.

So you would expect that if the bond lengths were measured there would be some differences, right !!!

Well, that isn't the case.

The bond lengths are all the same !!!

It is theorized that one pair of electrons is spread over all three bonds. These are called **delocalized** electrons.

### **Key terms:**

Resonance,

Resonance Hybrid,

Delocalisation

Draw the Lewis structures for:  $\text{CO}_3^{-2}$

$\text{HCOO}^{-1}$

### Covalent compounds with fewer than eight outer shell electrons per atom

When the elements with fewer than four outer-shell electrons per atom form compounds they usually lose those electrons to form ions.

However, for small atoms, the relevant ionization energies may be so high that covalent bonding occurs instead.

Since there are fewer than four electrons available for sharing, there will be fewer than eight outer – shell electrons per atom in the resulting compound.

Look at the ionic radii of elements with fewer than four electrons in their outer shells and select the three most likely to form covalent compounds. Explain your choice.

$\text{Be}^{+2}$ ,  $\text{B}^{+3}$ , and  $\text{Al}^{+3}$  have the smallest radii.

This implies that ionisation energies are high, therefore these ions are least likely to be formed.:

Ion	I. $E_1$ (kJ mol <sup>-1</sup> )	ionic radii (10 <sup>-12</sup> m)
$\text{Be}^{+2}$	900	30
$\text{B}^{+3}$	799	168
$\text{Al}^{+3}$	577	45

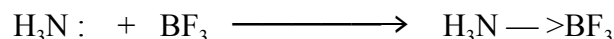
Draw Lewis structures for the following:



How many outer-shell electrons are there around the central atom?

The above molecules exist in certain conditions, but in each case there is a tendency for the ‘stable octet’ to be reached by means of **coordinate bonding**.

Example: The molecule formed by the combination between  $\text{NH}_3$  and  $\text{BF}_3$



For the second period elements,  $\text{Li} \longrightarrow \text{F}$ , which have only s and p orbitals available, 8 is the maximum number of valence electrons that can be accommodated.

### Covalent compounds with more than eight outer-shell electrons per atom

If the noble gas rule or the octet rule always applied, no atom could have more than eight electrons in its outer shell.

As a result, no atom could have more than four single covalent bonds (or the equivalent) associated with it.

The octet rule always applies for elements in the first two periods of the Periodic Table (H  $\longrightarrow$  Ne), but many other elements show a covalency greater than four in some of their compounds.

Examples:



Outermost shells of twelve electrons are quite common.

**Only elements in the third and subsequent rows can do this because they make use of the unused d-orbitals.**

**Elements in Period 2 can never exceed an octet, because their valence shell ( $n = 2$ ) can have  $2n^2 = 8$  maximum of electrons .**

*The heavier noble gases do form a few compounds. Why?*

Neil Bartlett at the University of BC prepared the first Noble gas compounds.

### Paramagnetism

Compounds with unpaired electrons, example NO, exist.

In these compounds one or more electrons remain unpaired, the total number of valence electrons is an odd number.

They are called paramagnetic because the unpaired electron(s) is/are affected by a magnetic field.

Example:

$\text{ClO}_2$ , 19 valence electrons, unstable and explosive, red-yellow gas, m.p =  $-59^\circ\text{C}$ , b.p =  $9.9^\circ\text{C}$

## Lewis Structures: Covalent Bonding

Lewis Structures are used to show which atoms are bonded together in a molecule.

A single bond between atoms occurs when one pair of electrons (i.e. two electrons) are shared between 2 atoms. A double bond results when two electron pairs are shared and the sharing of three electron pairs is a triple bond.

### STEPS FOR LEWIS STRUCTURE CONSTRUCTION

STEP 1: Decide which atoms are bonded together and arrange the atoms on your page to reflect your decision, (see the “skeletal structures, p.225). It helps to first determine a “central atom”, an atom to which many of the other atoms are bonded. Usually, the central atom is the atom which requires the most bonds to complete its valence octet. Another way to determine the central atom is usually the least electronegative (i.e. Si in  $\text{SiF}_4$  or S in  $\text{SOCl}_2$ ) Caution - this does not always work, especially where hydrogen is involved. Hydrogen is never the central atom.

STEP 2: Count all the valence electrons.

Example:  $\text{BF}_3$ : TOTAL valence electrons = 24 e

$\text{B} \rightarrow 1 \text{ atom} \times 3 \text{ valence electrons} = 3 \text{ e} + \text{F} \rightarrow 3 \text{ atoms} \times 7 \text{ valence electrons} = 21 \text{ e}$

NOTE: The charge on an ion indicates whether it contains extra electrons (negative ions) or has lost electrons (positive ions). Be sure to take these gains and losses into account where necessary.

Example:  $\text{SO}_4^{2-}$  -add two electrons to the total number of valence electrons contributed by one atom of S and four atoms of O

$\text{NH}_4^{1+}$  -subtract one electron from the total number of valence electrons contributed by one atom of N and 4 atoms of H

STEP 3: Place 2 electrons (i.e. one pair of electrons) in each bond, i.e. a bonding pair for each bond.

STEP 4: Complete the octets of the atoms attached to the central atom by adding electrons in pairs.

STEP 5: Place any remaining electrons on the central atom.

STEP 6: If the central atom does not have an octet, form double bonds. If necessary, form triple bonds.

### NOTE: There are EXCEPTIONS to the Octet Rule

1. The valence shell for H is completed by 2 electrons (1 electron pair).
2. The valence shell for Li and all members of its family is completed by 2 electrons (1 electron pair).
3. The valence shell for Be is completed by 4 electrons (2 bonding pairs). NOTE: Although Be is an alkaline earth metal and therefore expected to form ionic compounds with non-metals, its ionization energy is too high for this to occur. Instead, it forms covalent bonds with a high degree of ionic character.

4. The valence shell for B is completed by 6 electrons (3 bonding pairs).  
NOTE: Although the other members of its family will form ionic compounds with most non-metals, B doesn't for the same reason cited above for Be. It, too, will form covalent bonds with a high degree of ionic character.
5. Valence electrons of elements of the third and subsequent rows of the Periodic Table may absorb enough energy during bonding so that some or all are excited into their own **unfilled d-orbital** (one electron per orbital). This means that many more bonds than expected may form, (e.g. P with 5 valence electrons may form up to 5 bonds and S with 6 valence electrons may form up to 6 bonds).
6. Some atoms, ions and molecules have orbitals containing a single unpaired electron. These are called **paramagnetic** because the unpaired electron(s) is/are affected by a magnetic field. Paramagnetic substances have an ODD number of valence electrons so no matter how hard you try, your Lewis structure will always show an unpaired electron. e.g. NO and NO<sub>2</sub>

### Assignment

1. Complete the chart on Lewis Structures.
2. Draw the Lewis electron dot structure for:  
(a) CH<sub>4</sub> (b) CH<sub>2</sub>Cl<sub>2</sub> (c) NH<sub>3</sub> (d) H<sub>2</sub>O (e) PCl<sub>3</sub> (f) H<sub>2</sub>S (g) PO<sub>4</sub><sup>-3</sup> (h) BrO<sub>3</sub><sup>-1</sup> (i) NO<sup>+1</sup>  
(j) HCN (k) CH<sub>2</sub>O (l) PH<sub>2</sub><sup>-1</sup> (m) PH<sub>4</sub><sup>+1</sup>
3. Draw the Lewis electron dot structure for:  
(a) SO<sub>3</sub> (b) O<sub>3</sub> (c) NO<sub>3</sub><sup>-1</sup> (d) NO<sub>2</sub><sup>-1</sup> (e) CO<sub>3</sub><sup>-2</sup> (f) HCOO<sup>-1</sup>



## Shapes of Molecules and Ions: Valence Shell Electron Pair Repulsion Theory (VSEPR)

Molecular geometry has become an important area of study. For instance, the effectiveness of many drugs can be attributed to their geometry being just right so they can either aid or hinder some biochemical process. Many drugs today are first being designed theoretically on a computer. A sound knowledge of the geometry of molecules is necessary. Once a drug has been designed in theory, it is then up to the bench chemist to design a synthesis in as few steps as possible. Some drugs are found accidentally through empirical evidence. Finding the structure of these molecules is also necessary in order to learn what kind of action it may have on the target molecules.

The key to understanding molecular geometry is knowing what arrangement atoms or groups of atoms will take around the central atom(s) in a molecule or an ion.

A method which is surprisingly accurate called **Valence Shell Electron Pair Repulsion Theory or VSEPR** for short.

The molecular shapes are named according to the geometric shapes of the solid figures defined by the bonds between the central atom and the atoms attached to it.

The basic premise of the method is that electron pairs in the valence shell of a polyvalent ion (an atom capable of forming more than one covalent bond) are always arranged in a way so as to minimize the repulsions between them. This arrangement applies to both bonding pairs (shared) and non-bonded pairs (lone pairs) of electrons.

### Main concepts of VSEPR:

1. The geometric shape of a molecule can be predicted by focussing attention on the structure's central atom(s) and the mutually repulsive valence shell electron pairs surrounding it. This approach is known as the valence shell electron pair repulsion (**VSEPR**) approach.
2. Two kinds of valence electron pairs may populate the central atom(s) of a molecule:  
-bonding pairs and non-bonding pairs (lone pairs). Repulsions between adjacent pairs of electrons vary in strength depending upon whether they are bond pair-bond pair (BP-BP), bond pair-lone pair (BP-LP), or lone pair-lone pair (LP-LP). The repulsion order is considered to be:



- this concept helps explain the spatial distribution of electron pairs; lone pairs spontaneously arrange themselves to be as far apart as possible, bond pair-lone pairs are next, and bond pair-bond pairs are found to be the closest.
3. In the VSEPR approach, electron pairs on the central atom(s) are viewed as assuming positions around that atom that minimize electron pair-electron pair repulsions. The resulting electron pair geometry about the central atom determines the placement of the atoms bonded to the central atom(s). The resulting arrangement of bonded atoms determines the molecular geometry.
  4. Molecular geometries may be classified according to the number of lone pairs and bonding pairs of electrons surrounding the central atom. e.g.:  
two bonding pairs = linear; three bonding pairs = trigonal planar; two bonding pairs and one lone pair = angular (bent); and so forth.
  5. Molecules containing one or more polar covalent bonds may either be polar or non-polar, based on the extent of the bond polarities and molecular geometry.
  6. The shape and polarity (or lack of polarity) of a given molecule helps determine the general properties of the substance composed of these molecules.

## Assignment

1. Using all the Lewis structures that were drawn, predict the shape of each of the structure.
2. The molecules  $\text{SiF}_4$ ,  $\text{SF}_4$ , and  $\text{XeF}_4$  all have molecular formulas of the type  $\text{XF}_4$ , but the molecules have different molecular geometries. Predict the shape of each molecule and explain the origin of the differing shapes.
3. The three species  $\text{NO}_2^+$ ,  $\text{NO}_2$ , and  $\text{NO}_2^-$  all have a central nitrogen atom. The O-N-O bond angles in the three species are  $180^\circ$ ,  $134^\circ$ , and  $115^\circ$ , respectively. Explain this variation in bond angles.
4. The H—P—H bond angle in  $\text{PH}_3$  is  $93^\circ$ ; in  $\text{PH}_4^+$  it is  $109.5^\circ$ . Account for this difference.

## Predicting the Polarity of Molecules

Use the molecular structures that were derived from the VSEPR model along with electronegativities to predict whether or not molecules are polar.

Recall that polar bonds involve an unequal sharing of electrons, the presence of which, in certain compounds can make the molecule polar.

### In order to determine if a molecule is polar:

1. Determine if the molecule has polar bonds.
2. Determine the shape of the molecule.

A molecule that contains polar bonds will not necessarily be a polar molecule.

If the shape of a molecule is such that the polar bonds are **symmetrically** arranged around the central atom, then their **effects may cancel, i.e. their dipoles will cancel** and there will be **no charge separation**, thus the molecule as a whole will be non-polar.

### **Symmetrical Molecules have the following basic geometries:**

Linear, trigonal planar, tetrahedral, trigonal pyramidal, octahedral.

If a molecule is one of these shapes- **with identical atoms attached to a central atom**, the molecule is said to be **symmetrical and non-polar**.

### **For a molecule to be polar:**

It must contain polar bonds, **and** its shape must be such that the **dipoles do not cancel** out.

The **dipole moment** is a measure of the polarity of a molecule.

(Dipole moment is measured in units of Debye)

Non-polar molecules have a zero dipole moment.

The more polar a molecule, the greater the dipole moment.

## Assignment

1. Using all the Lewis structures that were drawn, predict the shape of each of the structure, and further predict whether each molecule is polar or non-polar.
2. The  $\text{PF}_3$  molecule has a dipole moment of 1.03 D, but  $\text{BF}_3$  has dipole moment of zero. How can you explain the difference.
3. Despite the larger electronegativity difference between the bonded atoms,  $\text{BeCl}_{2(g)}$  has no dipole moment whereas  $\text{SCl}_{2(g)}$  does possess one. Account for this difference in polarity,