



# NATIONAL MATH + SCIENCE INITIATIVE

## AP CHEMISTRY

### Bonding, Lewis, and Molecular Geometries

2016 EDITION  
PRESENTER

# Periodic Table of the Elements

|                    |  |                    |  |                     |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                   |  |                    |  |
|--------------------|--|--------------------|--|---------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|--------------------|--|-------------------|--|--------------------|--|
| 1<br>H<br>1.0079   |  |                    |  |                     |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  | 2<br>He<br>4.0026  |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  |                   |  |                    |  |
| 3<br>Li<br>6.941   |  | 4<br>Be<br>9.012   |  |                     |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  | 5<br>B<br>10.811   |  | 6<br>C<br>12.011   |  | 7<br>N<br>14.007   |  | 8<br>O<br>16.00    |  | 9<br>F<br>19.00    |  | 10<br>Ne<br>20.179 |  |                    |  |                   |  |                    |  |
| 11<br>Na<br>22.99  |  | 12<br>Mg<br>24.30  |  |                     |  |                    |  |                    |  |                    |  |                    |  |                    |  |                    |  | 13<br>Al<br>26.98  |  | 14<br>Si<br>28.09  |  | 15<br>P<br>30.974  |  | 16<br>S<br>32.06   |  | 17<br>Cl<br>35.453 |  | 18<br>Ar<br>39.948 |  |                    |  |                   |  |                    |  |
| 19<br>K<br>39.10   |  | 20<br>Ca<br>40.08  |  | 21<br>Sc<br>44.96   |  | 22<br>Ti<br>47.90  |  | 23<br>V<br>50.94   |  | 24<br>Cr<br>52.00  |  | 25<br>Mn<br>54.938 |  | 26<br>Fe<br>55.85  |  | 27<br>Co<br>58.93  |  | 28<br>Ni<br>58.69  |  | 29<br>Cu<br>63.55  |  | 30<br>Zn<br>65.39  |  | 31<br>Ga<br>69.72  |  | 32<br>Ge<br>72.59  |  | 33<br>As<br>74.92  |  | 34<br>Se<br>78.96  |  | 35<br>Br<br>79.90 |  | 36<br>Kr<br>83.80  |  |
| 37<br>Rb<br>85.47  |  | 38<br>Sr<br>87.62  |  | 39<br>Y<br>88.91    |  | 40<br>Zr<br>91.22  |  | 41<br>Nb<br>92.91  |  | 42<br>Mo<br>93.94  |  | 43<br>Tc<br>(98)   |  | 44<br>Ru<br>101.1  |  | 45<br>Rh<br>102.91 |  | 46<br>Pd<br>106.42 |  | 47<br>Ag<br>107.87 |  | 48<br>Cd<br>112.41 |  | 49<br>In<br>114.82 |  | 50<br>Sn<br>118.71 |  | 51<br>Sb<br>121.75 |  | 52<br>Te<br>127.60 |  | 53<br>I<br>126.91 |  | 54<br>Xe<br>131.29 |  |
| 55<br>Cs<br>132.91 |  | 56<br>Ba<br>137.33 |  | 57<br>*La<br>138.91 |  | 72<br>Hf<br>178.49 |  | 73<br>Ta<br>180.95 |  | 74<br>W<br>183.85  |  | 75<br>Re<br>186.21 |  | 76<br>Os<br>190.2  |  | 77<br>Ir<br>192.2  |  | 78<br>Pt<br>195.08 |  | 79<br>Au<br>196.97 |  | 80<br>Hg<br>200.59 |  | 81<br>Tl<br>204.38 |  | 82<br>Pb<br>207.2  |  | 83<br>Bi<br>208.98 |  | 84<br>Po<br>(209)  |  | 85<br>At<br>(210) |  | 86<br>Rn<br>(222)  |  |
| 87<br>Fr<br>(223)  |  | 88<br>Ra<br>226.02 |  | 89<br>†Ac<br>227.03 |  | 104<br>Rf<br>(261) |  | 105<br>Db<br>(262) |  | 106<br>Sg<br>(263) |  | 107<br>Bh<br>(262) |  | 108<br>Hs<br>(265) |  | 109<br>Mt<br>(266) |  | 110<br>§<br>(269)  |  | 111<br>§<br>(272)  |  | 112<br>§<br>(277)  |  | §Not yet named     |  |                    |  |                    |  |                    |  |                   |  |                    |  |

\*Lanthanide Series:

†Actinide Series:

|        |        |        |        |       |        |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 58     | 59     | 60     | 61     | 62    | 63     | 64     | 65     | 66     | 67     | 68     | 69     | 70     | 71     |
| Ce     | Pr     | Nd     | Pm     | Sm    | Eu     | Gd     | Tb     | Dy     | Ho     | Er     | Tm     | Yb     | Lu     |
| 140.12 | 140.91 | 144.24 | (145)  | 150.4 | 151.97 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.04 | 174.97 |
| 90     | 91     | 92     | 93     | 94    | 95     | 96     | 97     | 98     | 99     | 100    | 101    | 102    | 103    |
| Th     | Pa     | U      | Np     | Pu    | Am     | Cm     | Bk     | Cf     | Es     | Fm     | Md     | No     | Lr     |
| 232.04 | 231.04 | 238.03 | 237.05 | (244) | (243)  | (247)  | (247)  | (251)  | (252)  | (257)  | (258)  | (259)  | (260)  |

# AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

## ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

$E$  = energy

$\nu$  = frequency

$\lambda$  = wavelength

Planck's constant,  $h = 6.626 \times 10^{-34}$  J s

Speed of light,  $c = 2.998 \times 10^8$  m s<sup>-1</sup>

Avogadro's number =  $6.022 \times 10^{23}$  mol<sup>-1</sup>

Electron charge,  $e = -1.602 \times 10^{-19}$  coulomb

## EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

### Equilibrium Constants

$K_c$  (molar concentrations)

$K_p$  (gas pressures)

$K_a$  (weak acid)

$K_b$  (weak base)

$K_w$  (water)

## KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

$k$  = rate constant

$t$  = time

$t_{1/2}$  = half-life

## GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity,  $M$  = moles of solute per liter of solution

$$A = abc$$

$P$  = pressure

$V$  = volume

$T$  = temperature

$n$  = number of moles

$m$  = mass

$M$  = molar mass

$D$  = density

$KE$  = kinetic energy

$v$  = velocity

$A$  = absorbance

$a$  = molar absorptivity

$b$  = path length

$c$  = concentration

Gas constant,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 760 \text{ mm Hg}$$

$$= 760 \text{ torr}$$

STP =  $0.00^\circ\text{C}$  and  $1.000 \text{ atm}$

## THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

$q$  = heat

$m$  = mass

$c$  = specific heat capacity

$T$  = temperature

$S^\circ$  = standard entropy

$H^\circ$  = standard enthalpy

$G^\circ$  = standard free energy

$n$  = number of moles

$E^\circ$  = standard reduction potential

$I$  = current (amperes)

$q$  = charge (coulombs)

$t$  = time (seconds)

Faraday's constant,  $F = 96,485 \text{ coulombs per mole of electrons}$

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

## 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.*

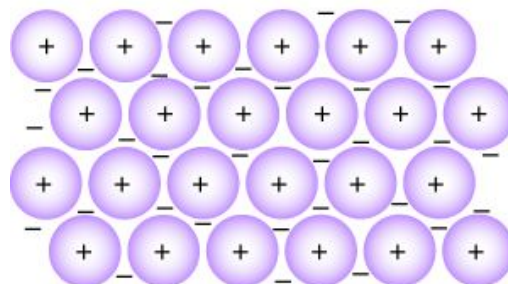
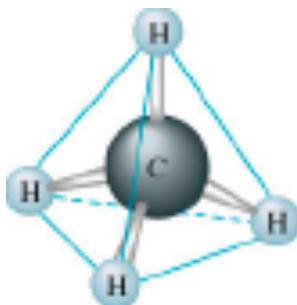
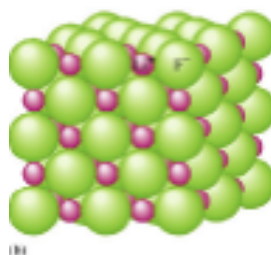
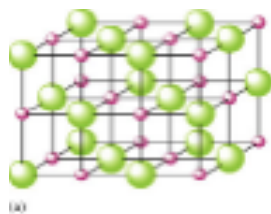
#### IMPORTANT

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.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |



### Ionic Bonding – *It's All About Coulomb's Law*

Results form the net attraction between oppositely charged ions, closely packed together as a regular array of cations and anions called a crystal lattice.

This systematic arrangement maximizes the attractive forces while minimizing the repulsive forces. Bonding is all about maximizing attraction and minimizing repulsion.

|                                 |                                                                                                                                                                                                                      |
|---------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $U_E \propto \frac{q^+ q^-}{d}$ | Coulombs' law indicates the more highly charged the ions the stronger the attraction; and smaller ions will form stronger attractions than larger ions because of the decreased in distance separating the two ions. |
|---------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

### Metallic Bonding – *It's a Sea of Electrons*

Metallic bonding describes an array of positively charged metal cores surrounded by a sea of mobile valence electrons.

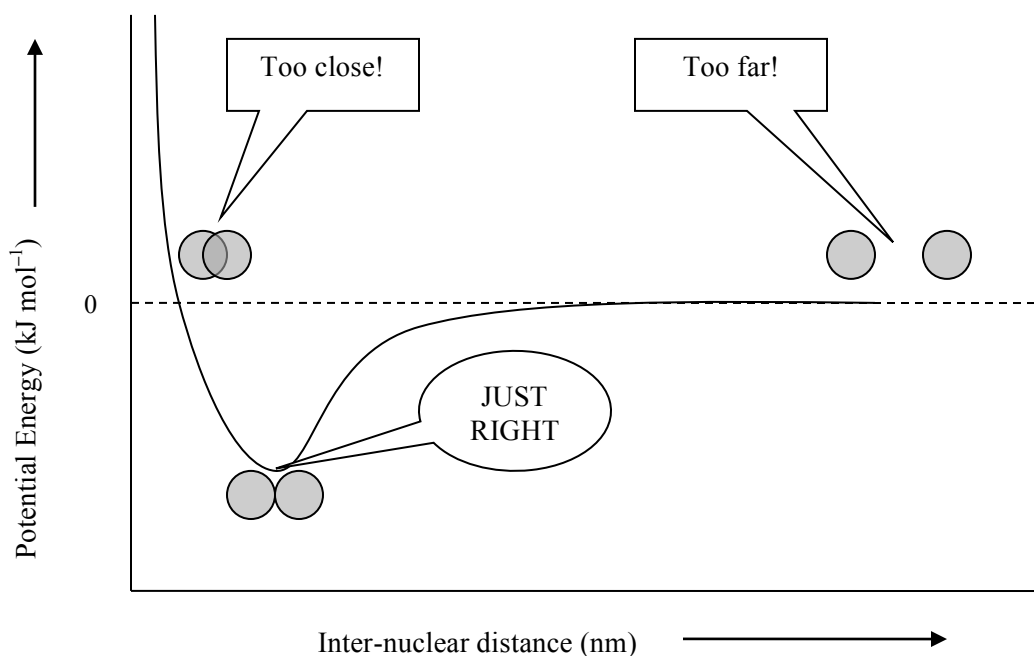
The valence electrons from the metal atoms are considered to be delocalized and not associated with an individual atom.

- Metallic bonding can be represented as an array of positive metal ions with valence electrons drawn among them, as if the electrons were moving (i.e., a sea of electrons).
- The electron sea model can be used to explain several properties of metals, including electrical conductivity, malleability, ductility, and low volatility.
- The number of valence electrons involved in metallic bonding, via the shell model, can be used to understand patterns in these properties.

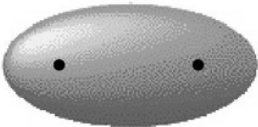
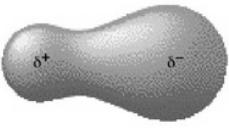
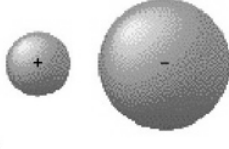
Metallic solids may also be mixtures of metals called alloys. Some properties of alloys can be understood in terms of the size of the component atoms:

- Interstitial alloys form between atoms of different radii, where the smaller atoms fill the spaces between the larger atoms.
  - Steel is an example in which carbon occupies the interstices in iron.
  - The interstitial atoms make the lattice more rigid, decreasing malleability and ductility.
- Substitutional alloys form between atoms of comparable radii, where one atom substitutes for the other in the lattice.
  - Brass is an example in which some copper atoms are substituted with a different element, usually zinc.
  - The alloy remains malleable and ductile.
- Alloys typically retain a sea of mobile electrons and so remain conducting. However, in some cases, alloy formation alters the chemistry of the surface.
  - An example is formation of a chemically inert oxide layer in stainless steel.

| 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 <b><i>too close together</i></b> , 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 <b><i>too far apart</i></b> , 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 <b><i>just right</i></b> , 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 <b><i>bond length</i></b> . <ul style="list-style-type: none"> <li>The <b><i>bond energy</i></b> is the energy required for the dissociation of the bond. Typically given in a per mole basis (i.e. <math>\text{kJ mol}^{-1}</math>)</li> </ul> |                             |



Bond Polarity – *Why all the negativity, electronegativity that is?*

|                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  <p>(a)</p> | <p>Electronegativity is the ability of an atom in a molecule to attract shared electrons to it.</p> <ul style="list-style-type: none"> <li>Two or more valence electrons shared between atoms of <i>identical</i> electronegativity constitute a nonpolar covalent bond.</li> <li>Two or more valence electrons shared between atoms of unequal electronegativity constitute a polar covalent bond.</li> </ul>                                                                                                                                                                                                                                                                                                                      |
|  <p>(b)</p> | <p><b>Polar Covalent Bonds</b></p> <ul style="list-style-type: none"> <li>The atom with a higher electronegativity will develop a partial negative charge relative to the other atom in the bond.             <ul style="list-style-type: none"> <li>For diatomic molecules, the partial negative charge on the more electronegative atom is equal in magnitude to the partial positive charge on the less electronegative atom.</li> </ul> </li> <li>Greater differences in electronegativity lead to greater partial charges, and consequently greater bond dipoles, thus the bond is <b>MORE</b> polar</li> <li>The sum of partial charges in any molecule or ion must be equal to the overall charge on the species.</li> </ul> |
|  <p>(c)</p> | <p>All bonds have some ionic character, and the difference between ionic and covalent bonding is not distinct but rather a continuum.</p> <ul style="list-style-type: none"> <li>The difference in electronegativity is not the only factor in determining if a bond is designated ionic or covalent.</li> <li>Generally, bonds between a metal and nonmetal are ionic, and between two nonmetals the bonds are covalent.</li> <li>Examination of the properties of a compound is the best way to determine the type of bonding.</li> </ul>                                                                                                                                                                                         |

Lewis Diagrams – *It's All About those Localized Electrons and VSEPR*

Lewis diagrams can be constructed according to a well-established set of principles.

- Typically atoms bond in a manner that allows for an complete octet (8) of electrons in the atom's valence shell
- In cases where more than one equivalent Lewis structure can be constructed, resonance must be included as a refinement to the Lewis structure approach in order to provide qualitatively accurate predictions of molecular structure and properties (in some cases).
- 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.

The VSEPR model uses the Coulombic repulsion between electrons as a basis for predicting the arrangement of electron pairs around a central atom. Remember, maximize attraction and minimize repulsion...

The combination of Lewis diagrams with the VSEPR model provides model for predicting structural properties of many covalently bonded molecules and polyatomic ions, including the following:

- Molecular geometry
- Bond angles
- Relative bond energies based on bond order
- Relative bond lengths (multiple bonds, effects of atomic radius)
- Presence of a dipole moment

### 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, NO<sub>2</sub>, and ClO<sub>2</sub> 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 sp<sup>2</sup> hybridized
- 109°, the central atom is sp<sup>3</sup> 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  $\sigma$  bond and one  $\pi$  bond
- Triple bond – three pairs of electrons shared: one  $\sigma$  bond and two  $\pi$  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!

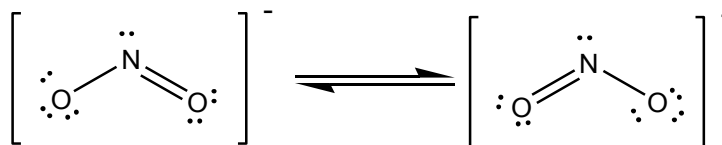
| Bond Strength                                                       | Bond Length                                |
|---------------------------------------------------------------------|--------------------------------------------|
| Sigma ( $\sigma$ ) bonds are stronger than pi ( $\pi$ ) bonds;  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

### Resonance – Where Oh Where Does that Double Bond Go?

When a molecule has equally different positions where a double or triple bond can be placed, you must draw resonance structures.

In terms of “bond properties” it is as if the multiple bond “resonates” between all the possible positions, giving the bond length and bond strengths a value somewhere between that of a pure single or double bond.

The bonds are more equivalent to a “bond and  $\frac{1}{2}$ ” in terms of length and strength.



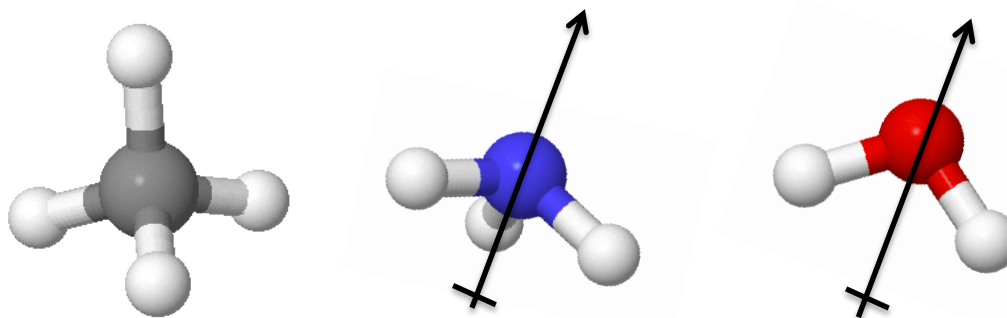
### Polarity – O’ Dipole, Dipole, wherefore art thou Dipole?

Like with bonds, molecules can be polar or non-polar; i.e. they exhibit an electron density (cloud) that is not symmetrically distributed about the molecule.

- This creates the presence of a dipole moment – one side of the molecule has more electrons than the other, thus that side is more negative than the other.

Determining molecular polarity

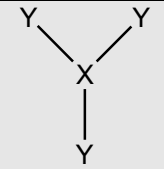
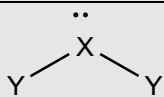
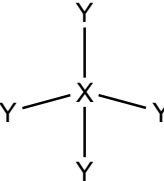
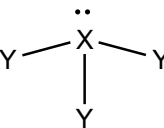
- If lone pairs are present on the central atom the molecule is *typically* polar.
- There are a couple of exceptions to this.
  - Trigonal bipyramidal structures that have a molecular shape that is **linear**
  - Octahedral structures that have a molecular shape that is **square planar**
- Why do lone pair electrons on the central atom typically make the molecule polar?
  - Their presence creates increased electron repulsion and thus, an unequal distribution of electron density, which repels the other electron regions (bonds) more.
  - Look at the molecules for  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  – all have 4 electron domains.

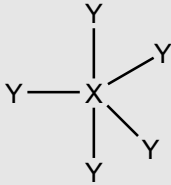
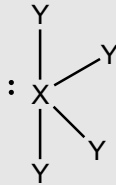
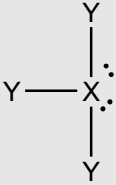
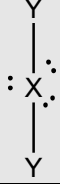
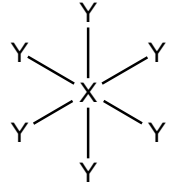
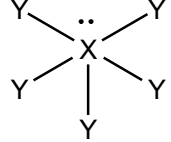
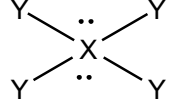


- $\text{CH}_4$  has 4 bonds with the same terminal atoms (H) thus it has an equal distribution of electron density and DOES NOT have a net dipole moment so the molecule is NONPOLAR
- $\text{NH}_3$  has 3 bonds and 1 lone electron pair (not shown) thus it has an unequal distribution of electron density and DOES have a net dipole moment so the molecule is POLAR
- $\text{H}_2\text{O}$  has 2 bonds and 2 lone electron pairs (not shown) thus it has an unequal distribution of electron density and DOES have a net dipole moment so the molecule is POLAR

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°     |               |

| Number of electron domains (bond pairs and lone pairs) | Number of lone pairs | Electronic Geometry  | Molecular Geometry   | Structure                                                                            | Bond Angles             | Hybridization |
|--------------------------------------------------------|----------------------|----------------------|----------------------|--------------------------------------------------------------------------------------|-------------------------|---------------|
| 5                                                      | 0                    | Trigonal Bipyramidal | Trigonal bipyramidal |    | $120^\circ; 90^\circ$   |               |
|                                                        | 1                    |                      | See-saw              |    | $<120^\circ; <90^\circ$ |               |
|                                                        | 2                    |                      | T-shaped             |   | $90^\circ$              |               |
|                                                        | 3                    |                      | Linear               |  | $180^\circ$             |               |
| 6                                                      | 0                    | Octahedral           | Octahedral           |  | $90^\circ$              |               |
|                                                        | 1                    |                      | Square pyramidal     |  | $90^\circ$              |               |
|                                                        | 2                    |                      | Square planar        |  | $90^\circ$              |               |

### 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.

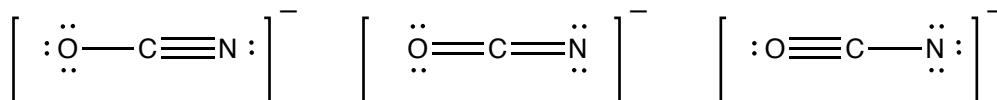
$$\text{Formal Charge} = \# \text{ of valence electrons} - \# \text{ of lone pair electrons} - \frac{1}{2} \# \text{ of bonding electrons}$$

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  $\text{OCN}^-$

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 (+ $\Delta H$ )

Bond Formation – EXOTHERMIC (- $\Delta H$ )

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

## Key Formulas and Relationships

When answering questions about Ionic bond strength, justify your response using Coulomb's law:

$$U_E \propto \frac{q^+ q^-}{d}$$

If the charges are greater and distances similar, the greater charged compound will have more ion-ion attraction; thus it will require more energy to dissociate. This is useful in justifying melting points, solubility, and lattice energy differences between two ionic compounds.

## Key Concepts and Phrases

|                                                                                                       |                                                                                  |
|-------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| Be able to determine what type of bonding is present by looking at the chemical formula;              | Never ever forget that ionic bonds are merely electrostatic attractions (forces) |
| Be able to sketch Lewis structures and determine their shape, bond angle, polarity, and hybridization | You MUST memorize the structural pair (electronic) and molecular geometries      |
| Breaking bonds takes in energy (endothermic; $+\Delta H$ )                                            | Forming bonds RELEASES energy (exothermic; $-\Delta H$ )                         |

## Connections to Other Chapters

|                                            |                                                                            |
|--------------------------------------------|----------------------------------------------------------------------------|
| Periodicity – especially electronegativity | Atomic Structure – especially understanding orbitals and valence electrons |
|--------------------------------------------|----------------------------------------------------------------------------|

## What to write, or not to write: That is the question...

NEVER use the term “happy” when referring to atoms or molecules. Everything is about energy, not emotion!!

When justifying polarity, indicate there is either “an asymmetrical distribution of electron density”, “unequal distribution of charge on the molecule” AND THEREFORE the molecule has “a net dipole moment”... DO NOT refer to the molecule as being asymmetrical or unbalanced.

When lone pairs are present on the central atom, they will distort the “expected” bond angle. Explain your response by indicating... lone pairs have more repulsive forces compared to bonding pairs since they are only attracted to one nucleus.

When discussing “expanded valence” recall only the elements in Period 3 and below can expand their valence shell. Be sure to explain that elements that do not have “d” sublevels available (elements in Periods 1 and 2) cannot have an expanded octet. They need d orbitals to have trigonal bipyramidal and octahedral arrangements.

Remember we stressed: maximize attraction and minimize repulsion

- In the trigonal bipyramidal structure, when lone pairs are present on the central atom, they will locate themselves on the equatorial plane (around the triangle) because they best minimize repulsion at  $120^\circ$ .
- In the octahedral structure, when lone pairs are present on the central atom, they will locate themselves on the axial position (on “top” and “bottom”).

And finally.....

### **ALWAYS DRAW THE LEWIS STRUCTURE**

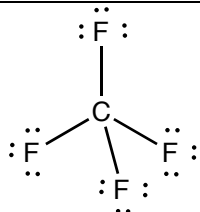
Even if it's not “required” it helps answer many questions; such as shape, bond angle, polarity, type of IMF, etc...

## NMSI SUPER PROBLEM

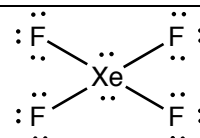
Answer the following questions about the molecules and reactions containing fluorine atoms.

(a) Draw the Lewis structures for

i.  $\text{CF}_4$

|                                                                                   |                                                                                                |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
|  | <b>1 point</b> for the correct Lewis structure; atoms must show lone pair electrons if present |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|

ii.  $\text{XeF}_4$

|                                                                                   |                                                                                                |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
|  | <b>1 point</b> for the correct Lewis structure; atoms must show lone pair electrons if present |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|

(b) Although  $\text{CF}_4$  and  $\text{XeF}_4$  *both* have the 4 atoms of fluorine around the central atom they have different molecular shapes. Explain this difference. Be sure to state the correct molecular geometry of both molecules in your explanation.

|                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| $\text{CF}_4$ molecules are tetrahedral in their molecular geometry whereas molecules of $\text{XeF}_4$ are square planar. Although they both have four fluorine atoms the Xe atom has 2 sets of lone pair electrons – or 6 regions of electron density and the C atom only has the 4 regions of electron density – it has no lone pairs, therefore they will have different molecular geometries. | <b>1 point</b> for correct explanation<br><br><b>1 point</b> for stating both molecular geometries |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|

(c) Identify the hybridization about the C atom in  $\text{CF}_4$ .

|               |                                                                        |
|---------------|------------------------------------------------------------------------|
| $\text{sp}^3$ | <b>1 point</b> for the correct hybridization, consistent with part (a) |
|---------------|------------------------------------------------------------------------|

(d) Indicate whether molecules of  $\text{XeF}_4$  are polar or nonpolar. Justify your answer.

|                                                                                                                                                                                            |                                                            |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|
| Nonpolar; because the molecule has an equal distribution of electron density there is no NET DIPOLE moment as the individual dipoles cancel each other out due to the square planar shape. | <b>1 point</b> for the correct polarity with justification |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|

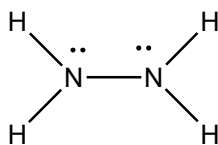
- (e) Explain why nitrogen only forms the fluoride  $\text{NF}_3$  but arsenic forms both  $\text{AsF}_3$  and  $\text{AsF}_5$ .

|                                                                                                                |                                                                                                                   |
|----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| Nitrogen can't form an expanded octet since it lacks the $d$ orbitals which are required to form $\text{NF}_5$ | <b>1 point</b> for the lack of $d$ orbitals                                                                       |
| Arsenic has $d$ orbitals that can allow for an expanded octet.                                                 | <b>1 point</b> for stating that As has empty $d$ orbitals available for electrons. (or similar correct argument). |

Fluorine reacts with hydrazine,  $\text{N}_2\text{H}_4$ , as shown in the reaction below at  $25^\circ\text{C}$  and 1 atm.

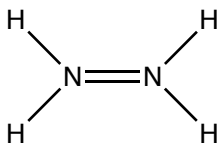


- (f) Determine the number of *both* sigma and pi bonds in  $\text{N}_2\text{H}_4$ . The Lewis structure for  $\text{N}_2\text{H}_4$  is shown below.



|                           |                                                              |
|---------------------------|--------------------------------------------------------------|
| 5 sigma bonds; 0 pi bonds | <b>1 point</b> for correct number of both sigma and pi bonds |
|---------------------------|--------------------------------------------------------------|

- (g) A student drew the following competing structure for hydrazine. Use the concept of formal charge to support which Lewis diagram best represent a molecule of hydrazine.



|                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                              |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| In the first Lewis diagram of hydrazine the formal charge on the Nitrogen atom is zero ( $5-2-3$ ). In the Lewis diagram of hydrazine with the double bond the formal charge on the Nitrogen atom is +1 ( $5-0-4$ ). Thus the first (with lone electron pairs on the nitrogen atoms) Lewis diagram best represents a molecule of hydrazine. | <b>1 point</b> for selecting the first Lewis diagram as the best representation of hydrazine with correct justification using formal charge. |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|

(h) Using the table of bond enthalpies below, calculate the enthalpy of an N–H bond.

| Bonds | Bond Enthalpies<br>(kJ/mol) |
|-------|-----------------------------|
| N—N   | 160                         |
| N=N   | 418                         |
| N≡N   | 941                         |
| F—H   | 565                         |
| F—F   | 154                         |
| N—H   | ???                         |

|                                                                                                                                                                                                                                                                                         |                                                                                                                                                                      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\Delta H^\circ_{\text{rxn}} = \text{Sum of Bonds Broken} - \text{Sum of Bonds Formed}$<br>$-1169 \text{ kJ/mol} = [160 + 4(\text{BE}_{\text{N-H}}) + 2(154)] - [(941) + 4(565)]$<br>$1564 \text{ kJ/mol} = 4(\text{BE}_{\text{N-H}})$<br>$\text{BE}_{\text{N-H}} = 391 \text{ kJ/mol}$ | <p><b>1 point</b> for correct sign for the enthalpy of reaction</p> <p><b>1 point</b> for correct substitution</p> <p><b>1 point</b> for correct N–H bond energy</p> |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|

(i) Is the average kinetic energy of the nitrogen gas, N<sub>2</sub>, greater than, less than, or equal to the average kinetic energy of hydrogen fluoride gas, HF, when both are at the same temperature? Justify your answer.

|                                                                                                                |                                                                                                                                                     |
|----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| Since both gases are at the same temperature, the average kinetic energy of N <sub>2</sub> and HF is the same. | <b>1 point</b> for stating both substances have the same average kinetic energy because they are at the same temperature; or similar justification. |
|----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|

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(8 points)

Use the information in the table below to respond to the statements and questions that follow. Your answers should be in terms of principles of molecular structure and intermolecular forces.

| Compound    | Formula                            | Lewis Electron-Dot Diagram                                                                                                                                                                 |
|-------------|------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ethanethiol | CH <sub>3</sub> CH <sub>2</sub> SH | $  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\ddot{\text{S}}:\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $ |
| Ethane      | CH <sub>3</sub> CH <sub>3</sub>    | $  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $                 |
| Ethanol     | CH <sub>3</sub> CH <sub>2</sub> OH | $  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\ddot{\text{O}}:\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $ |
| Ethyne      | C <sub>2</sub> H <sub>2</sub>      | $  \begin{array}{c}  \text{H}:\text{C}::\text{C}:\text{H} \\  \text{or} \\  \text{H}-\text{C}\equiv\text{C}-\text{H}  \end{array}  $                                                       |

(a) Draw the complete Lewis electron-dot diagram for ethyne in the appropriate cell in the table above.

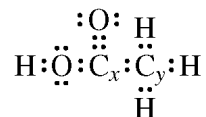
|                                              |                                                      |
|----------------------------------------------|------------------------------------------------------|
| See the lower right cell in the table above. | One point is earned for the correct Lewis structure. |
|----------------------------------------------|------------------------------------------------------|

(b) Which of the four molecules contains the shortest carbon-to-carbon bond? Explain.

|                                                                                                                                                                   |                                                                                                            |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| Ethyne, which contains a triple bond, has the shortest C-to-C bond. The other molecules have single C-to-C bonds, and triple bonds are shorter than single bonds. | <p>One point is earned for the correct choice.</p> <p>One point is earned for the correct explanation.</p> |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|

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- (c) A Lewis electron-dot diagram of a molecule of ethanoic acid is given below. The carbon atoms in the molecule are labeled *x* and *y*, respectively.



Identify the geometry of the arrangement of atoms bonded to each of the following.

- (i) Carbon *x*

|                 |                                               |
|-----------------|-----------------------------------------------|
| Trigonal planar | One point is earned for the correct geometry. |
|-----------------|-----------------------------------------------|

- (ii) Carbon *y*

|                                                          |                                               |
|----------------------------------------------------------|-----------------------------------------------|
| Distorted tetrahedral, tetrahedral or trigonal pyramidal | One point is earned for the correct geometry. |
|----------------------------------------------------------|-----------------------------------------------|

- (d) Energy is required to boil ethanol. Consider the statement “As ethanol boils, energy goes into breaking C–C bonds, C–H bonds, C–O bonds, and O–H bonds.” Is the statement true or false? Justify your answer.

|                                                                                                                                                                                                                                   |                                                                |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| The statement is false. All of the bonds described are intramolecular; these bonds are not broken during vaporization. When ethanol boils, the added energy overcomes <u>intermolecular</u> , not <u>intramolecular</u> , forces. | One point is earned for the correct choice with justification. |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|

- (e) Identify a compound from the table above that is nonpolar. Justify your answer.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                              |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|
| <p>Either ethane or ethyne may be identified as nonpolar.</p> <p>The ethane/ethyne molecule is nonpolar because all of the bond dipoles in the molecule cancel.</p> <p style="text-align: center;"><b>OR</b></p> <p>The ethane/ethyne molecule is nonpolar because the molecule is symmetric.</p> <p><u>Note:</u> Explanation must refer to the shape of the molecule. Statements such as: “all hydrocarbons are nonpolar”, “the carbons are surrounded by hydrogens” or “there are no lone pairs” do not earn this point.</p> | One point is earned for a correct choice with justification. |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|

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- (f) Ethanol is completely soluble in water, whereas ethanethiol has limited solubility in water. Account for the difference in solubilities between the two compounds in terms of intermolecular forces.

Ethanol is able to form strong hydrogen bonds with water whereas ethanethiol does not have similar capability. The formation of hydrogen bonds increases the attraction between molecules of ethanol and molecules of water, making them more soluble in each other.

Note: The answer must clearly focus on the solute-solvent interaction. Just the mention of hydrogen bonding does not earn the point.

One point is earned for the correct explanation.

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(2 points)

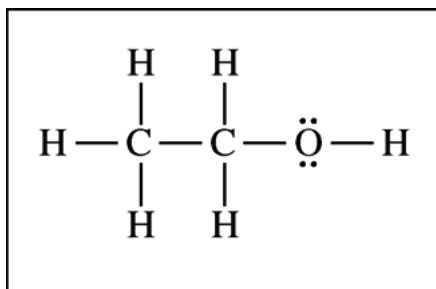
Answer the following questions using principles of molecular structure and intermolecular forces.

| Compound | Empirical Formula               | Solubility in Water | Boiling Point (°C) |
|----------|---------------------------------|---------------------|--------------------|
| 1        | C <sub>2</sub> H <sub>6</sub> O | Slightly soluble    | −24                |
| 2        | C <sub>2</sub> H <sub>6</sub> O | Soluble             | 78                 |

Compounds 1 and 2 in the data table above have the same empirical formula, but they have different physical properties.

(a) The skeletal structure for one of the two compounds is shown below in Box X.

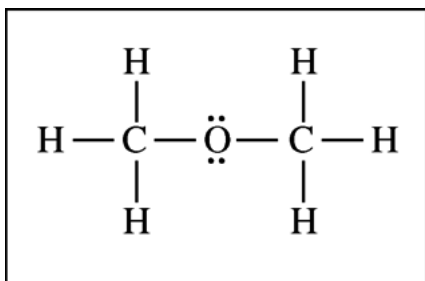
- (i) Complete the Lewis electron-dot diagram of the molecule in Box X. Include any lone (nonbonding) pairs of electrons.



Box X

1 point is earned for a correct Lewis diagram.

- (ii) In Box Y below, draw the complete Lewis electron-dot diagram for the other compound, which is a structural isomer of the compound represented in Box X. Include any lone (nonbonding) pairs of electrons.

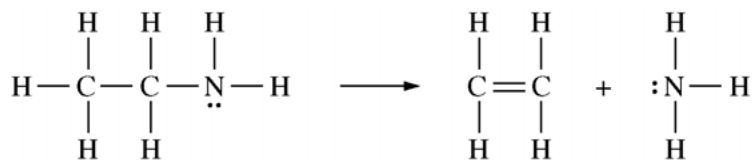


Box Y

1 point is earned for a correct Lewis diagram.

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(3 points)



A sample of  $\text{CH}_3\text{CH}_2\text{NH}_2$  is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

- (a) Using the data in the table below, calculate the value, in  $\text{kJ/mol}_{\text{rxn}}$ , of the standard enthalpy change,  $\Delta H^\circ$ , for the reaction at 298 K.

| Bond                           | C–C | C = C | C–H | C–N | N–H |
|--------------------------------|-----|-------|-----|-----|-----|
| Average Bond Enthalpy (kJ/mol) | 348 | 614   | 413 | 293 | 391 |

$\Delta H^\circ = \text{enthalpy of bonds broken} - \text{enthalpy of bonds formed}$

$$\begin{aligned}
 \Delta H^\circ &= [5(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}}) + 2(\Delta H_{\text{N-H}})] - \\
 &\quad [4(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C=C}}) + 3(\Delta H_{\text{N-H}})] \\
 &= [5(413) + 293 + 348 + 2(391)] - [4(413) + 614 + 3(391)] = 49 \text{ kJ/mol}_{\text{rxn}}
 \end{aligned}$$

**OR**

$$\begin{aligned}
 \Delta H^\circ &= [(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}})] - [(\Delta H_{\text{C=C}}) + (\Delta H_{\text{N-H}})] \\
 &= [413 + 293 + 348] \text{ kJ/mol} - [614 + 391] \text{ kJ/mol} = 49 \text{ kJ/mol}_{\text{rxn}}
 \end{aligned}$$

1 point is earned for the correct bond count and use of values from table.

1 point is earned for the correct setup in terms of bonds broken minus bonds formed and calculated  $\Delta H^\circ$ .

- (b) Based on your answer to part (a), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

The temperature of the contents should decrease because the reaction is endothermic, as indicated by the positive  $\Delta H^\circ$ .

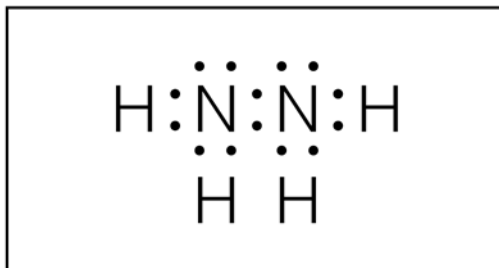
1 point is earned for the correct choice with explanation.

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SCORING GUIDELINES**

**4 Points**

Hydrazine is an inorganic compound with the formula  $\text{N}_2\text{H}_4$ .

- (a) In the box below, complete the Lewis electron-dot diagram for the  $\text{N}_2\text{H}_4$  molecule by drawing in all the electron pairs.



The correct Lewis diagram has single bonds between each pair of atoms and a lone pair of electrons on each N atom (a total of  $14 e^-$ ).

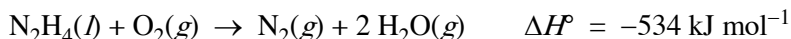
1 point is earned for the correct Lewis diagram.

- (b) On the basis of the diagram you completed in part (a), do all six atoms in the  $\text{N}_2\text{H}_4$  molecule lie in the same plane? Explain.

No, they do not. The molecular geometry surrounding both nitrogen atoms is trigonal pyramidal. Therefore the molecule as a whole cannot have all the atoms in the same plane.

1 point is earned for a correct answer with a valid explanation.

$\text{N}_2\text{H}_4$  reacts in air according to the equation below.



- (c) Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

The reaction is an oxidation-reduction reaction. The oxidation state of N changes from  $-2$  to  $0$  while that of O changes from  $0$  to  $-2$ .

1 point is earned for the correct choice with a valid justification.

- (g) Indicate whether the statement written in the box below is true or false. Justify your answer.

The large negative  $\Delta H^\circ$  for the combustion of hydrazine results from the large release of energy that occurs when the strong bonds of the reactants are broken.

The statement is false on two counts. First, energy is released not when bonds are broken, but rather when they are formed. Second, the bonds in the reactants are relatively weak compared to the bonds in the products.

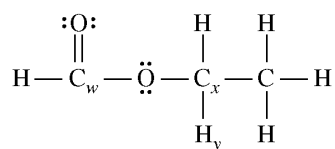
1 point is earned for correctly identifying the statement as false along with a valid justification.

# AP<sup>®</sup> CHEMISTRY SCORING GUIDELINES

(3points)

Use principles of molecular structure, intermolecular forces, and kinetic molecular theory to answer the following questions.

- (a) A complete Lewis electron-dot diagram of a molecule of ethyl methanoate is given below.



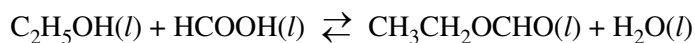
- (i) Identify the hybridization of the valence electrons of the carbon atom labeled  $\text{C}_w$ .

|        |                                           |
|--------|-------------------------------------------|
| $sp^2$ | 1 point is earned for the correct answer. |
|--------|-------------------------------------------|

- (ii) Estimate the numerical value of the  $\text{H}_y - \text{C}_x - \text{O}$  bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.

|                                                                                                                                                    |                                                                          |
|----------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------|
| The $\text{C}_x$ is the central atom in a tetrahedral arrangement of bonding electron pairs; thus the angle would be approximately $109.5^\circ$ . | 1 point is earned for the correct angle with an appropriate explanation. |
|----------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------|

- (b) Ethyl methanoate,  $\text{CH}_3\text{CH}_2\text{OCHO}$ , is synthesized in the laboratory from ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , and methanoic acid,  $\text{HCOOH}$ , as represented by the following equation.



- (i) In the box below, draw the complete Lewis electron-dot diagram of a methanoic acid molecule.

|                                                                                                                    |                                          |
|--------------------------------------------------------------------------------------------------------------------|------------------------------------------|
| $  \begin{array}{c}  \text{:O:} \\  \parallel \\  \text{H} - \text{C} - \ddot{\text{O}} - \text{H}  \end{array}  $ | 1 point is earned for a correct diagram. |
|--------------------------------------------------------------------------------------------------------------------|------------------------------------------|