

Bonding

Types, Lewis Structures, and Molecular Shapes

What I Absolutely Have to Know to Survive the AP Exam

The following might indicate that the question deals with bonding and/or molecular geometry: Electronic or molecular geometry; type of bond; VSEPR; Lewis diagram; hybridization; polar or non-polar; dipole moment; shape of the molecule; bond angle; resonance; bond length/strength; sigma/pi bonds, formal charge

BOND, CHEMICAL BOND...

The strong electrostatic forces of attractions holding atoms together in a unit are called chemical bonds.

Covalent bonds, ionic bonds, and metallic bonds are distinct from (and significantly stronger than) typical intermolecular interactions. Do NOT confuse the intra-particle interactions with inter-particle attractive forces

The system is achieving the lowest possible energy state by bonding.

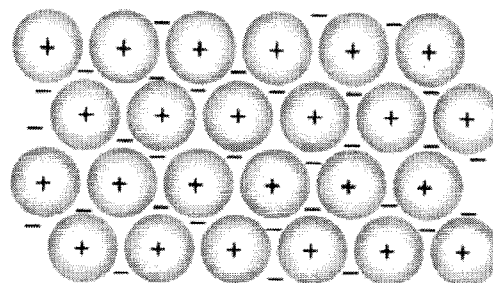
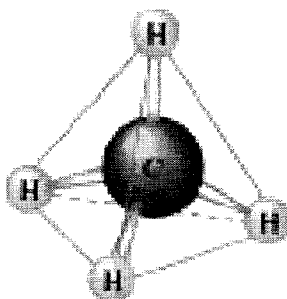
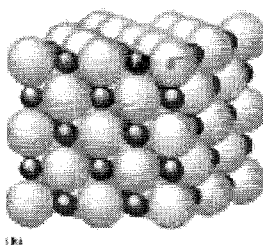
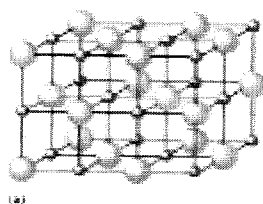
IMPORTANT

Energy is RELEASED when a bond is formed

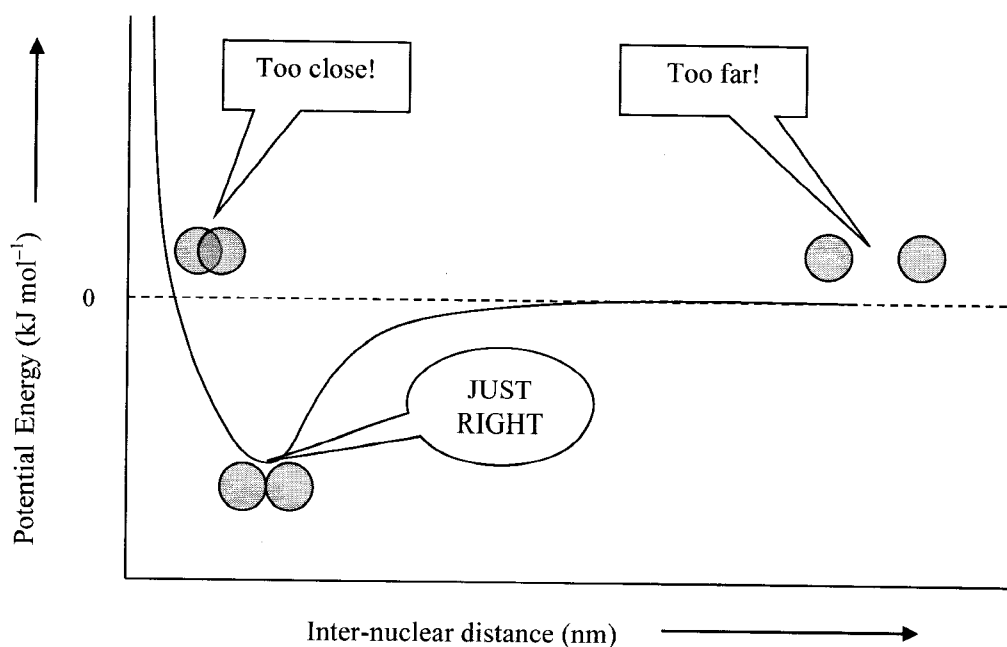
Energy is REQUIRED to break a bond

TYPES OF CHEMICAL BONDS – An Overview

Ionic	Ionic bonding is the phrase used to describe the strong Coulombic interaction between ions in an ionic substance.
Covalent	Covalent chemical bonds can be modeled as the sharing of one or more pairs of valence electrons between two atoms in a molecule. The extent to which this sharing is unequal can be predicted from the relative electronegativities of the atoms involved; the relative electronegativities can generally be understood through application of the shell model and Coulomb's law. The Lewis structure model, combined with valence shell electron pair repulsion (VSEPR), can be used to predict many structural features of covalently bonded molecules and ions.
Metallic	The bonding in metals is characterized by delocalization of valence electrons.



Covalent Bonding – Maximize the Attraction Minimize the Repulsion	
Attractive Forces	Repulsive Forces
Proton–electron attraction	Electron–electron repulsion
	Proton–proton repulsion
When the attractive forces offset the repulsive forces, the energy of the two atoms decreases and a <i>bond</i> is formed. This happens when attraction outweighs repulsion!	
Remember, nature is striving for a LOWER ENERGY STATE	
THINK GOLDBLOCKS	
If the atoms are <i>too close together</i> , the repulsive forces outweigh the attractive forces and the atoms do not reach a lower energy state; therefore they DO NOT form a chemical bond!	
If the atoms are <i>too far apart</i> , the two atoms do not effectively interact; i.e. the attractive forces are not sufficient enough to reach a lower energy state; therefore they DO NOT form a chemical bond!	
If the atoms are <i>just right</i> , the attractive forces offset the repulsive forces and the atoms reach a lower energy state; therefore they form a chemical bond! The distance between the 2 nuclei where the potential energy is at a minimum (attractive and repulsive forces are balanced) represents the <i>bond length</i> .	
<ul style="list-style-type: none"> The <i>bond energy</i> is the energy required for the dissociation of the bond. Typically given in a per mole basis (i.e. kJ mol^{-1}) 	



Lewis Diagrams and Molecular Geometry – *It's All About Localized Electrons and VSEPR* con't

As with any model, there are limitations to the use of the Lewis structure model, particularly in cases with an odd number of valence electrons. Please recognize that Lewis diagrams have limitations but are still great models of covalent bonding.

- Odd-electron compounds – A *few* stable compounds have an odd number of valence electrons; thus do not obey the octet rule. NO, NO₂, and ClO₂ are common examples.

Bond formation is associated with overlap between atomic orbitals.

Chemists commonly use the terms “hybridization” and “hybrid orbital” to describe the arrangement of electrons around a central atom. When there is a bond angle of

- 180°, the central atom is said to be sp hybridized
- 120°, the central atom is sp² hybridized
- 109°, the central atom is sp³ hybridized.
- When an atom has more than four pairs of electrons surrounding the central atom, students are only responsible for the shape of the resulting molecule.

Some atoms bond with more than 4 pairs of electrons on the central atom. Whoa, what do you mean more than four pairs (8 total) electrons on the central atom..?

- Can only happen if the central atom is from the 3rd or higher period
 - Why? *d* orbitals are needed for the expansion – the combination of 1 *s* orbital and 3 *p* orbitals provides the four bonding sites that make up typical 4 bonding pairs when an atom bonds; the additional “*d*” orbitals allow for expansion to either 5 or 6 bonding sites around the central atom.

In multiple bonds, such overlap leads to the formation of both sigma and pi bonds. This is what we are talking about with DOUBLE and TRIPLE bonds

- The overlap is stronger in sigma than pi bonds, which is reflected in sigma bonds having larger bond energy than pi bonds.
- The presence of a pi bond also prevents the rotation of the bond, and leads to structural isomers.
 - In systems, such as benzene, where atomic p-orbitals overlap strongly with more than one other p-orbital, extended pi bonding exists, which is delocalized across more than two nuclei.
 - Such descriptions provide an alternative description to resonance in Lewis structures.
 - A useful example of delocalized pi bonding is molecular solids that conduct electricity.

MULTIPLE BONDS ARE MOST OFTEN FORMED by C,N,O,P and S ATOMS — say “C-NOPS”

- Double bond – two pairs of electrons shared: one σ bond and one π bond
- Triple bond – three pairs of electrons shared: one σ bond and two π bonds

MULTIPLE BONDS

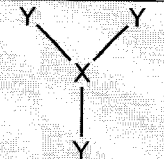

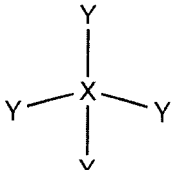
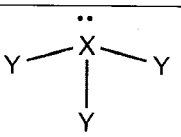
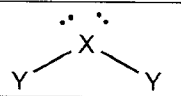
- Increase the electron density between two nuclei
- This decreases the repulsions between the 2 nuclei (+ charges remember!)
- The added electrons enhance the attractions between both nuclei and the increased electron density

The nuclei can move closer together; thus the bond length is shorter for a double than a single, and triple is shortest of all!

Bond Strength	Bond Length
Sigma (σ) bonds are stronger than pi (π) bonds;	Single Bonds are the longest
Pi bonds never exist alone	Double bonds are shorter than single bonds
Combinations of σ and π are stronger than σ alone	Triple bonds are the shortest of all

Molecular Geometry – *Shape it Up!*

- You MUST KNOW the molecular shapes!
- It all revolves around what is on the central atom!
- The charts in the following pages give examples of the shapes, names, hybridizations, and bond angles you must know.

Number of electron domains (bond pairs and lone pairs)	Number of lone pairs	Electronic Geometry	Molecular Geometry	Structure	Bond Angles	Hybridization
2	0	Linear	Linear	Y—X—Y	180°	sp
3	0	Trigonal Planar	Trigonal planar		120°	sp^2
	1		Bent		<120°	
4	0	Tetrahedral	Tetrahedral		109.5°	sp^3
	1		Pyramidal		<109.5°	
	2		Bent		<109.5°	

Formal Charge – *How Fictitious!*

Formal charge is a fictitious charge assigned to each atom in a Lewis diagram that helps distinguish it from other competing Lewis diagrams for the same molecule. It is essentially the calculated charge for each atom if you completely ignore the effects of electronegativity – which isn't very realistic – but in this case it is helpful.

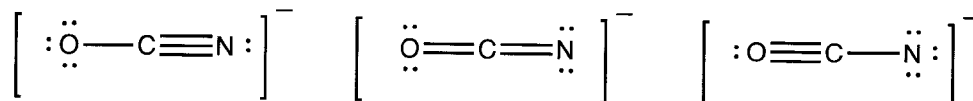
$$\text{Formal Charge} = \# \text{ of valence electrons} - \# \text{ of lone pair electrons} - \frac{1}{2} \# \text{ of bonding electrons}$$

Formal charge can be used as a criterion for determining which of several possible valid Lewis diagrams provides the best model for predicting molecular structure and properties. Generally you use these parameters to help decide:

- Neutral molecules must have a total formal charge (sum) of ZERO
- Ions must have a total formal charge (sum) that equals the charge on the ion
- Small (or zero) formal charges on each atom are preferred to larger (+ or –) ones
- When formal charges are unavoidable, the most electronegative atom should have a negative formal charge

For example – the cyanate ion OCN^-

If given this on the AP exam and asked which is correct, use formal charge to make that determination.



	A				B				C		
	O	C	N		O	C	N		O	C	N
Valence e^-	6	4	5		6	4	5		6	4	5
Lone e^-	6	0	2		4	0	4		2	0	6
$\frac{1}{2}$ bonding e^-	1	4	3		2	4	2		3	4	2
Formal Charge	-1	0	0		0	0	-1		+1	0	-2

All three structures have a net formal charge of -1; they better as the ion has a charge of -1. Structure C has the most formal charges and a +2 on a very electronegative oxygen atom – so it is OUT! Between A and B, A has the negative formal charge on the most electronegative atom (O is more electronegative than N). Thus structure A provides the best model for predicting molecular structure and properties for the cyanate ion.

Bond Energy – *Breaking Up is Hard to Do!*

Say this over and over and over...

Breaking Bonds ABSORBS energy and forming bonds RELEASES energy!

Bond Breaking – ENDOTHERMIC (+ ΔH)

Bond Formation – EXOTHERMIC (- ΔH)

You often will be asked to determine the overall energy change for a chemical reaction based on BOND ENERGIES for the reactants and the products. In order to answer these you really need to consider:

- The balanced equation
- The Lewis structures of the reactants and the products
- Bond Energies of each bond being broken and those being formed

To solve the problem you need to think about what is happening and realize:

$$\Delta H^\circ = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}}$$

Just remember: $\Delta H = \text{BONDS BROKEN} - \text{BONDS FORMED}$