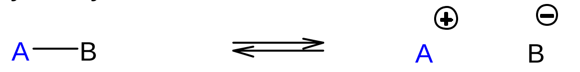
Chapter 2: The Nature of Bonds and Structure of Organic Molecules

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.



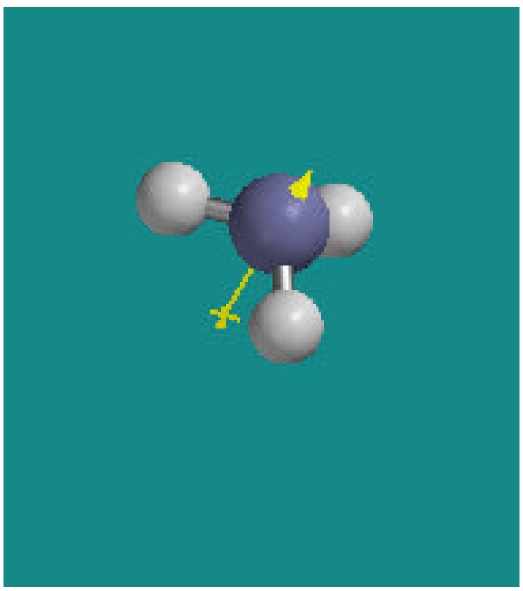
covalent
low EN difference

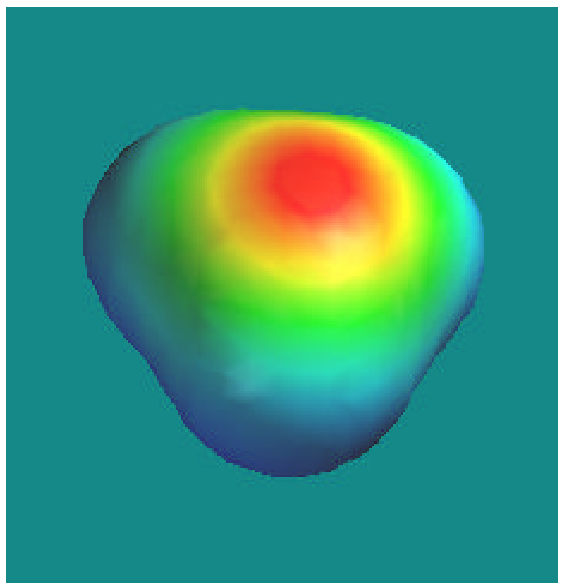
ionic
large EN difference

What is the definition of electronegativity?

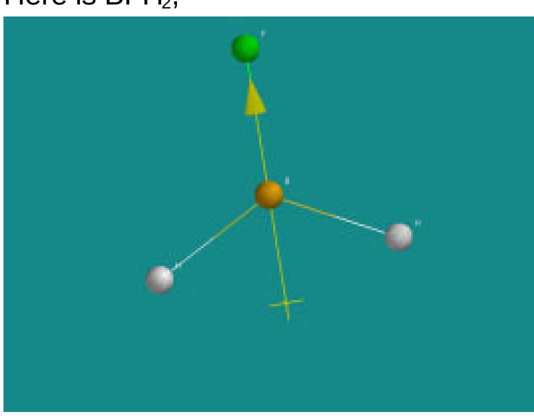
What is a dipole? A dipole μ is proportional to the charge x charge x distance between them. The dipole moment is drawn as a crossed arrow with the direction going towards the positive end of the molecule. Here are some examples:

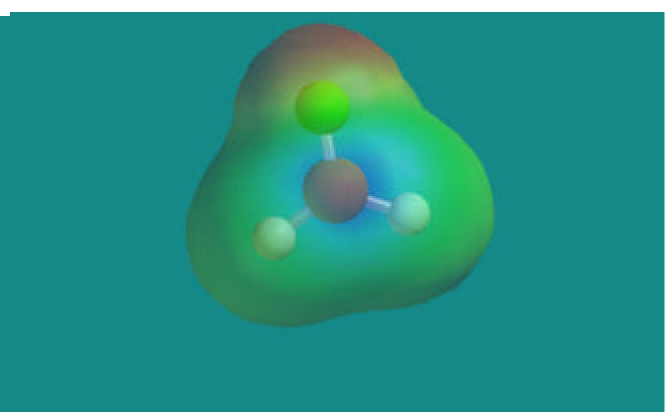
Ammonia :NH_3 On the left, there is the dipole arrow. Right, there is charge density picture with red indicating negative charge and blue indicating positive.





Here is BFH_2,





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

Non-polar covalent

Polar covalent

Ionic

Metals and Non-Metals
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

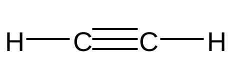
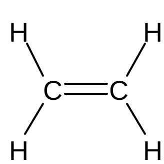
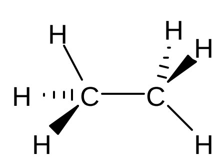
Classify these ficticious bonds as non-polar or polar and if polar show the d+ and d-.

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

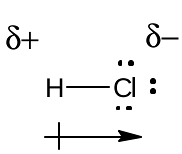
For some real bonds. Classify as non-polar or polar and if polar show the d+ and d-.

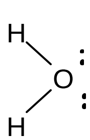
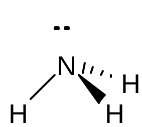
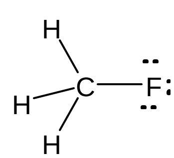
C – N	C -- H	B – H	Al – H	C – O	C – F	Li -- H
F -- F	B – Cl	Li – Al	Al – O	B – O	Li – Li	C – Li

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:

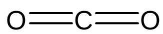
How about molecules with polar bonds: Here the polar vectors must be added based on the shape. Here are some simple examples.

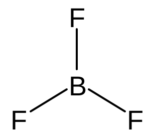


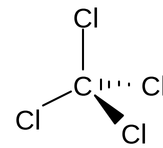




Polar Covalent Bonds and Polar Molecules.

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







Shape

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:

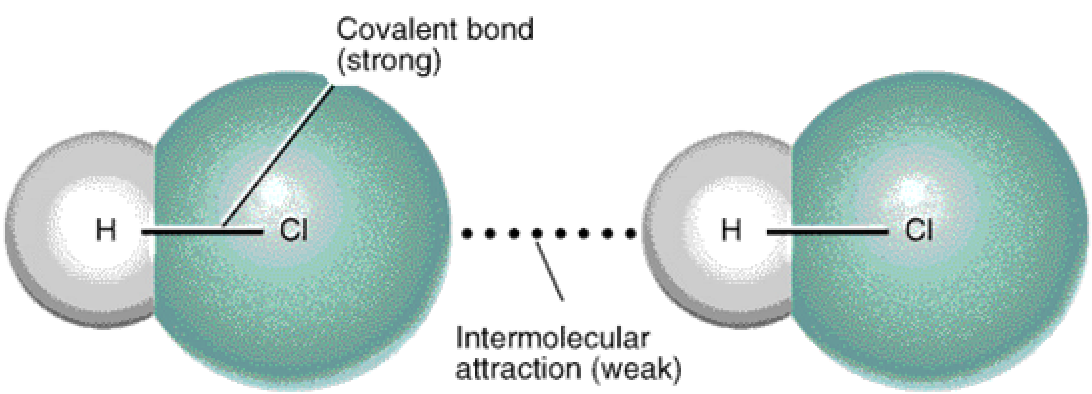
Physical property	Low	High
Melting point	Strong Weak Forces	Strong Weak Forces
Boiling point	Strong Weak Forces	Strong Weak Forces

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)

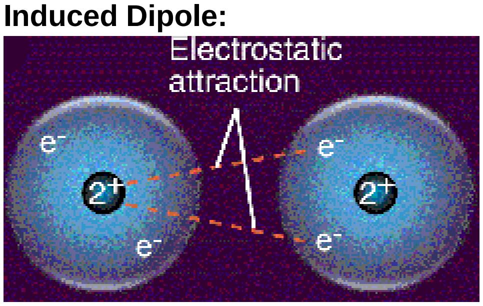
Relative magnitudes of forces

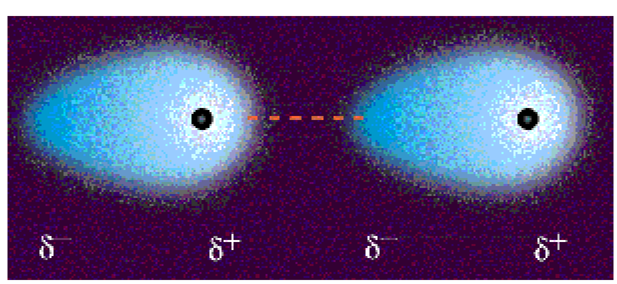
Attractive Force	Covalent bonds	H-bonding	Dipole-dipole	London forces
Energy	~100 kcal/mole	5-10 kcal/mole	< 5 kcal/mole	< 1 kcal/mole



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

Induced Dipole:

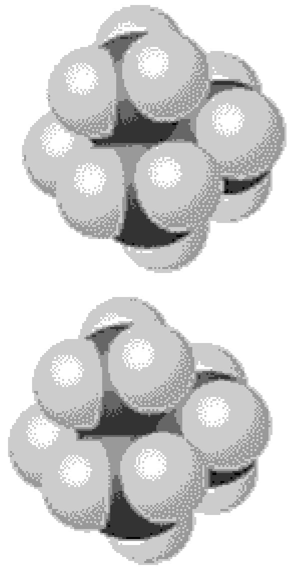
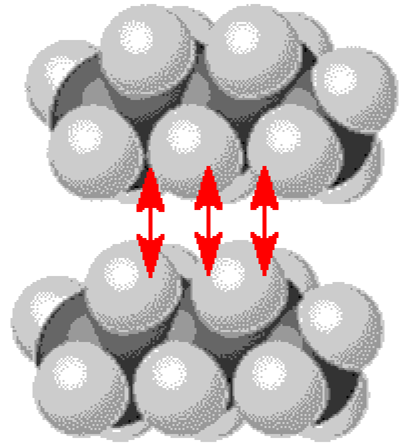




See http://www.chm.bris.ac.uk/webprojects2003/swinerd/forces/forces.htm

Shape and Size

Since the interactions between the two atoms or molecules depends on the surface area between the two bodies, the **shape** is important:

Sphere – Sphere = small contact area	Rod—Rod = large contact area
 Neopentane (bp = 282.7 K)	Interactions between electron clouds increases with larger surface. There are more electron-electron interactions.  *n*-Pentane (bp = 309.4 K)

Boiling Points (ºC) of Selected Elements and Compounds --Mass in ()

Increasing Size

Atomic	Ar (40) -186	Kr (83) -153	Xe (131) -109	
Molecular	CH_4 (16) -161	$(CH_3)_4C$ (72) 9.5	$(CH_3)_4Si$ (88) 27	CCl_4 (154) 77

Molecular Shape

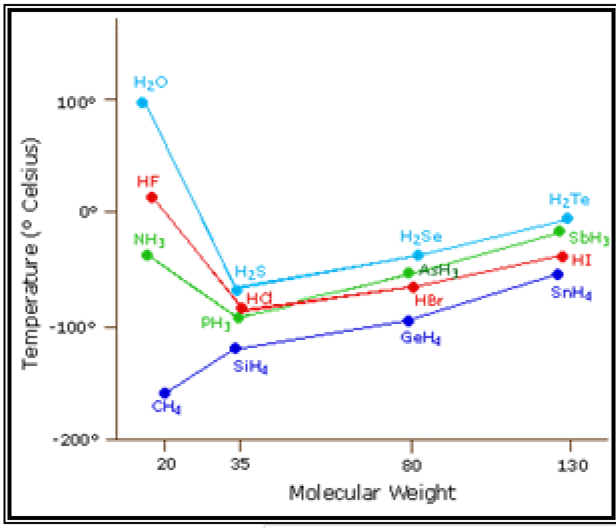
Spherical:	$(CH_3)_4C$ (72) 9.5	$(CH_3)_2CCl_2$ (113) 69	$(CH_3)_3CC(CH_3)_3$ (114) 106
Linear:	$CH_3(CH_2)_3CH_3$ (72) 36	$Cl(CH_2)_3Cl$ (113) 121	$CH_3(CH_2)_6CH_3$ (114) 126

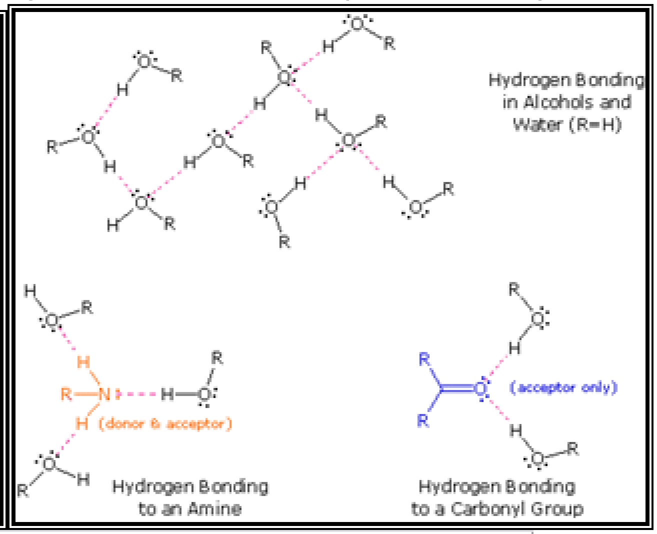
Molecular Polarity

Non-polar:	$H_2C{=}CH_2$ (28) -104	F_2 (38) -188	$CH_3C{=}CCH_3$ (54) -32	CF_4 (88) -130
Polar:	$H_2C{=}O$ (30) -21	$CH_3CH{=}O$ (44) 20	$(CH_3)_3N$ (59) 3.5	$(CH_3)_2C{=}O$ (58) 56
	$HC{=}N$ (27) 26	$CH_3C{=}N$ (41) 82	$(CH_2)_3O$ (58) 50	CH_3NO_2 (61) 101

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

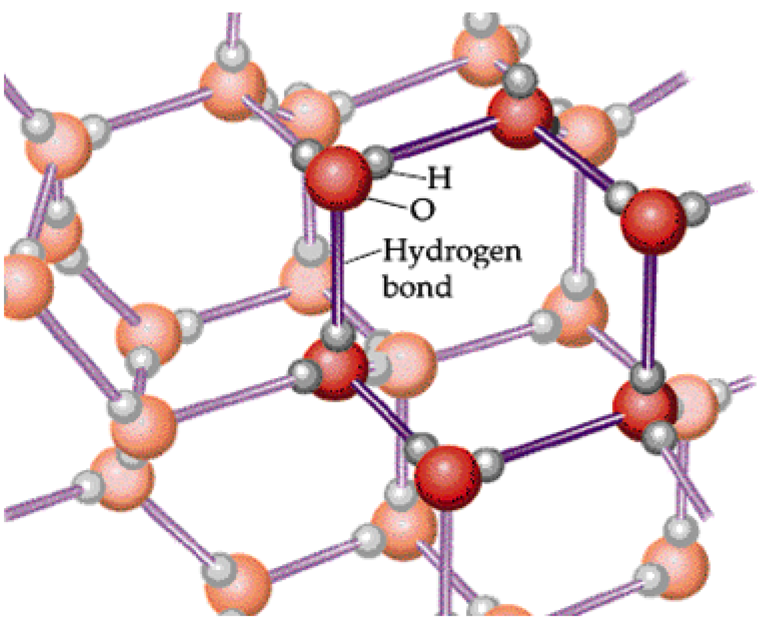
H-Bonds Boiling points of compounds containing N, O, F—H bonds compared to analogs.





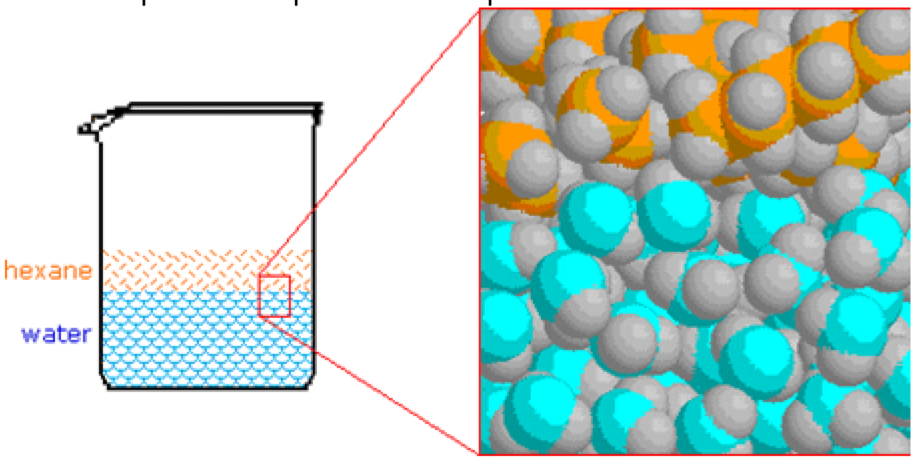
Compound	Formula	Mol. Wt.	Boiling Point	Melting Point
dimethyl ether	CH_3OCH_3	46	–24 ºC	–138 ºC
Ethanol	CH_3CH_2OH	46	78 ºC	–130 ºC
Propanol	$CH_3(CH_2)_2OH$	60	98 ºC	–127 ºC
diethyl ether	$(CH_3CH_2)_2O$	74	34 ºC	–116 ºC
propyl amine	$CH_3(CH_2)_2NH_2$	59	48 ºC	–83 ºC
Methylaminoethane	$CH_3CH_2NHCH_3$	59	37 ºC	
Trimethylamine	$(CH_3)_3N$	59	3 ºC	–117 ºC
Ethylene glycol	$HOCH_2CH_2OH$	62	197 ºC	–13 ºC
Acetic acid	CH_3CO_2H	60	118 ºC	17 ºC
ethylene diamine	$H_2NCH_2CH_2NH_2$	60	118 ºC	8.5 ºC

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



Cutout of the H-bonding in ice – responsible for the interesting structure of snow flakes

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.

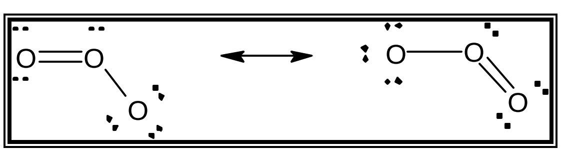
NaCl
HCl
$CH_3(CH_2)_5CH_3$ hexane
$CH_3C_6H_5$ toluene
CH_2Cl_2 Dichloromethane
$CH_3CH_2OCH_2CH_3$ Diethyl ether

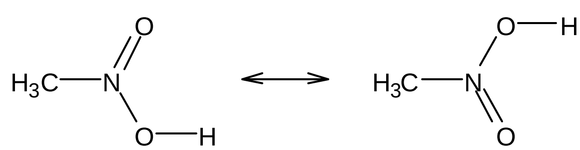
What functional groups are exceptions?

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

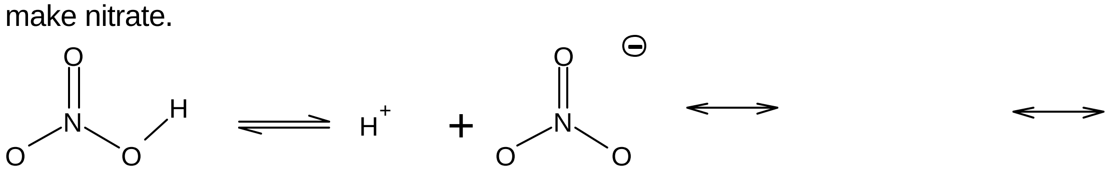
$$\text{Formal Charge} = \text{Valence Electrons in Neutral Atom} - \left(\text{Unshared Valence Electrons} + \text{Half of the Shared Electrons} \right)$$

or Half of the Shared Electrons = # of bonds.

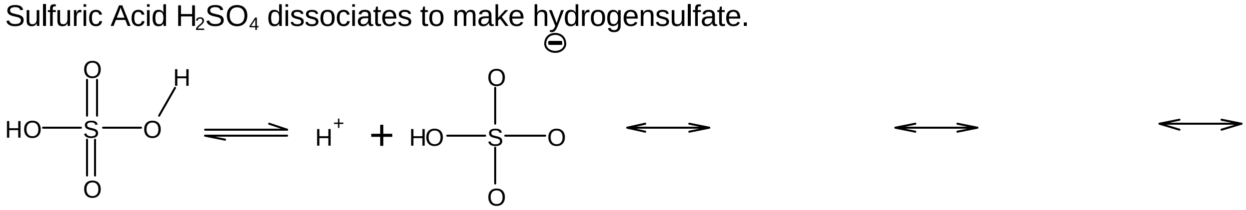




Here is the acid dissociation reaction of the following oxoacids. You must supply the formal charges. Make sure there is charge balance both on molecule and in the reaction. Nitric Acid HNO_3 dissociates to make nitrate.

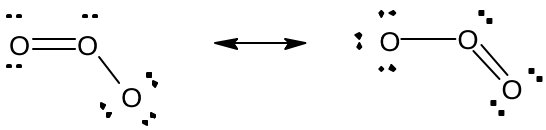


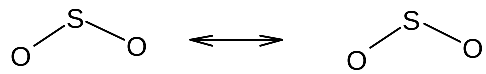
Sulfuric Acid H_2SO_4 dissociates to make hydrogensulfate.



Resonance

(1) Resonance repairs inadequacy of Lewis Structures.

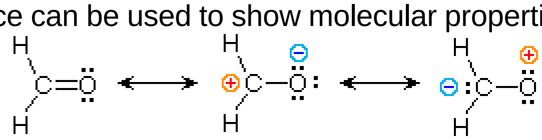




Experimentally ozone and SO_2 is bent (bond angle 120º) and has equal length S--O bonds (143.2 pm).
Resonance hybrids (the two structures) are always represented by a **double headed arrow**.
Draw the resonance structures for cyanate, $CNO^{(-)}$
Note formal charges.

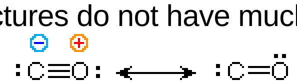
What does this imply about the bond order of these molecules? Which structure is more important? Why?

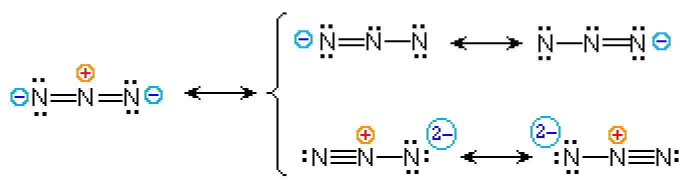
(2) Resonance can be used to show molecular properties:



formaldehyde
Which structures are more important?

(3) Wacky resonance structures do not have much effect.





Which structures of azide, N_3^- are important contributors? Which ones are not?

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 HCO_2H

Formate Anion $HCO_2^{(-)}$

Nitromethane CH_3NO_2

Methyl Nitrite $CH_3ON{=}O$

Diazomethane $CH_2{=}N{=}N$

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 HNO_3, HNO_2, and H_2SO_4 and their anions. Which is the best structure?

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

$HA \rightleftharpoons H^+ + A^-$

$Ka = [H^+][A^-]/[HA]$ 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 ΔG? Remember $\Delta G = -RTlnKa$
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 Ka of a strong acid is 10^{+x} Therefore, the pKa is positive or negative?

pKa Acidities of Some Common Hydrides

4	5	6	7
CH3-H ca. 50	NH2-H 34	HO-H 15.74	F-H 3.2
		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 compounds below.

$NH_4^{(+)}$ 9.24	$OH_3^{(+)}$ -1.74	$S\text{-}H^{(-)}$ 15 (pK2)	. $Se\text{-}H^{(-)}$ 11 (pK2)

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_4 50 $H_2C{=}CH_2$ 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

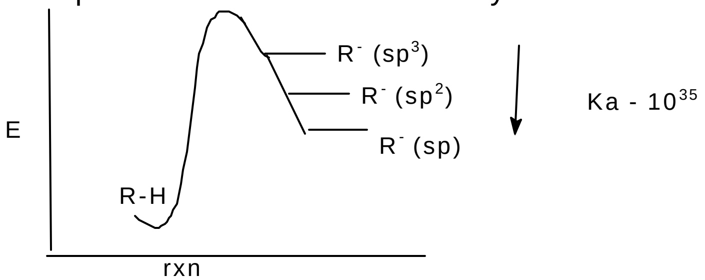
Most C-H acids are extremely weak.

$R_3C(sp^3)\text{-}H \rightleftharpoons H^+ + R_3C(sp^3)^-$ Ka = pKa=

$R_3C(sp^2)\text{-}H \rightleftharpoons H^+ + R_3C(sp^2)^-$ Ka = pKa=

$R_3C(sp)\text{-}H \rightleftharpoons H^+ + R_3C(sp)^-$ Ka = pKa=

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

Equilibrium and predicting reaction

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

Given pKa(HCl) = -5 and pKa(H_2O) = 16 and pKa(NH_3) = 33. pKa(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.

HCl $\rightleftharpoons$

H_2O $\rightleftharpoons$

NH_3 $\rightleftharpoons$

NH_4^+ $\rightleftharpoons$

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 Keq = $10^{+ \text{ or } -(pKa1-pKa2)}$. Left = -, Right = +. This can be derived algebraicly. Anyway you want, you're going to have to predict it.

Reactions.

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

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

(Acetylene)C-H + NH_2^- $\rightleftharpoons$ H-NH_2 + HCC^- Which direction will this reaction go and what will be the magnitude of the K_{eq}?

Practice:

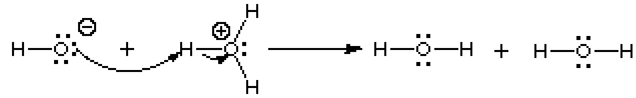
(1) Write the reaction of amide + ammonium and predict the direction.
(2) Given methanol CH_3OH pKa = 16 and water pKa = 16. Why can NaOH not completely deprotonate methanol?
(3) Hydride is a strong base, $H:^-$. What is the CA of hydride? That acid has a pKa of 38.

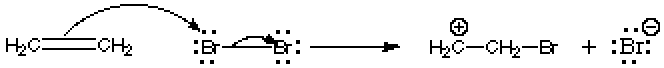
Extension to Organic Chemistry.

Acid/Base	Organic Chemistry
Acid = H^+	Electrophile = E^+
Base => goes after H^+	Nucleophile => goes after Nucleus

Introduction to Arrow Pushing:

Always draw the arrows from LP or bonds towards nuclei.

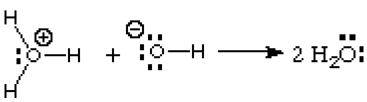


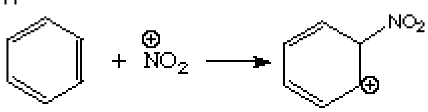


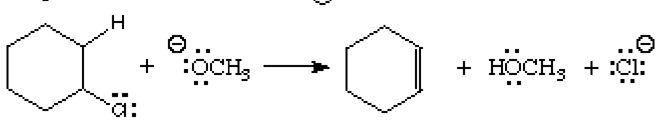
- New bonds are *formed* whenever a pair of electrons in a bond or LP is pushed towards a new atom; the flow is from **–** to **+.**
- A bond is *broken* when the electrons are pushed away from an atom in the bond. In the worked examples above note which bonds are formed and which bonds are broken.
- Note that formal charges often develop from arrow pushing. Formal charge is either calculated or just reasoned: if an atom gains an electron, it becomes -1; if an atom loses an electron, it becomes +1.

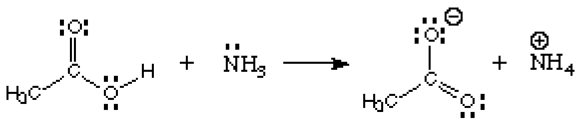
Additional practice is available from: http://www.abdn.ac.uk/curly-arrows/

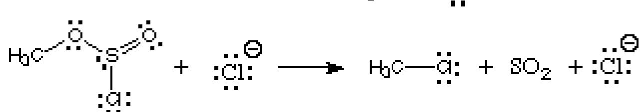
Provide arrows. Identify the nucleophile and the electrophile.

a. 

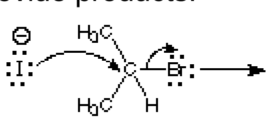
b. 

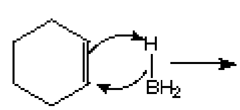
c. 

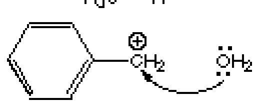
d. 

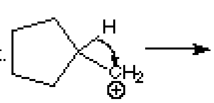
e. 

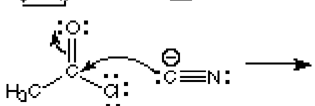
Provide products:

f. 

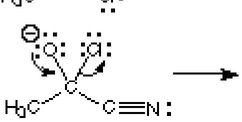
j. 

g. 

k. 

h. 

l. 

i. 

Figures from *Steven A. Hardinger and Harcourt Brace & Company* Answers available at http://web.chem.ucla.edu/%7Eharding/tutorials/curvedarrows/curvedarrows.html