

## CHEMICAL BONDS

### Chemical Bonds:

- The strong electrostatic forces of attraction holding atoms together in a unit are called chemical bonds (EU 2.C).
- Reflect a balance in the attractive and repulsive forces between electrically charged particles.
- Electronegativity can be used to reason about the type of bonding present between two atoms.

### Lewis Theory of Bonding:

- Electrons play a fundamental role in chemical bonding (especially valence electrons).
- Atoms tend to lose, gain or share electrons in order to attain noble gas configurations (called the **Octet rule** because most noble gases have 8 valence electrons BUT helium only has 2, therefore hydrogen, helium and beryllium will acquire a duet, not an octet).
- **Ionic bonds** - occur between metals and non-metals. Valence electrons are transferred from the metal to the non-metal giving cations and anions which are then electrostatically attracted to each other.
- **Covalent bonds** - involve non-metals. One or more pairs of valence electrons are shared.

All bonds have some ionic character and the difference between ionic and covalent bonds is not distinct but rather a continuum. The difference in electronegativity is not the only factor in determining if a bond is designated ionic or covalent. Generally, bonds between a metal and non-metal are ionic, and between two non-metals are covalent. Examination of the properties of a compound is the best way to determine the type of bonding. (EK 2.C.1.F)

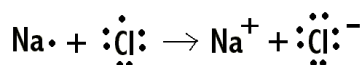
### Lewis Symbols:

- Uses the chemical symbol for the element surrounded by dots to represent the valence electrons.
- Example: Give Lewis symbols for magnesium, silicon, and phosphorus.

### IONIC BONDING:

- An atom gives up electrons to form a cation while the other gains the electrons to form an anion.
- The oppositely charged ions attract each other and form an **ion pair**.
- **Note:** The attractive force is not just limited to one ion - for example; in sodium chloride, each sodium ion strongly attracts six neighboring chloride ions and has a weaker attraction for further chloride ions. Each chloride ion strongly attracts six neighboring sodium ions and weakly attracts further sodium ions. The like-charged ions also repel each other. However, the net force is one of attraction - **ionic bonds**.
- In order to maximize the attractive forces among cations and anions, while minimizing the repulsive forces, ions in crystals are arranged in a systematic, periodic 3-D array.

### Lewis Symbols for Ionic Bonds:



Example: Use Lewis symbols to show the formation of ionic bonds between barium and fluorine.

## Lattice Energy:

- The change in energy that takes place when separated gaseous atoms are packed together to form an ionic solid.
- Lattice energy has a negative sign - energy is released (exothermic).
- Coulomb's Law describes the force of attraction between the cations and anions in an ionic crystal.
  - Because the force is proportional to the charge on each ion, larger charges lead to stronger interactions.
  - Because the force is inversely proportional to the square of the distance between the centers of the ions (nuclei), smaller ions lead to stronger interactions (EK 2.C.2.b)

## COVALENT BONDING:

- Electrons are shared between the nuclei of two atoms to form a molecule or polyatomic ion. Electronegativity differences between the two atoms account for the distribution of the shared electrons and the polarity of the bond (EK.2.C.1)

## Localized Electron Model

- Assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.
- Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms.
- **Bonding pairs** are shared pairs of electrons in a molecule and are found in the space between the atoms..
- **Lone pairs** (non-bonding or unshared pairs) are those pairs of electrons not participating in the bond and are localized on one atom.

**Lewis Structures** - Show the proportions in which atoms combine.

In most cases, the structure shows the bonded atoms obey the octet rule.

- **Bonding pairs** are shared pairs of electrons in a molecule.
- **Lone pairs** (non-bonding or unshared pairs) are those pairs of electrons not participating in the bond.
- **Coordinate covalent bonds** - when one atom provides both electrons of the shared pair.
- **Multiple covalent bonds** - when atoms share more than one pair of electrons.
- **Bond order** - single bond has a bond order of 1
- double bond has a bond order of 2
- triple bond has a bond order of 3
- Note that the Lewis structure is not always the one obtained from experimental evidence; there are limitations to the use of the Lewis structure model, especially where there are an odd number of valence electrons.

## Writing Lewis Structures:

### Guidelines:

1. The central element is the least electronegative element (EXCEPT H). It is usually the element written first.
2. Fluorine and hydrogen will be terminal atoms.
3. Oxygen atoms do not bond to each other except in O<sub>2</sub> and O<sub>3</sub> molecules, peroxides (containing O<sub>2</sub><sup>2-</sup> group) and rarely, superoxides (containing O<sub>2</sub><sup>-</sup> group).

4. In oxyacids (containing H, O and another element) H is usually bonded to O, NOT the central element.
5. Molecules and polyatomic ions usually have the most compact, symmetrical shape possible.

### Method:

1. Find the total number of valence electrons by adding the valence electrons for each atom in the formula. For polyatomic anions, add the charge to the total number of valence electrons. For polyatomic cations, subtract the charge from the total number of valence electrons.
2. Draw a single bond from the central element to each of the elements surrounding it.
3. Subtract the electrons used so far from the total number (remember each bond is two electrons).
4. Place the remaining electrons as pairs around the terminal atoms so that each has an octet (duet for H).
5. Any electrons left over go to the central atom(s).
6. If the central element does not have an octet, then one or two of the single bonds are changed to double bonds or one single bond is converted to a triple bond. If possible, make two double bonds before making one triple bond. The atoms most commonly involved in double bonds are C, N, O, and S. The atoms most often involved in triple bonds are C and N.

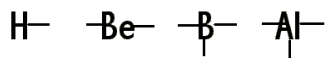
Examples: Write the Lewis structures of nitrogen trifluoride, phosgene ( $\text{COCl}_2$ ), and the chlorate ion ( $\text{ClO}_3^-$ )

### Exceptions to the octet rule:

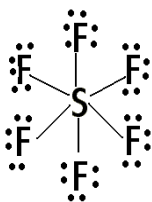
1. **Odd numbers of valence electrons:** molecules with odd numbers of valence electrons cannot satisfy the octet rule for all the atoms. There are few stable molecules with odd numbers of electrons.

**Free Radicals** are fragments of molecules with odd numbers of valence electrons. They are highly reactive and usually exist very briefly as intermediates in chemical reactions. Ex: Hydroxyl  $\bullet\text{OH}$  (g).

2. **Atoms with less than an octet:**



3. **Atoms with more than an octet (expanded valence shells):** Central elements from periods 3 and above can have more than octet due to the availability of low lying d orbitals. These can therefore have up to 18 electrons surrounding them.



Example: Write the Lewis structure for bromine pentafluoride.

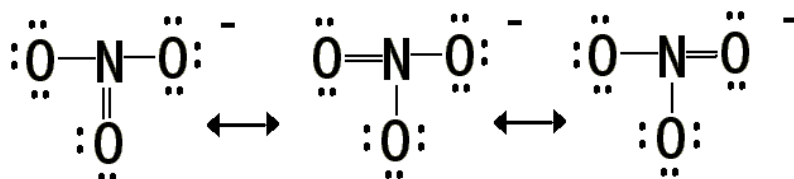
## Formal Charge:

- A bookkeeping system that counts bonding electrons as if they were equally shared between atoms - helps us write Lewis structures correctly.
- **FC = (atom's valence e<sup>-</sup>s in unbonded state) - (atom's valence e<sup>-</sup>s in bonded state).** Unbonded valence electrons are the group number. Bonded Valence electrons - in a bond, half of the shared electrons are assigned to each atom. All lone pair electrons are assigned to that atom.
- The most plausible Lewis structure is that which gives zero formal charge on all atoms.
- Formal charges should be as small as possible.
- Adjacent atoms in a structure should not carry formal charges of the same sign.
- The sum of all formal charges for a molecule should be zero for a neutral molecule and be equal to the charge on the ion for a polyatomic ion.

Example. Write the best Lewis structure for nitrosyl chloride (NOCl).

## Resonance (Delocalized Bonding):

- When there are multiple bonds present in a molecule or ion, one Lewis structure may not account for the physical and chemical properties.
- **Resonance structures:** differ only in the distribution of electrons. The atoms are located in the same place but the nonbonding electrons and multiple bond electrons may change locations.
- **Resonance hybrid:** the actual molecule is a hybrid of the resonance structures. It is represented by drawing the different resonance structures and putting a double-headed arrow between them.



- The more resonance structures (especially equivalent resonance structures) a species has, the more stable it is.
- **Major resonance contributors:** (i) All elements have an octet (other than exceptions previously discussed). (ii) Each element has a low formal charge. (iii) The most electronegative element has the most negative formal charge.
- **Minor resonance contributors:** (i) One of the elements has less than an octet. (ii) The most electronegative element does not have the most negative formal charge. (iii) Elements have high formal charges.
- **Localized electrons:** When resonance is not involved, electrons exist in well-defined regions between two atoms.
- **Delocalized electrons:** When resonance is involved, bonding electrons may spread out over several atoms.

Example: Write Lewis structures for the SO<sub>3</sub> molecule and the nitrate ion.

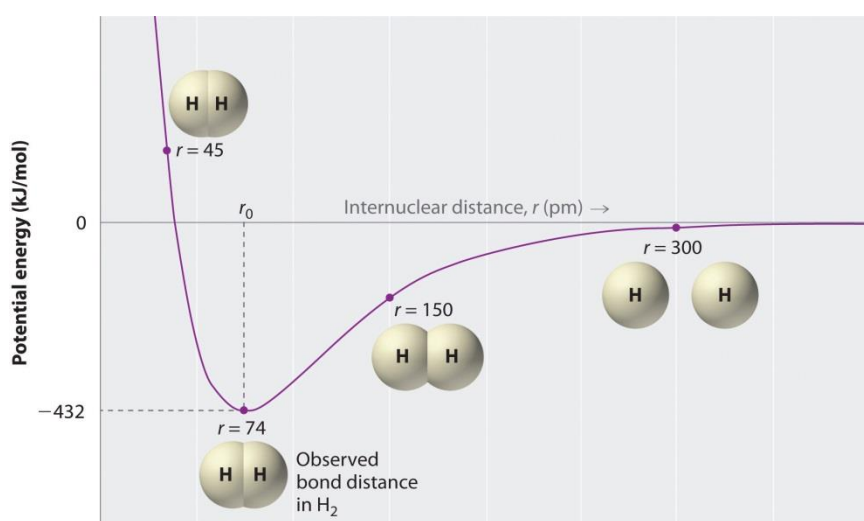
## Bond Length

- The distance between the nuclei of two covalently bonded atoms.

- Depends on the particular atoms and the bond order (does not usually differ no matter what the molecule is).
- In general - the length of the covalent bond joining two atoms is the sum of the covalent radii of the two atoms.
- Polar bonds are generally shorter and stronger than would be expected.
- Double and triple bonds are generally shorter and stronger than single bonds.

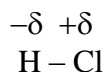
## Polarity of Bonds:

- **Nonpolar bonds** – two or more valence electrons shared between atoms of identical electronegativity constitute a non-polar bond.
- However, bonds between carbon and hydrogen are often considered to be non-polar even though carbon has a slightly higher electronegativity than hydrogen.
- The formation of a non-polar covalent bond can be expressed graphically as a plot of potential energy v's distance for the interaction of two identical atoms. Hydrogen atoms are often used as an example.



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- Energy profile as a function of the distance between the nuclei of two hydrogen atoms. As the atoms approach each other (right side) the energy decrease until the distance reaches 74 pm and then begins to increase again due to repulsions.
- The bond length (74 pm) is the distance between the bonded atoms' nuclei and is the distance of minimal potential energy, where the attractive and repulsive forces are balanced.
- The shape of the graph depends on the relative strengths of attractive and repulsive forces as a function of distance.
- **Polar bonds** – two or more valence electrons shared between atoms of unequal electronegativity.
- The electrons are drawn closer to the atom with the higher EN, causing a partial charge difference between the two atoms in the bond.



- For diatomic molecules such as the one above, the partial negative charge on the more electronegative atom is equal in magnitude to the partial positive charge on the less electronegative atom.
- Greater differences in electronegativity lead to greater partial charges and hence greater bond dipoles.
- The sum of all partial charges in any molecule or ion must equal the overall charge.

## Bond Energy:

- **Bond Dissociation Energy** - The energy absorbed in order to break 1 mole of covalent bonds between atoms in the gaseous state. This is the net energy of the stabilization of the bond compared to the two separated atoms.
- Double bonds have higher dissociation energies than single bonds, and triple are even higher.
- Dissociation energies depend on the environment, therefore **average bond energies** are used.

### Calculations:

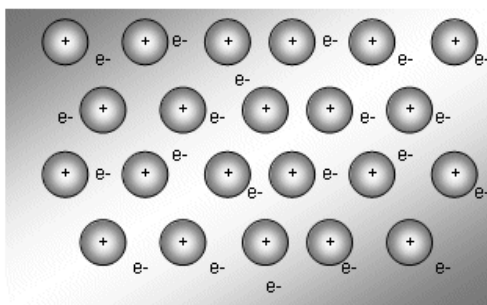
$$\Delta H = \Delta H_{\text{bonds broken}} + \Delta H_{\text{bonds formed}}$$

Example: 1. Use bond energies to determine the enthalpy of formation of gaseous hydrazine ( $\text{N}_2\text{H}_4$ ).

2. Calculate  $\Delta H$  for the reaction  $\text{C}_2\text{H}_6(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g}) + \text{HCl}(\text{g})$

## METALLIC BONDING

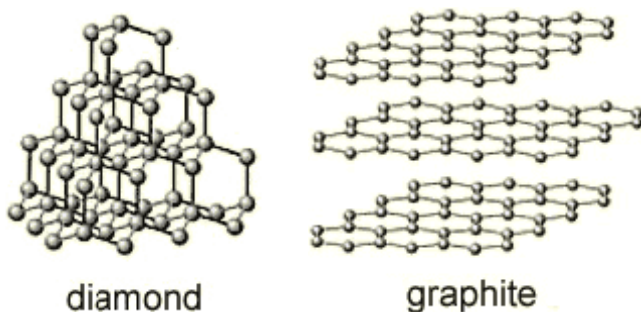
- The properties of metallic solids can be explained by the **electron sea model**. This envisions the metal as being composed of cations (or positive cores) consisting of the nucleus and inner electrons of each atom surrounded by a sea of mobile valence electrons.
- The valence electrons are delocalized and free to move.



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## COVALENT NETWORK BONDING

- Generally form in the carbon group because of their ability to form four covalent bonds.
- Covalent network solids consist of atoms that are covalently bonded together into a two-dimensional or three-dimensional network (a "giant molecule").
- Are only formed from non-metals.
- Can be elemental, such as diamond and graphite, or molecular, such as silicon dioxide and silicon carbide.



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