
Bonding & Molecular Shape

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The Nature of Bonding

Types

1. Ionic
2. Covalent
3. Metallic
4. Coordinate covalent

Driving force

For simple ionic and covalent bonding the octet rule provides a simple model. Having 8 electrons in the outer s and p sublevels results in a lower energy situation.

Having 8 electrons can be satisfied by sharing or transfer.

Is It Ionic or Covalent?

Usually a combination of both

Ionic Bonding – the transfer of electrons

- In ionic bonding there is more transfer than sharing. The usual criteria is an electronegativity difference of >1.67 (Some use 2.0).
- Bonds between the alkali and alkaline earth metals with chalcogens and halogens are very ionic. In general metals and nonmetals give compounds with appreciable ionic character.
- Ionic bonds give ionic compounds. Ionic compounds are also formed with polyatomic ions.
- Ionic solids consist of repeating positive and negative ions with strong interparticle forces.

Properties

1. High MP
2. Solubility in water
3. Well-defined crystals
4. Molten form conducts electricity as well as water solution

Prediction of MP and solubility

1. Ions are held together by electrostatic forces governed by Coulomb's Law. This law predicts that the force between two charged particles is directly proportional to the charge of the ions and inversely proportional to the square of the distance between them.

2. The larger the force between ions the higher the MP
3. The larger the force between ions the lower the solubility.

Thus the MP of $\text{NaCl} > \text{CsCl}$

and the solubility of $\text{CsCl} > \text{NaCl}$

Covalent Bonding – the sharing of electrons

- In covalent bonding there is more sharing than transfer. The usual criteria is an electronegativity difference of <1.67 (Some use 2.0).
- Bonds between nonmetals are very covalent. There can be appreciable covalent character with metals and nonmetals close to each other on the periodic table.
- Most organic (carbon containing compounds) are covalent so in the big picture most compounds are covalent.
- Most covalent solids and liquids consist of fairly neutral molecules. Thus the interparticle forces are much weaker than ionic compounds. Some macromolecules have covalent bonding between each particle.

Properties

1. Most have low MP but macromolecules have high MP
2. Usually have poor water solubility
3. Molten form does not conduct electricity, but solutions can give limited conduction

How to visualize bonding – Lewis structures - electron dot diagrams

These diagrams give a convenient way to represent bonding – especially simple covalent bonding between nonmetals (including hydrogen). The outermost (or valence) “s” and “p” electrons participate in simple covalent bonding and are shown as either shared pairs or unshared pairs (also called lone pairs). Shared pairs can be shown as a pair of dots between atoms or as a lines between atoms. Lone pairs are usually indicated by a pair of dots.

These Lewis structures (e dot diagrams) allow us to predict the geometry for a molecule. Since geometry dictates how the molecules will arrange themselves in matter, the geometry dictates physical and chemical properties. Once we know the geometry we are on our way to understanding the properties of covalent molecules.

Useful rules for writing Lewis structures

1. To help determine atom placement in the molecule remember that H is always a terminal atom and has 1 bond, F is always terminal as well.
The element with the lowest electronegativity is the central atom. (Review - Electronegativity is the attraction for additional electrons in a bonding situation and increases from left to right and decreases from top to bottom on the periodic table.)
2. Use all "s" and "p" valence electrons in the representation. Add electrons if a negative ion; subtract electrons if a positive ion. These are called the number of available electrons (AE).
AE = sum of "s" and "p" electrons in all atoms minus the electrical charge

3. Each nonmetal should have at least 8 electrons (4 pairs - the octet rule) around it. The number necessary to complete the octet rule using single pairs between atoms and no rings is called the number of needed electrons (NE).

$$NE = 2(\# \text{ of H atoms}) + 8(\# \text{ of non H atoms}) - 2(\# \text{atoms} - 1)$$

Thus if $AE = NE$ then the structure is drawn using rule one for atom arrangement and single bonds and lone pairs around the atoms. Draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms bonded to the central atom. Then complete the octet of the central atom using lone pairs.

Example: H_2O_2 , CH_4 , PCl_3

4. If the number of available electrons is less than the number of needed electrons ($AE < NE$) then there are three possibilities for the structure:
- multiple bonding (2 or 3 pairs shared between 2 atoms)
[Example: C_2H_2 , O_2]
 - rings [Example: P_4 , C_3H_6]
 - does not follow the octet rule and is electron deficient
[Example: BF_3]

If $AE < NE$ then apply the rule for drawing the structure as before. At the end you will need to either: (1) move electron pairs to have multiple pair bonding with the central atom, (2) move atoms into rings, or (3) declare that the compound does not follow the octet rule. Multiple bonding is the usual case.

5. If the number of available electrons exceeds the number of needed electrons ($AE > NE$) then the octet rule is exceeded for the central atom, meaning that more than four pairs of electrons can be put around the central atom. This occurs most often with nonmetals from the 3rd, 4th, and 5th period which have empty "d" sublevel spaces that can be used. Examples of elements which can have more than four pairs (8 electrons) when used as the central atom in a molecule include P, S, Se, Br, Kr, Xe.

Example: XeF_4 , PCl_5

If $AE > NE$ then draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms bonded to the central atom. Then complete the central atom using lone pairs. You will have extra electrons that will make the number of pairs of electrons on the central atom greater than 4, usually 5 or 6.

Bond order and bond length

Bond order - the # of shared pairs between 2 atoms

Bond length - the internuclear distance between 2 atoms in a bond

Trends:

- (1) The smaller the size of the atom the shorter the bond length
- (2) The larger the bond order the shorter the bond length

Resonance Structures

Resonance structures are 2 or more Lewis structures which have the same atom arrangement but different electron pair positions resulting in a different number of bond pairs between specific atoms.

[Note – another term you may have seen “isomer” refers to structures with different atom arrangements. Carbon compounds can exhibit many isomers.]

Examples: O_3 , C_6H_6 , $(NO_3)^{-1}$

Resonance structures result in extra stability for the molecule. The molecule does not “resonate” between structures but is an average of them all.

Formal charge

We have seen that it is possible to assign oxidation numbers in compounds that are covalently bonded or in ions that are covalently bonded. These numbers, although useful in balancing redox equations, do not give a true picture of the charge distribution in the molecule. A better indicator is the formal charge.

$$(\# \text{ of s and p } e^-) - \# \text{ of lone pair } e^- - 1/2 \text{ bonding } e^-$$

These formal charges are important in determining the importance of resonance structures.

Two guidelines apply:

- (1) Atoms should have formal charges as small as possible
- (2) A molecule is most stable when any negative charge resides on the most electronegative atom.

Molecular Shape

The simple idea that electron pairs about a central atom repel each other and will get as far away as possible allows us to predict shapes for simple covalently bonded molecules - especially those between nonmetal atoms.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

1. Draw a good Lewis structure
 2. Count the number of shared and unshared pairs around the central atom. This gives the structural pair geometry.
 3. If there are unshared pairs, then see how the structural pair geometry is distorted somewhat to get a different shape.
 4. Double and triple bonds are each counted as 1 pair of shared electrons.
- **The VSEPR dictionary should be understood, learned, committed to memory, and used to solve problems.

Bond Polarity

The polarity of a bond refers to the separation of charge between atoms in a covalent bond and is a term used to refer to a covalent bond's ionic character.

In a totally covalent situation there is no polarity (or ionic character). Bonds between the same type of atoms are 100% covalent; all other bonds have some degree of ionic character which can be quantified by the electronegativity difference between the atoms in the bond.

Why is bond polarity important?

Polar bonds can lead to polar molecules.

Polar Molecules

A polar molecule is a covalently bonded molecule that has a positive and a negative end as a result of the arrangement of polar bonds. The experimental measure of this is called the dipole moment, and a polar molecule is called a dipole.

Polar molecules:

- Have polar bonds
- Have bonds arranged asymmetrically so there is a positive and negative side to the molecule.
Another possibility is to have different bonds (with different polarities) arranged symmetrically.

Many molecules have some polarity; it is usually a question of how much polarity a molecule has which determines many of its properties.

The unusual properties of water come from the polarity of the molecule and the strong interparticle forces that result. For the same size molecule nonpolar molecules have weaker interparticle forces and a different set of properties. Large nonpolar molecules can have strong interparticle forces.

Many carbohydrates, proteins and nuclei acids are polar; fats and oils (lipids) are not.