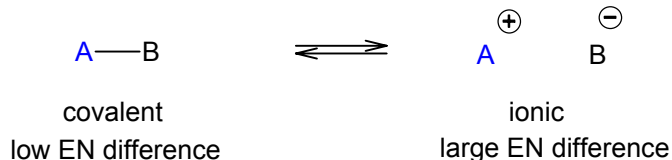


**Chapter 2: The Nature of Bonds and Structure of Organic Molecules**

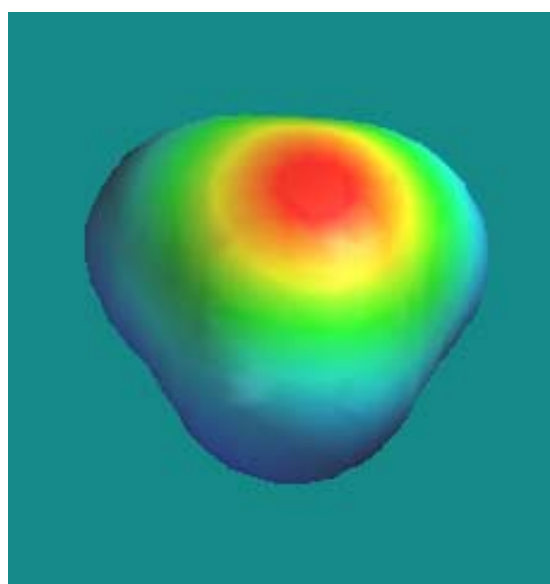
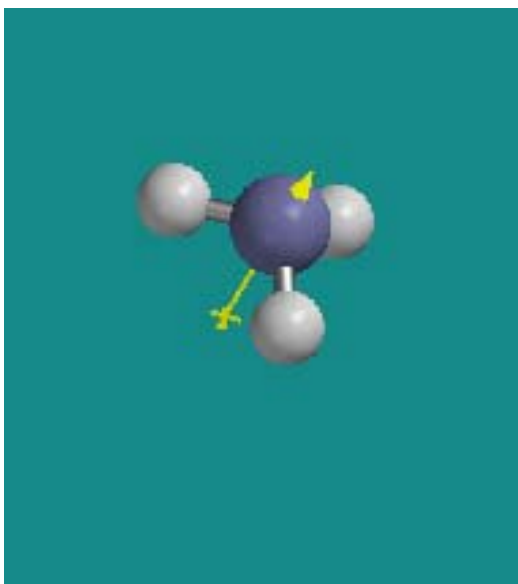
**Bonds and Polarity.** Bond polarity is based on the difference of the electronegativity of each individual atom in a bond. For the hypothetical bond A-B, the extreme picture would be either ionic or covalent. In reality many bonds are somewhere in between.



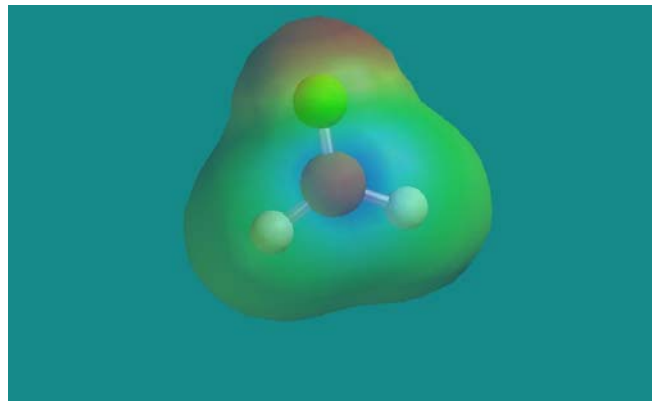
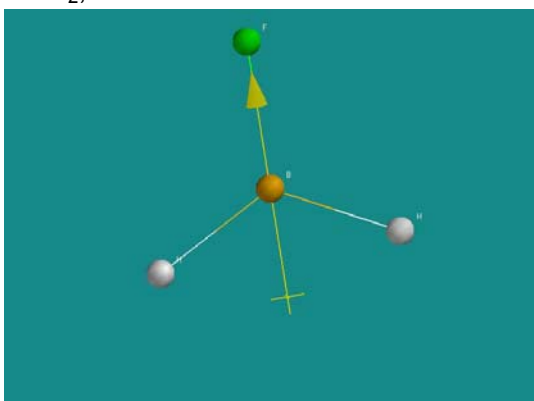
What is the definition of electronegativity?

What is a dipole? A dipole  $\mu$  is proportional to the charge x charge x distance between them. The dipole moment is drawn as a crossed arrow with the direction going towards the negative end of the molecule. Here are some examples:

Ammonia :NH<sub>3</sub>. On the left, there is the dipole arrow. Right, there is charge density picture with red indicating negative charge and blue indicating positive.



Here is BFH<sub>2</sub>,



What is the difference between a non-polar, polar-covalent and ionic bond?

Non-polar covalent

Polar covalent

Ionic

**Metals, Non-Metals, and Polarity**

Metals tend to be electropositive – easy to lose electrons.  
These have low EN values.

Non-metals (called main group elements) approach the most electronegative element F.  
H is not really a metal. It is compatible with the main group elements. C is average for a non-metal.

H 2.2	Electronegativity Values for Some Elements					
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 0.9	Mg 1.2	Al 1.5	Si 1.7	P 2.1	S 2.4	Cl 2.8
K 0.8	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.7

Table taken from Bill Reusch, <http://www.cem.msu.edu/~reusch/VirtualText/intro2.htm#strc2>

Classify these fictitious bonds as non-polar or polar and if polar show the  $\delta^+$  and  $\delta^-$ .

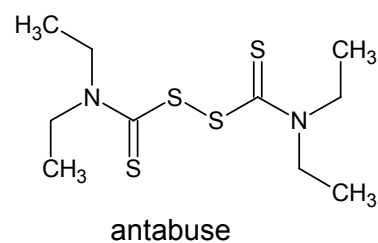
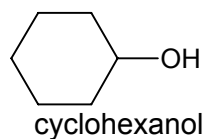
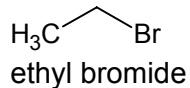
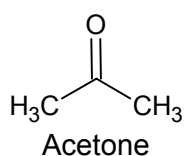
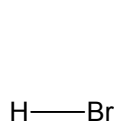
Polar	A -- B	$EN_A \gg EN_B$
Polar	A -- B	$EN_B \gg EN_A$
Non-polar	A -- B	$EN_A \sim EN_B$ (usually $< .4-.5$ )

For some real bonds. Classify as non-polar or polar and if polar show the  $\delta^+$  and  $\delta^-$ .

C – N	C -- H	B – H	Al – H	C – O	C – F	Li -- H
F -- F	B – Cl	Li – Al	Al – O	B – O	Li – Li	C – Li

**Summary of Polarity concepts:****1. What is polarity?****2. Why is polarity important in molecules.**

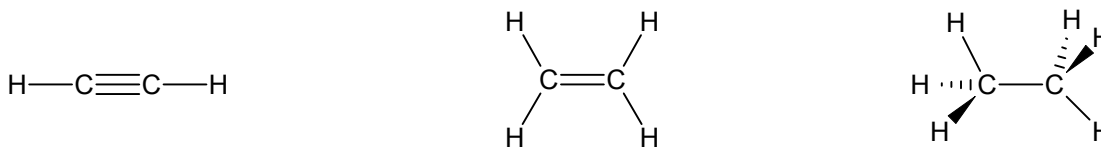
Assign  $\delta^+$  and  $\delta^-$  in the molecules below



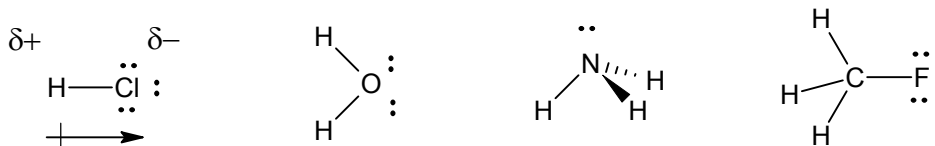
**Molecular Polarity and Intermolecular Forces**

To understand the overall polarity of a molecule, the polarity of each bond and the arrangement of the bonds in the molecule have to be considered.

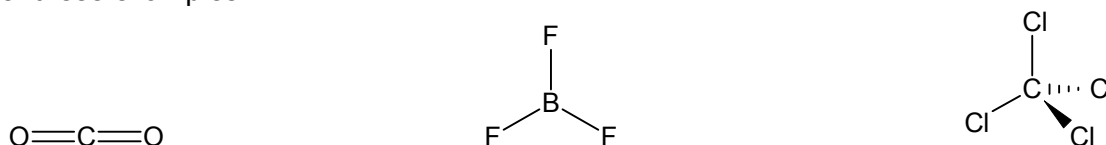
For a molecule with non-polar bonds, it's easy to see that the molecule overall is non-polar. Consider these molecules:



How about **molecules with polar bonds**: Here the polar vectors must be added based on the shape. Here are some simple examples.

**Polar Covalent Bonds and Polar Molecules.**

Just having polar bonds does not make the molecule polar. Consider these examples

**Intermolecular Forces:**

Just as there are attractions within molecules to hold the atoms together, there are forces between molecules that give the ensemble of molecules their physical properties:

Physical property	Low	High
Melting point	Strong Weak Forces+	Strong Weak Forces+
Boiling point	Strong Weak Forces	Strong Weak Forces

+Melting points and boiling points are based on two different pictures.

BP is the liquid  $\rightarrow$  gas.

Molecules are not locked in any arrangement.

MP is solid  $\rightarrow$  liquid.

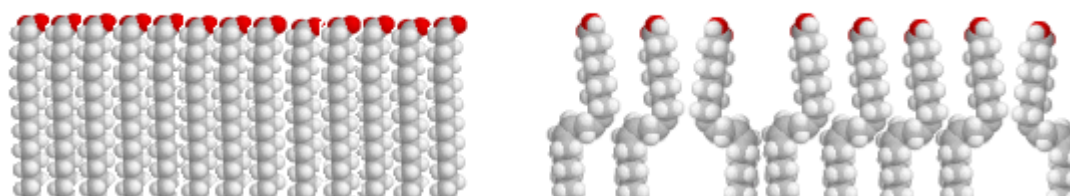
Molecules are locked in a lattice in the solid. This involves orientation.

Lattice prefers regular shapes.

Irregular shapes are liquids.

Fat

Oil



[http://bioweb.wku.edu/courses/BIOL115/Wyatt/Biochem/Lipid/Fat\\_oil.gif](http://bioweb.wku.edu/courses/BIOL115/Wyatt/Biochem/Lipid/Fat_oil.gif)

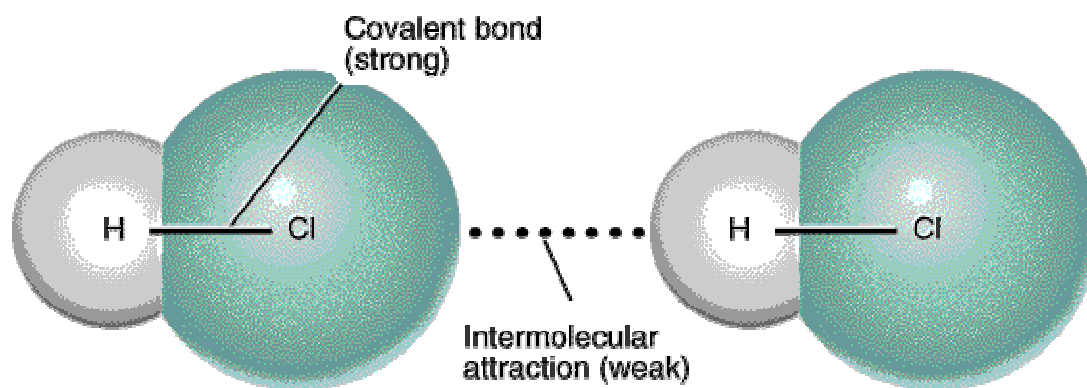
There are 3 main classes of intermolecular forces:

- **Dipole-Dipole** (permanent)
- **H-Bonding**: The elements N, O, and F can share H's between them. This is a very special force.
- **London, Van der Waals, or Dispersion** (induced dipole)

**Relative magnitudes of forces**

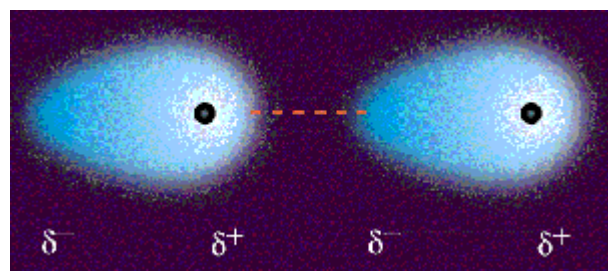
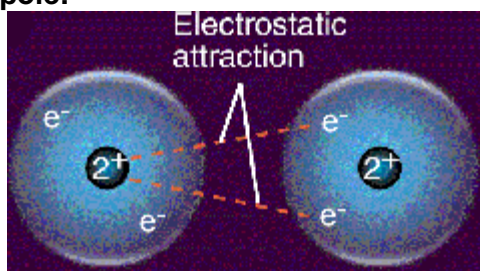
Attractive Force	Covalent bonds	H-bonding	Dipole-dipole	London forces
Energy	~100 kcal/mole	5-10 kcal/mole	< 5 kcal/mole	< 1 kcal/mole

What is the difference between intra and intermolecular forces?



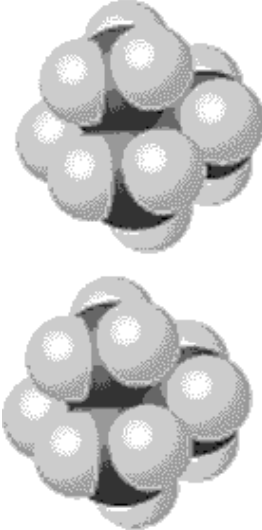
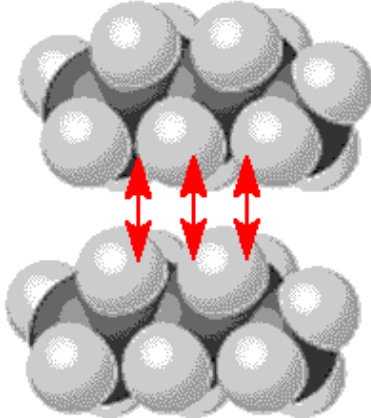
Picture from <http://scidiv.bcc.ctc.edu/wv/08/0008-0012-interforce.htm>

### Induced Dipole:



See <http://www.chm.bris.ac.uk/webprojects2003/swinerd/forces/forces.htm>

**Shape is important**, since the interactions between the two atoms or molecules depends on the surface area between the two bodies. These two molecules have the formula  $C_5H_{12}$

Sphere – Sphere = small contact area	Rod—Rod = large contact area
 <p data-bbox="342 1724 537 1787">Neopentane (bp = 282.7 K)</p>	<p data-bbox="829 1171 1453 1276"><b>Interactions between electron clouds increases with larger surface. There are more electron-electron interactions.</b></p>  <p data-bbox="987 1734 1193 1797"><i>n</i>-Pentane (bp = 309.4 K)</p>

## Boiling Point Trends of Compounds correlated to Molecular Mass ( )

**Increasing Size**

Atomic	Bp (C°)	Molecular	Bp (C°)
He (4)	-271	CH <sub>4</sub> (16)	-161
Ar (40)	-186	(CH <sub>3</sub> ) <sub>4</sub> C (72)	-9.5
Kr (83)	-153	(CH <sub>3</sub> ) <sub>4</sub> Si (88)	27
Xe (131)	-109	CCl <sub>4</sub> (154)	77

**Molecular Shape**

Spherical	Bp (C°)	Linear	Bp (C°)
(CH <sub>3</sub> ) <sub>4</sub> C (72)	9.5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> (72)	36
(CH <sub>3</sub> ) <sub>2</sub> CCl <sub>2</sub> (113)	69	Cl(CH <sub>2</sub> ) <sub>3</sub> Cl (113)	121
[(CH <sub>3</sub> ) <sub>3</sub> C] <sub>2</sub> (114)	106	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> (114)	126

**Molecular Polarity**

Non-polar	Bp (C°)	Polar	Bp (C°)
H <sub>2</sub> C=CH <sub>2</sub> (28)	-104	H <sub>2</sub> C=O (30)	-21
F <sub>2</sub> (38)	-188	CH <sub>3</sub> CH=O (44)	20
CH <sub>3</sub> C≡CCH <sub>3</sub> (54)	-32	(CH <sub>2</sub> ) <sub>3</sub> O (58)	50
CF <sub>4</sub> (88)	-130	(CH <sub>3</sub> ) <sub>2</sub> C=O (58)	56

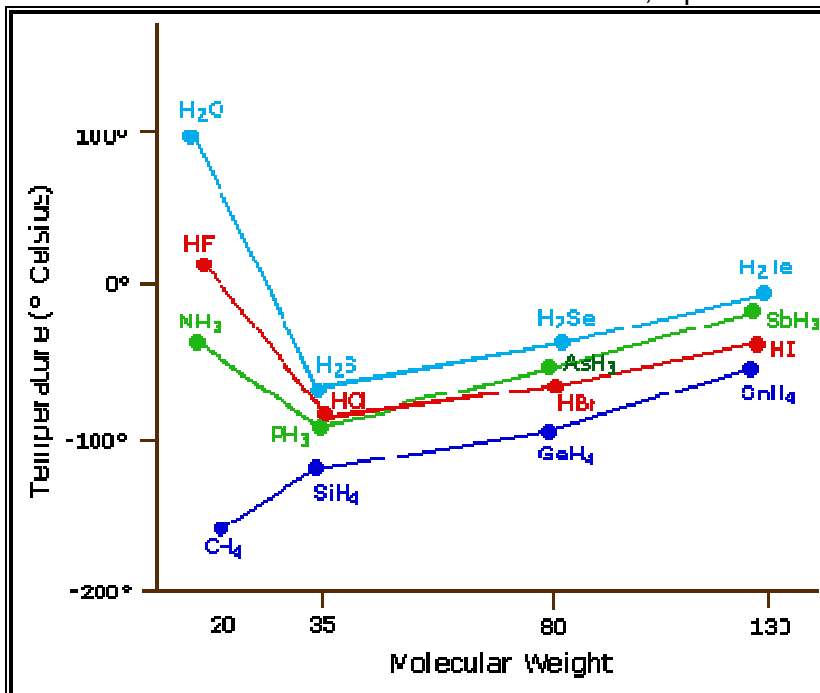
Table adapted from Bill Reusch, <http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4>

**H-Bonds** involve N, O, F sharing bonds with H.

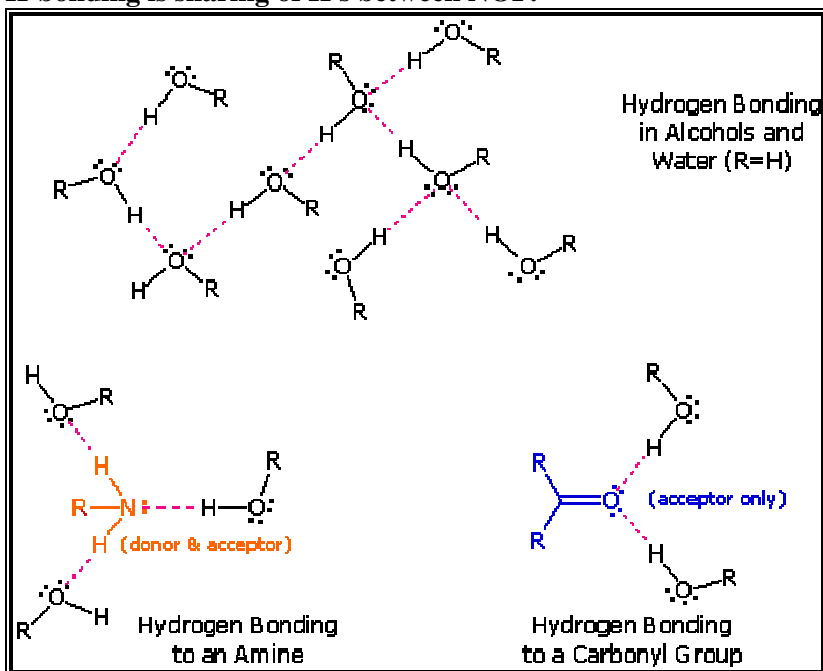
- H bonds are very strong and you always need to be on the lookout for H-bonds.
- H-bonds occur through LP electrons on the highly electronegative atom.
- When a H bonds to a LP, we call this a donor H-bond.
- When a LP bonds to a H, we can call this an acceptor H-bond.

H-bonds are the reason why water boils at such a high T.

Consider these trends of molecules that involve H-bonds, dipole and dispersion forces.



<http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4>

**H-bonding is sharing of H's between NOF.**

<http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4>

Determine if these molecules can be H-bond donors, acceptors or both.

H-F      H<sub>2</sub>S      H<sub>2</sub>O      CH<sub>3</sub>OH      H<sub>2</sub>C=O

CH<sub>3</sub>-O-CH<sub>3</sub>      (CH<sub>3</sub>)<sub>3</sub>N      CH<sub>3</sub>NH<sub>2</sub>      H<sub>2</sub>Se

Molecular Properties affected by Hydrogen Bonding				
Compound	Formula	Mol. Wt.	Boiling Point	Melting Point
Dimethyl ether	CH <sub>3</sub> OCH <sub>3</sub>	46	-24 °C	-138 °C
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	46	78 °C	-130 °C
Propanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	60	98 °C	-127 °C
Diethyl ether	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O	74	34 °C	-116 °C
Propyl amine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	59	48 °C	-83 °C
Methylaminoethane	CH <sub>3</sub> CH <sub>2</sub> NHCH <sub>3</sub>	59	37 °C	
Trimethylamine	(CH <sub>3</sub> ) <sub>3</sub> N	59	3 °C	-117 °C
Ethylene glycol	HOCH <sub>2</sub> CH <sub>2</sub> OH	62	197 °C	-13 °C
Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	60	118 °C	17 °C
Ethylene diamine	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	60	118 °C	8.5 °C

Table taken from Bill Reusch, <http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4>

True or False:

Dipole-Dipole is the strongest intermolecular force?

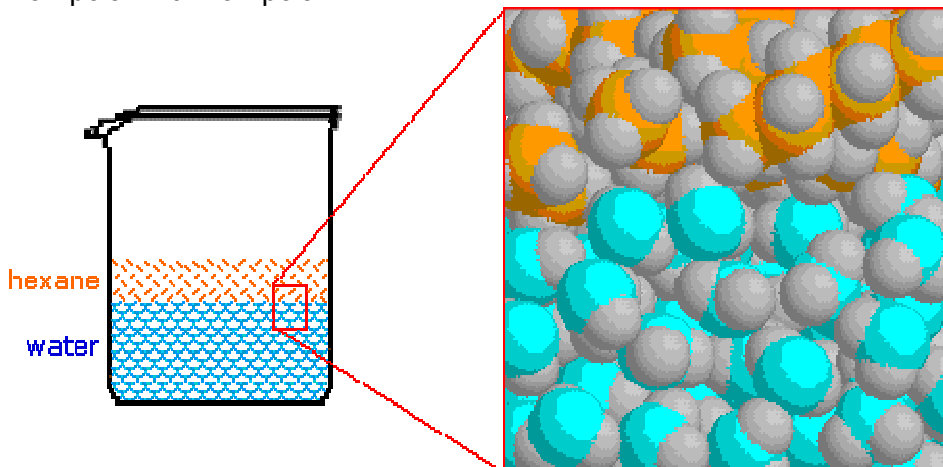
Electronegativity is the same thing as intermolecular force?

Boiling points increase as intermolecular forces increase?

Melting points increase as intermolecular forces increase?

A molecule with polar bonds must have high intermolecular forces?

**Solubility:** In general like dissolves like.  
Polar with polar. Non-polar with non-polar.



<http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp6>

Predict solubilities of the following in water.

NaCl

HCl (g)

$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$  hexane

$\text{CH}_3\text{OH}$  methanol

$\text{CH}_3\text{C}_6\text{H}_5$  toluene

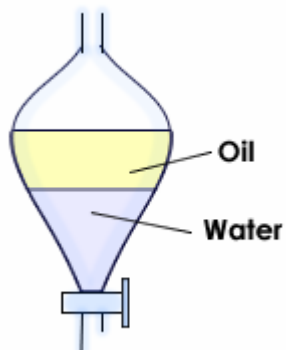
$\text{CH}_2\text{Cl}_2$  Dichloromethane

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  Diethyl ether

$\text{I}_2(\text{s})$

What organic functional groups are usually soluble in water?

### Liquid/Liquid Extraction



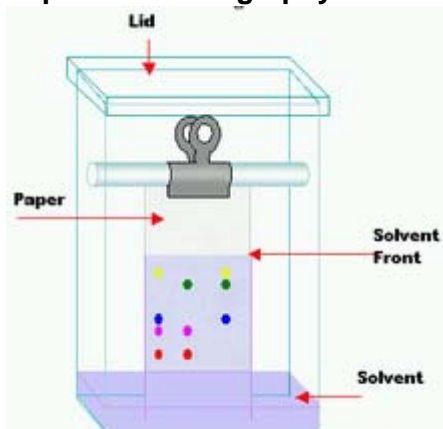
Here is the water/hexane (oil) system. Why is hexane on top?

If we put nonpolar solute in the system, which layer will it go to?

If we put polar solute in the system, which layer will it go to?

Image from [http://en.wikipedia.org/wiki/Separatory\\_funnel](http://en.wikipedia.org/wiki/Separatory_funnel)

### Paper Chromatography



Paper is polar. Solvent carries the solutes through the paper.

Which moves faster polar or non-polar solute?

Which moves slower polar or non-polar solute?

3 compounds have similar components:

Red, pink, blue, and green.

Which component is least polar?

Most polar?

[http://en.wikipedia.org/wiki/Paper\\_chromatography](http://en.wikipedia.org/wiki/Paper_chromatography)

**Classifying Polarity in Bonds in terms of Valence Bond Models****Formal Charges**

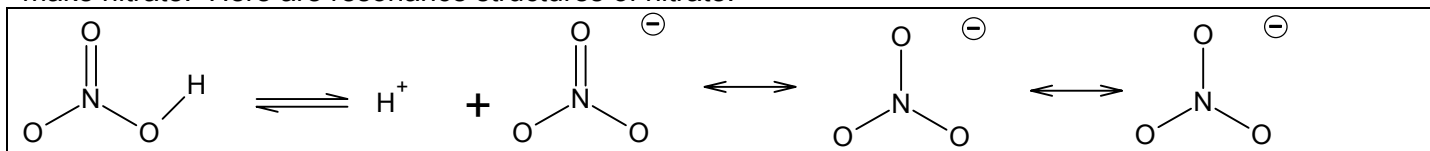
$$\text{Formal Charge} = \text{Valence Electrons in Neutral Atom} - \left( \text{Unshared Valence Electrons} + \text{Half of the Shared Electrons} \right)$$

or Half of the Shared Electrons = # of bonds.

Here is the acid dissociation reaction of the following oxoacids. You must supply the formal charges. Make sure there is charge balance both on molecule and in the reaction.

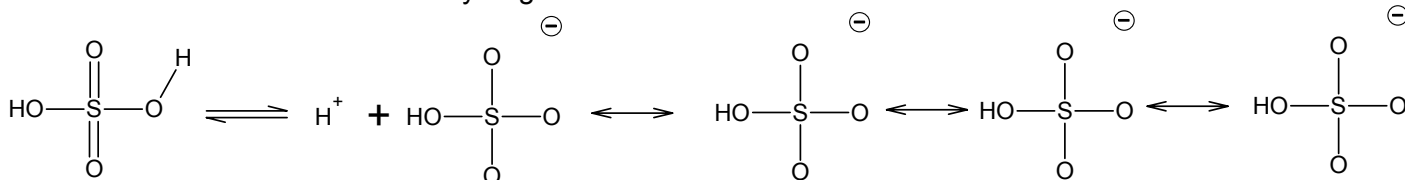
Nitric Acid  $\text{HNO}_3$  dissociates to

make nitrate. Here are resonance structures of nitrate.



Sulfuric Acid  $\text{H}_2\text{SO}_4$  dissociates to make hydrogensulfate.

Here are resonance structures of hydrogensulfate.



**Generally, the best Lewis structure has the least separation of formal charge!**

How does the overall charge of a molecule relate to the formal charge of individual atoms?

How does formal charge relate to number of bonds of individual atoms?

**Formal charge vs Oxidation State**

Formal charge is of how charge gets distributed in *pure* covalent compounds.

In *pure* ionic compounds, the atomic charge is thought of being split by oxidation number.

Which model is better at explaining charge separation in molecules? Oxidation or formal charge?

Consider water,  $\text{H}_2\text{O}$ , What is the oxidation state of H?

the oxidation of O?

Consider HCl. What is the oxidation state of H?

the oxidation state of Cl?

$\text{MgBr}_2$  What is the oxidation state of Mg?

the oxidation state of Br?

Consider Mn. What is the oxidation state of Mn?

The most oxidized form of Mn is permanganate,  $\text{MnO}_4^-$  What is the oxidation state of Mn?

Another form of Mn is  $\text{MnO}_2$ . What is the oxidation state of Mn?

$\text{CH}_4$

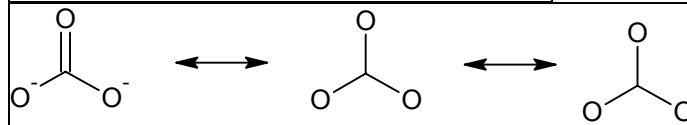
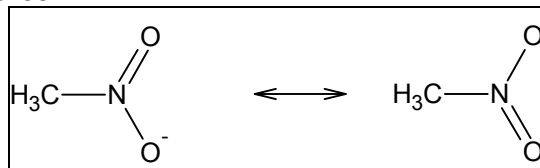
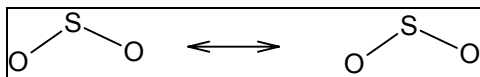
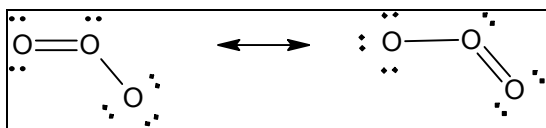
$\text{H}_2\text{C}=\text{O}$

the most oxidized form of C?



**Resonance**

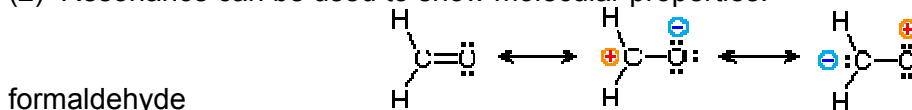
(1) Resonance repairs inadequacy of Lewis Structures.

Experimentally ozone and SO<sub>2</sub> is bent (bond angle 120°) and has equal length S--O bonds (143.2 pm).**Resonance hybrids** (the two structures) are always represented by a **double headed arrow**.Draw the resonance structures for cyanate, CNO<sup>-</sup>

Note formal charges.

What does this imply about the bond order of these molecules? Which structure is more important? Why?

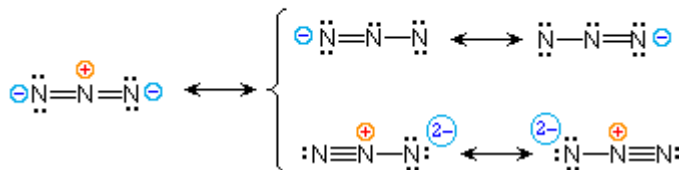
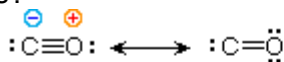
(2) Resonance can be used to show molecular properties:



formaldehyde

Which structure(s) are more important?

(3) Wacky resonance structures do not have much effect on the actual properties of the molecule. What is weird about these structures?

**Resonance Summary:**

Resonance structures involve molecules with the same molecular structure and number of electrons.

Resonance hybrids have different types of electronic localization.

The following factors are important in evaluating the contribution each of these canonical structures makes to the actual molecule.

1. **The number of covalent bonds in a structure.** (The greater the bonding, the more important and stable the contributing structure.)
2. **Formal charge separation.** (Other factors aside, charge separation decreases the stability and importance of the contributing structure.)
3. **Electronegativity of charge bearing atoms and charge density.** (High charge density is destabilizing. Positive charge is best accommodated on atoms of low electronegativity, and negative charge on high electronegative atoms.)

Based on <http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm#strc7>

Practice: For the compounds and ions listed below, write Lewis / Kekulé structures for as many reasonable canonical forms as you can.

Formic Acid  $\text{HCO}_2\text{H}$

Formate Anion  $\text{HCO}_2^{(-)}$

Nitromethane  $\text{CH}_3\text{NO}_2$

Methyl Nitrite  $\text{CH}_3\text{ON}=\text{O}$

Considering the resonance hybrid forms written here, which three of these compounds or ions will exhibit the greatest resonance stabilization?

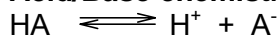
Practice: Reconsider the resonance of  $\text{HNO}_3$  and  $\text{HNO}_2$  and their anions. Which is the best structure for each?

True or False?

The more resonance structures you can draw for a molecule the more stable?

All resonance structures have the same effect on the actual structure of a molecule?

Resonance structures are important for chemical structure because electrons want to occupy the most number of positions in a molecule?

**Acid/Base chemistry is based on acid dissociation: We talk about Ka and pKa.**

$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  in general products / reactants.

Why don't we talk about  $pK_b$ ?

When is the ratio  $> 1$ ?

When is the ratio  $< 1$ ?

What about the  $\Delta G$ ? Remember  $\Delta G = -RT \ln K_a$

When is the ratio  $> 1$ ?

When is the ratio  $< 1$ ?

Some acid reactions are very favorable. What do we call this kind of acid? \_\_\_\_\_

Name the 6 main acids in this group? Are any organic acids?

The  $K_a$  of a strong acid is  $10^{+x}$

Are the  $pK_a$ 's of strong acids positive or negative?

pKa Acidities of Some Common Hydrides							
Gr 4	pKa	Gr 5	pKa	Gr 6	pKa	Gr 7	pKa
CH <sub>3</sub> -H	ca. 50	NH <sub>2</sub> -H	34	HO-H	15.74	F-H	3.2
Not important for this course.				HS-H	6.97 (pK1)	Cl-H	-3
				Hse-H	3.8 (pK1)	Br-H	-6
				Hte-H	2.6 (pK1)	I-H	-7

pKa of neutral hydrides above and selected charged hydrogen compounds below.

NH <sub>4</sub> <sup>(+)</sup>	9.24	OH <sub>3</sub> <sup>(+)</sup>	-1.74	S-H <sup>(-)</sup>	15 (pK2)	Se-H <sup>(-)</sup>	11 (pK2)
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<http://www.cem.msu.edu/~reusch/VirtualText/suppmnt2.htm#top4>

The main X-H bonds in organic chemistry are C-H, N-H, O-H. Rank them in acidity:

Now let's look at the acidity of H in respect to X-H bond. With respect to elements, what determines the acid strength? \_\_\_\_\_.

Make sure that you understand this order and what the pKa means.

C-H depends on the electronic state of C? How do we classify these hybrid states?

Of the three states above, rank them in order of acidity: (p.287)

Typical pKa's of these acids are approximately

CH<sub>4</sub> 50                      H<sub>2</sub>C=CH<sub>2</sub> 45                      HC≡CH 25

Now let's review magnitudes.  $10^x$

A photon of light is about  $10^x$  m

A pore in a good water purifier is  $10^x$  m

The thickness of this paper is about  $10^x$  m

The length of a child is about  $10^x$  m

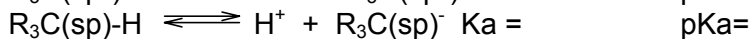
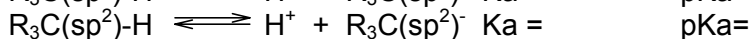
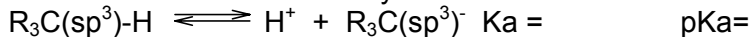
The number of students in this OCHEM course is about  $10^x$

The thickness of McMurray is about  $10^x$  pages

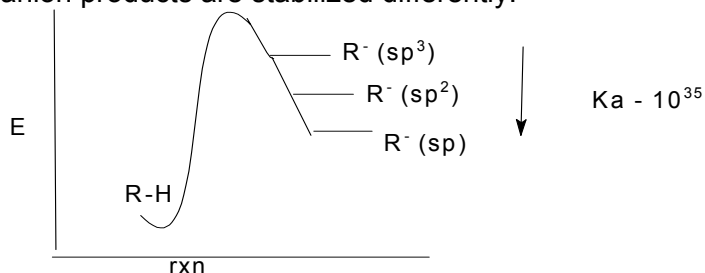
The federal deficit is about  $\$10^x$

**Unlikely acids**

Most C-H acids are extremely weak.



We explain this based on the stability of the anion. The C-H species are all about the same stability, but the anion products are stabilized differently.



N-H acids,

What are some N-H acids?

pKa's of N-H:

pKa's of  $N^+-H$

O-H acids?

What are some O-H acids?

pKa's of O-H:

pKa's of  $O^+-H$

**Summary of weak acids**

C-H

N-H

O-H

$N^+-H$

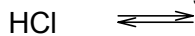
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 $O^+-H$

What about other strong acids.

**Equilibrium and predicting reaction**

To calculate the extent of an acid base reaction is crucial.

Given  $pK_a(HCl) = -5$  and  $pK_a(H_2O) = 16$  and  $pK_a(NH_3) = 33$ .  $pK_a(NH_4^+) = 9$ . Note N-H can have more than one acid strength depending if N is neutral or positive. Write these reactions as ionization reactions.



**Strategy:** (1) Find the acid on left and conjugate acid (CA) on right. (2) The reaction proceeds towards the side with the highest pKa. (3) The magnitude of the  $K_{eq} = 10^{+ \text{ or } - (pK_{a1} - pK_{a2})}$ .

Left = -, Right = +. This can be derived algebraically. Anyway you want, you're going to have to predict it.

**Reactions.**

$\text{HO}^- + \text{H-Cl} \rightleftharpoons \text{H-OH} + \text{Cl}^-$  Which direction and what will be the magnitude of the  $K_{\text{eq}}$ ?

$\text{HC}\equiv\text{C-H} + \text{OH}^- \rightleftharpoons \text{H-OH} + \text{HC}\equiv\text{C}^-$  Which direction will this reaction go and what will be the magnitude of the  $K_{\text{eq}}$ ?

$(\text{Acetylene})\text{C-H} + \text{NH}_2^- \rightleftharpoons \text{H-NH}_2 + \text{HC}\equiv\text{C}^-$  Which direction will this reaction go and what will be the magnitude of the  $K_{\text{eq}}$ ?

**Practice:**

(1) Write the reaction of amide + ammonium and predict the direction.

(2) Given methanol  $\text{CH}_3\text{OH}$   $\text{pK}_a = 16$  and water  $\text{pK}_a = 16$ . Why can  $\text{NaOH}$  not completely deprotonate methanol?

(3) Hydride is a strong base,  $\text{H}^-$ . What is the CA of hydride? That acid has a  $\text{pK}_a$  of 38.

**Extension to Organic Chemistry:**

Acid/Base	Organic Chemistry
Acid = $\text{H}^+$	Electrophile = $\text{E}^+$
Base => goes after $\text{H}^+$	Nucleophile => goes after Nucleus

**Summaries:**

1. What is an ionic bond? A covalent bond? a polar bond? A non-polar bond?
2. When is a molecule polar? When is a molecule nonpolar?
3. Be able to predict trends in electronegativity of atoms – going down and across the periodic table..
4. Determine dipole moments and direction of the dipole vector based on electronegativity of atoms and the  $\delta^+$  and  $\delta^-$ .
5. Know the 3 intermolecular forces. How do intermolecular forces affect boiling and melting points.
6. Predict trends in intermolecular forces of molecules that contain atoms going across or down the periodic table.
7. Understand volatility. Be able to predict the volatility of molecules based on intermolecular forces.
8. Predict solubility of molecules in water based on molecular similarity.
9. Be able to calculate formal charges of atoms in molecules. You should be able to write structures with correct formal charge.
10. Be able to write resonance structures.
11. Determine if a resonance structure is important for representing the properties of a molecule.
12. Know approximate  $\text{pK}_a$ 's of C-H, N-H and O-H.
14. Be able to explain why  $\text{C}\equiv\text{C-H}$  is more acidic than  $(\text{sp}^3)\text{C-H}$
15. Know the strong acids. What kind of acids are most organic compounds? What is the significance of this fact?
16. Be able to predict trends in  $\text{pK}_a$ 's of Y-H bonds going across or down the periodic table.
17. Be able to predict the direction and magnitude of reactions based on  $\text{pK}_a$ 's of the acid and conjugate acids.