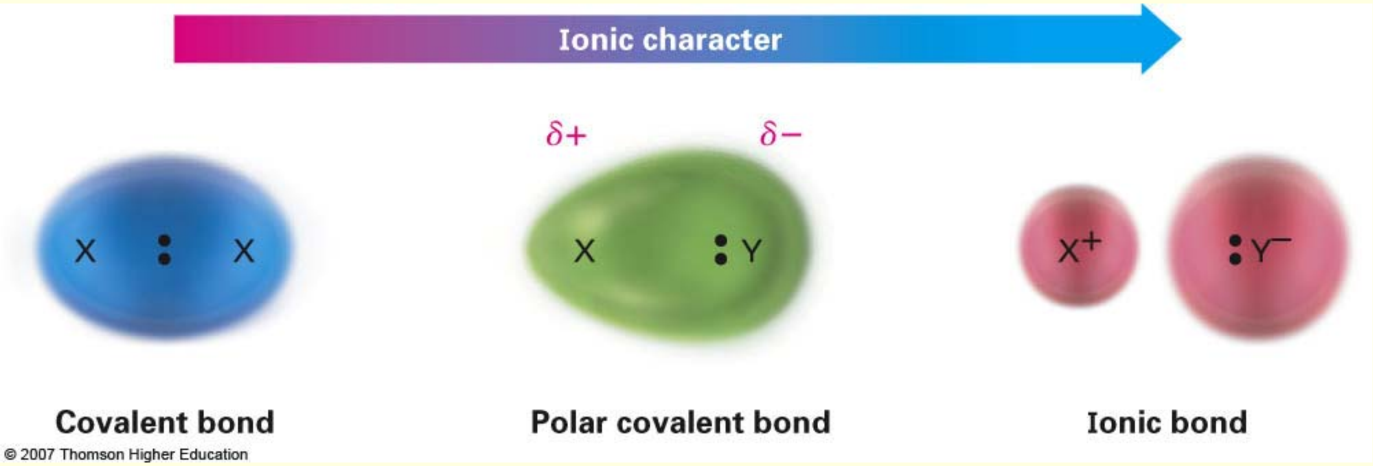
Polar Covalent Bonds: Electronegativity

- Covalent bonds can have ionic character
- These are **polar covalent bonds**
  - Bonding electrons attracted more strongly by one atom than by the other
  - Electron distribution between atoms is not symmetrical



Bond Polarity and Electronegativity

Symmetrical Covalent Bonds

C – C

C – H

(non-polar)

Polar Covalent Bonds

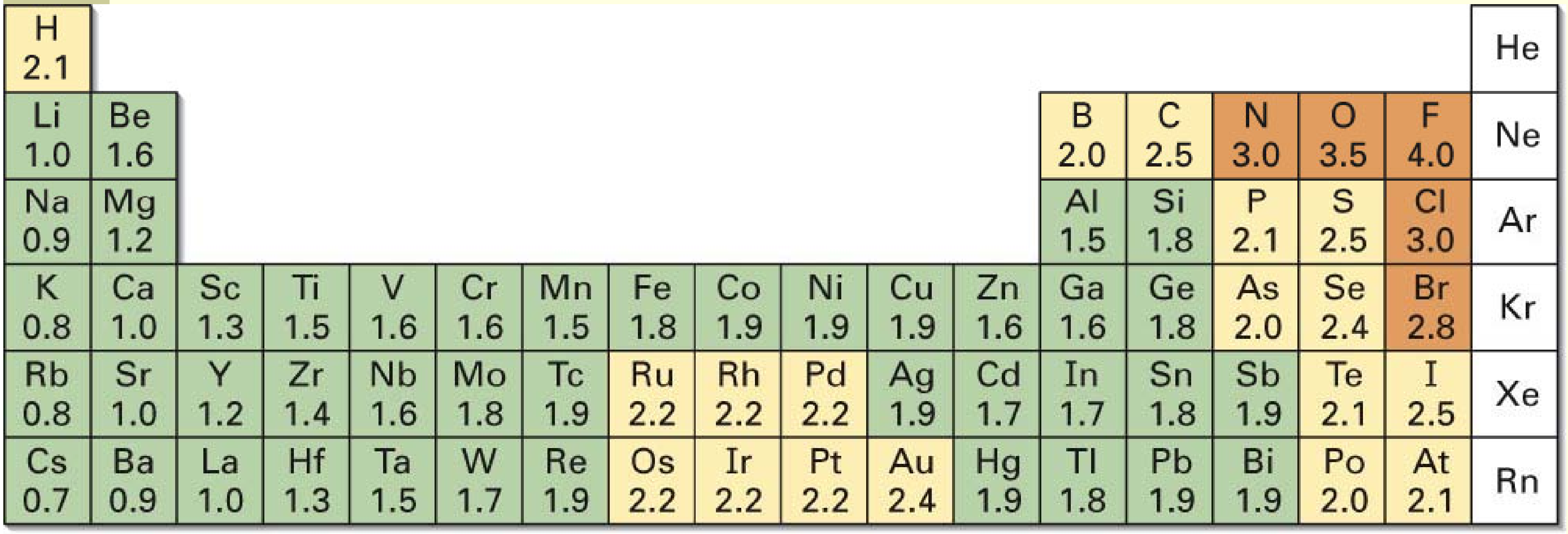
$^{\delta+}\mathrm{C} - \mathrm{O}^{\delta-}$

$+\!\!\!\longrightarrow$

(polar)

- **Electronegativity (EN):** intrinsic ability of an atom to attract the shared electrons in a covalent bond
- **Inductive Effect:** shifting of sigma bonded electrons in response to nearby electronegative atom

The Periodic Table and Electronegativity



H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

C – H
(non-polar)

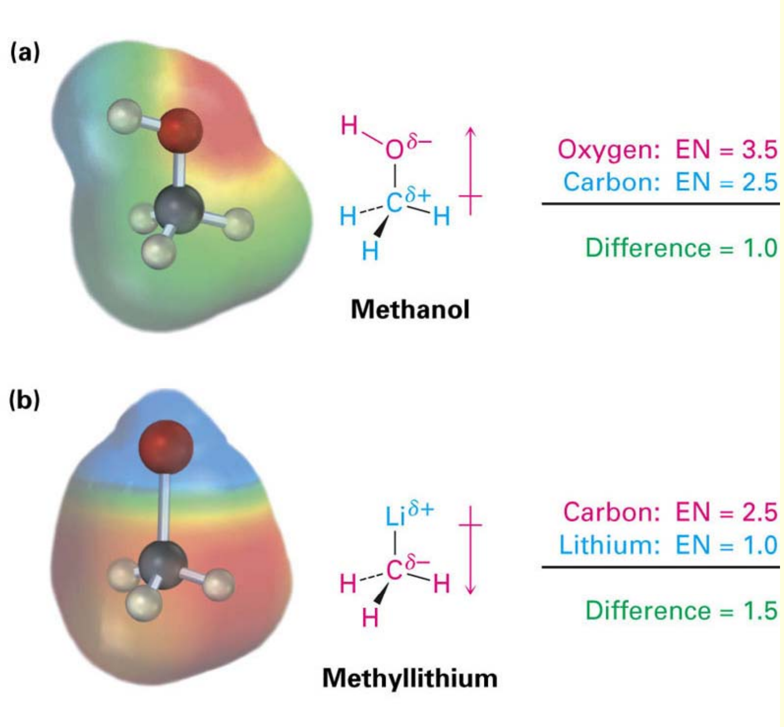
C - Br and C - I
(polar)

Bond Polarity and Inductive Effect

- **Nonpolar Covalent Bonds**: atoms with similar EN
- **Polar Covalent Bonds**: Difference in EN of atoms < 2
- Ionic Bonds: Difference in EN > 2
  - C–H bonds, relatively nonpolar C-O, C-X bonds (*more* electronegative elements) are polar
- Bonding electrons shift toward electronegative atom
  - C acquires partial positive charge, $\delta+$
  - Electronegative atom acquires partial negative charge, $\delta-$
- **Inductive effect:** shifting of electrons in a bond in response to EN of nearby atoms

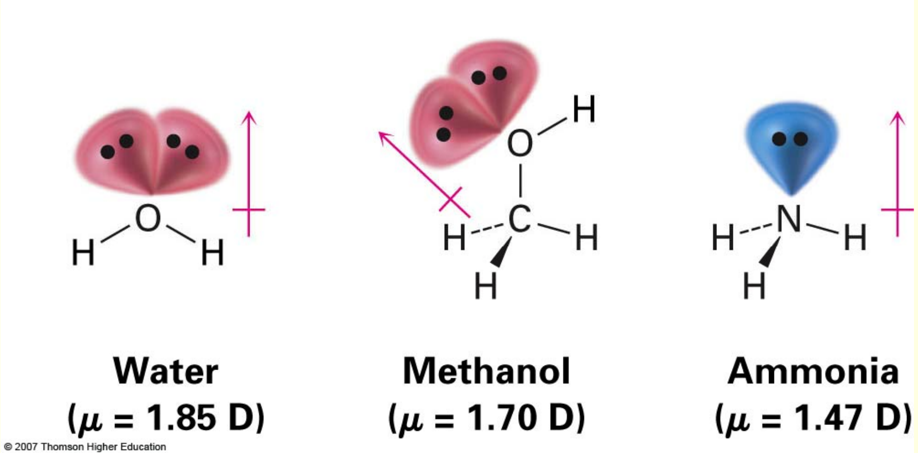
Electrostatic Potential Maps

- **Electrostatic potential maps** show calculated charge distributions
- Colors indicate electron-rich (red) and electron-poor (blue) regions
- Arrows indicate direction of bond polarity



Polar Covalent Bonds: Net Dipole Moments

- Molecules as a whole are often polar from vector summation of individual bond polarities and lone-pair contributions
- Strongly polar substances soluble in polar solvents like water; nonpolar substances are insoluble in water.
- **Dipole moment (μ) -** Net molecular polarity, due to difference in summed charges
  - μ - magnitude of charge *Q* at end of molecular dipole times distance *r* between charges
    - $\mu = Q \times r$, in *debyes* (D), 1 D = 3.336 × 10–30 coulomb meter
    - length of an average covalent bond, the dipole moment would be 1.60 × 10–29 C·m, or 4.80 D.



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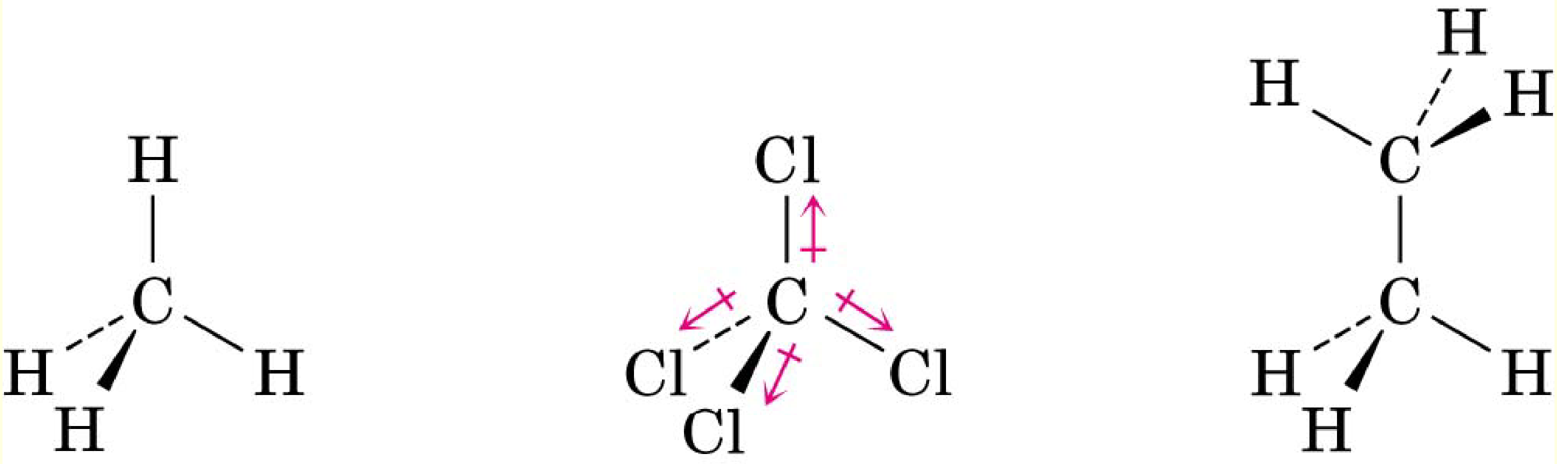
Absence of Net Dipole Moments

- In symmetrical molecules, the dipole moments of each bond has one in the opposite direction
- The effects of the local dipoles cancel each other



Methane (**$\mu = 0$ D**)

Tetrachloromethane (**$\mu = 0$ D**)

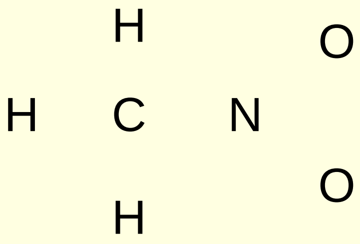
Ethane (**$\mu = 0$ D**)

Drawing Lewis Structures

- **Draw molecular skeleton:** this will come with practice, remember atom valence
- **Determine number of available valence electrons:** add an electron for each negative charge, remove an electron for each positive charge
- **Draw all single covalent bonds and lone pairs:** give as many atoms as possible full octets, assigning lone pairs to most electronegative atoms
- **Convert lone pairs to multiple bonds if needed:** to satisfy octet rule for as many atoms as possible
- **Assign formal charges to all atoms:** the sum of all charges must equal total charge of the molecule

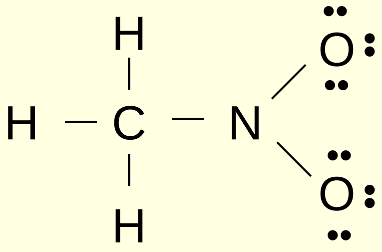
Example: Nitromethane: CH_3NO_2

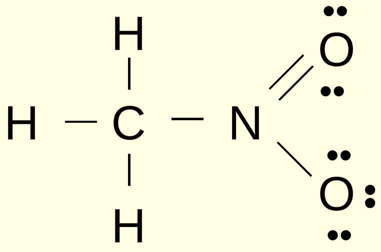
Step 1&2



Valence E = 3(1) + 1(4) + 1(5) + 2(6) = 24 e^-

Step 3&4

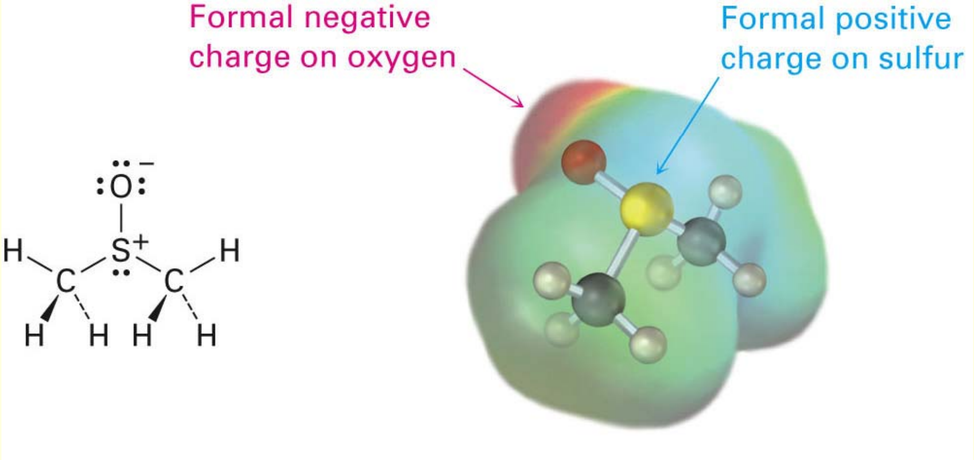




Step 5……………

Formal Charges

- Sometimes it is necessary to have structures with *formal charges* on individual atoms
- We compare the bonding of the atom in the molecule to the valence electron structure
- If the atom has one more electron in the molecule, it is shown with a "-" charge
- If the atom has one less electron, it is shown with a "+" charge
- Neutral molecules with both a "+" and a "-" are **dipolar**

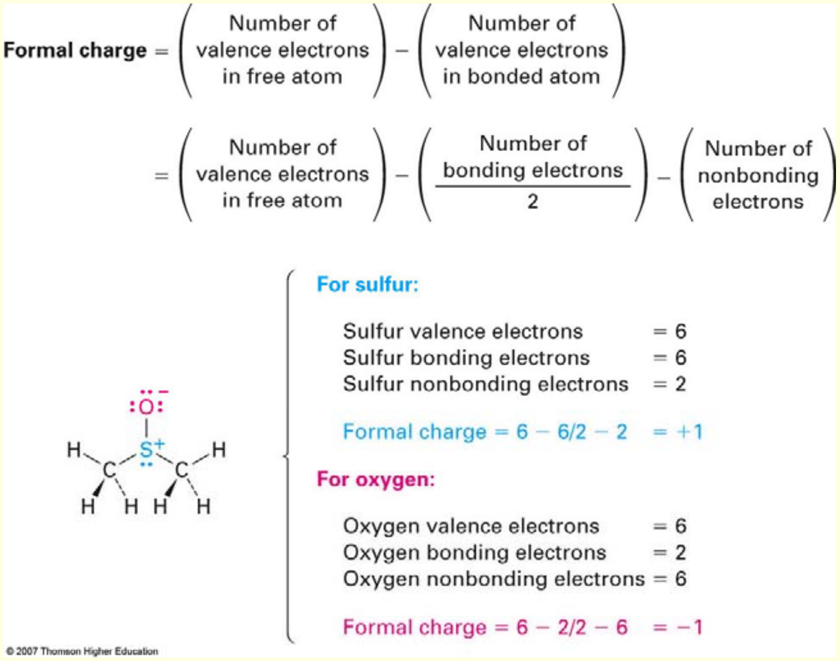


Formal negative charge on oxygen

Formal positive charge on sulfur

Dimethyl sulfoxide

- • Atomic sulfur has 6 valence electrons.
- Dimethyl suloxide sulfur has only 5.
- • It has lost an electron and has positive charge.
- • Oxygen atom in DMSO has gained electron and has (-) charge.



$$\textbf{Formal charge} = \begin{pmatrix}\text{Number of}\\ \text{valence electrons}\\ \text{in free atom}\end{pmatrix} - \begin{pmatrix}\text{Number of}\\ \text{valence electrons}\\ \text{in bonded atom}\end{pmatrix}$$

$$= \begin{pmatrix}\text{Number of}\\ \text{valence electrons}\\ \text{in free atom}\end{pmatrix} - \begin{pmatrix}\dfrac{\text{Number of bonding electrons}}{2}\end{pmatrix} - \begin{pmatrix}\text{Number of}\\ \text{nonbonding}\\ \text{electrons}\end{pmatrix}$$

For sulfur:

Sulfur valence electrons = 6
Sulfur bonding electrons = 6
Sulfur nonbonding electrons = 2

Formal charge = 6 − 6/2 − 2 = +1

For oxygen:

Oxygen valence electrons = 6
Oxygen bonding electrons = 2
Oxygen nonbonding electrons = 6

Formal charge = 6 − 2/2 − 6 = −1

Common Formal Charges

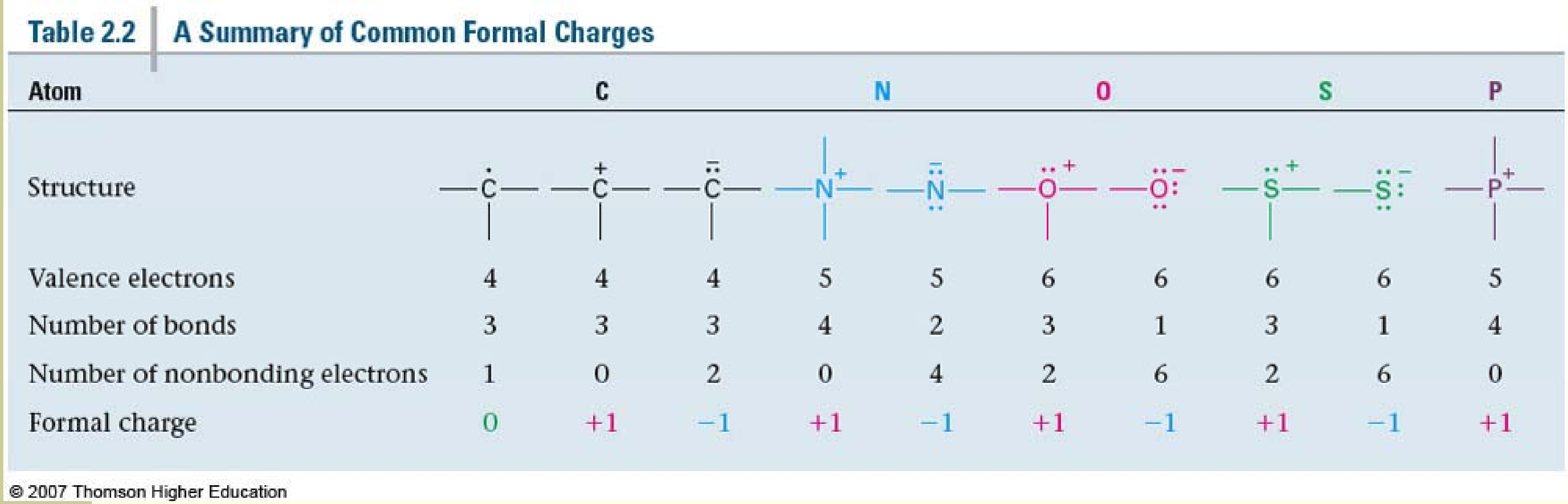
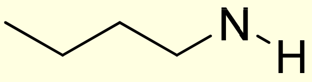


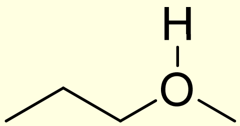
Table 2.2 **A Summary of Common Formal Charges**

Atom	C			N		O		S		P
Structure	$-\dot{\mathrm{C}}-$	$-\mathrm{C}^{+}-$	$-\ddot{\mathrm{C}}^{-}-$	$-\mathrm{N}^{+}-$	$-\ddot{\mathrm{N}}^{-}-$	$-\ddot{\mathrm{O}}^{+}-$	$-\ddot{\mathrm{O}}\mathrm{:}^{-}$	$-\ddot{\mathrm{S}}^{+}-$	$-\ddot{\mathrm{S}}\mathrm{:}^{-}$	$-\mathrm{P}^{+}-$
Valence electrons	4	4	4	5	5	6	6	6	6	5
Number of bonds	3	3	3	4	2	3	1	3	1	4
Number of nonbonding electrons	1	0	2	0	4	2	6	2	6	0
Formal charge	0	+1	−1	+1	−1	+1	−1	+1	−1	+1

charges are typically shown (not necessarily the lone pairs)

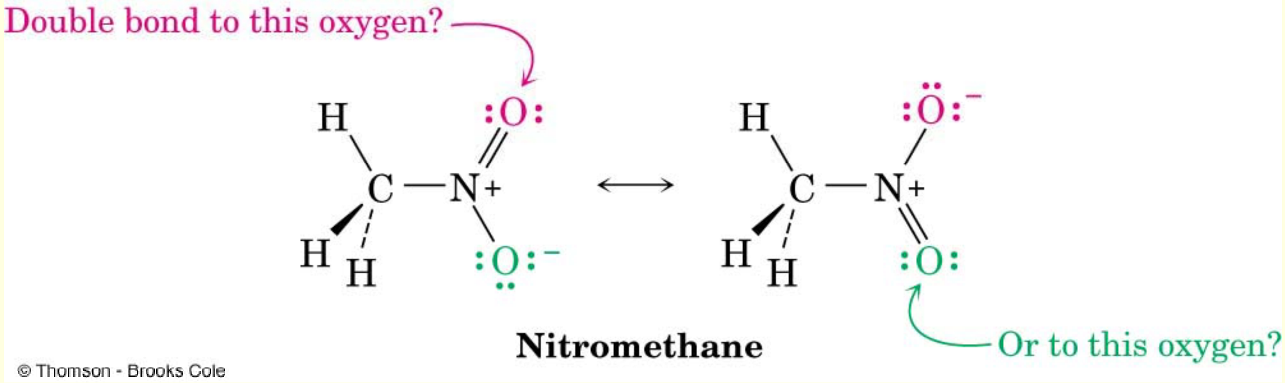
add necessary lone pairs and charges to the following compounds:





Resonance

- Some molecules have structures that cannot be shown with a single representation
- In these cases we draw structures that contribute to the final structure but which differ in the position of the π bond(s) or lone pair(s)
- Such a structure is delocalized and is represented by **resonance forms**
- The resonance forms are connected by a **double-headed** arrow



Nitromethane

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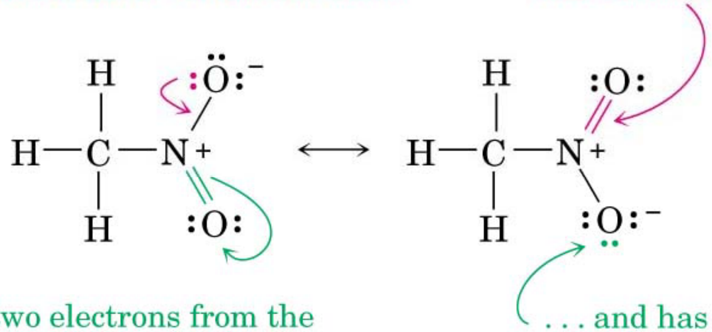
We say the pi bond is delocalized, and valence bond theory cannot describe where
Pi bond and one lone pair are located. This is why we must draw multiple versions
And use molecular orbital theory to show delocalization

Curved Arrows and Resonance Forms

- We can imagine that electrons move in pairs to convert from one resonance form to another
- A curved arrow shows that a pair of electrons moves *from* the atom or bond at the tail of the arrow *to* the atom or bond at the head of the arrow

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of an N=O double bond.

The new resonance structure has a double bond here . . .



Simultaneously, two electrons from the N=O double bond move onto the bottom oxygen atom to become a lone pair.

. . . and has a lone pair of electrons here.

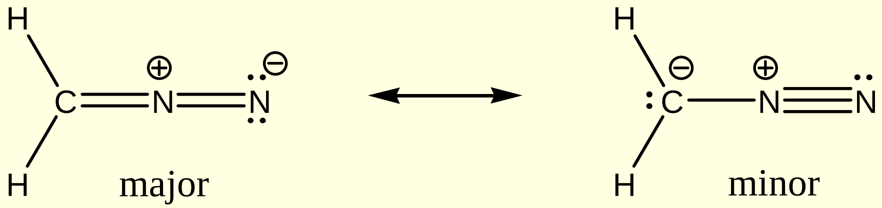
Drawing Resonance Forms

- Redraw all atoms and sigma bonds in same position
- Only move pi electrons and lone pair electrons (note that electrons must remain with same atom) using curved arrows to illustrate
- All resonance forms must have same net charge
- Never violate the octet rule for 2nd row atoms
- Resonance forms may be equivalent (degenerate) but do not have to be
- Not all resonance forms contribute equally to the overall resonance hybrid
- There are two additional resonance structures for nitromethane, can you draw them???

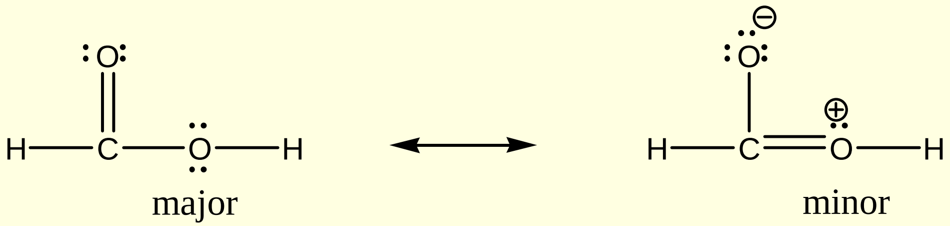
Guidelines to determine major resonance contributor

- 1. Structures with maximum octets are preferred

- 2. Charges should be located on atoms with compatible electronegativity

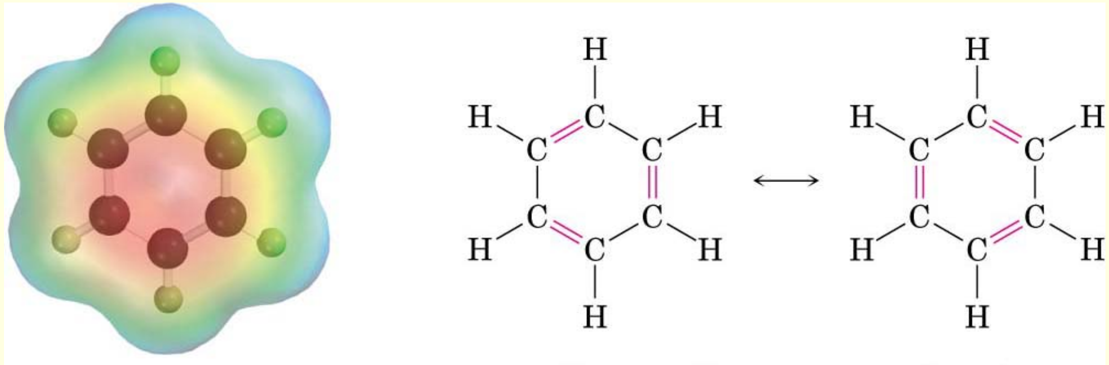


- 3. Structures with minimum charge separation are preferred



Resonance Hybrids

- A structure with resonance forms does not alternate between the forms (individual resonance forms are imaginary)
- Instead, it is a *hybrid* of all resonance forms, so the structure is called a **resonance hybrid**
- For example, benzene (C_6H_6) has two resonance forms with alternating double and single bonds
  - In the resonance hybrid, the actual structure, all its C-C bonds equivalent, midway between double and single



Benzene (two resonance forms)

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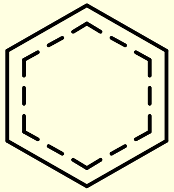
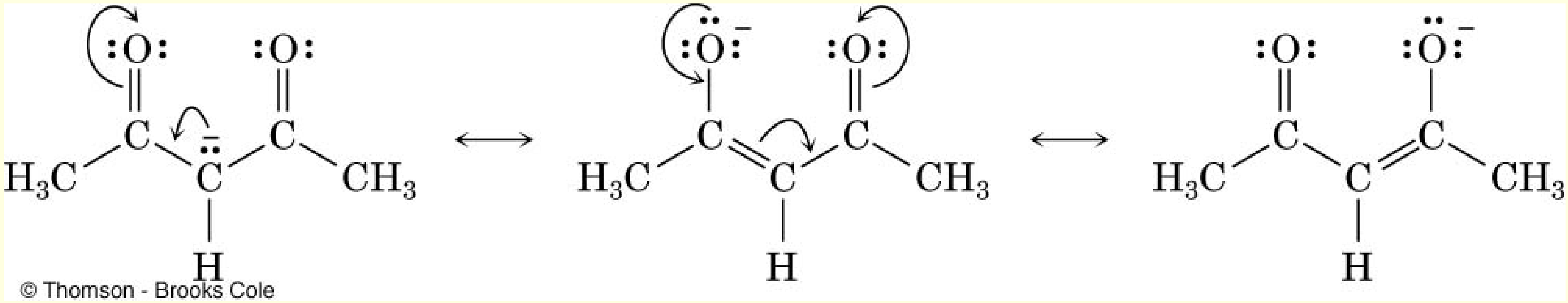
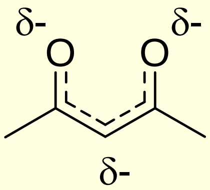


Different Atoms in Resonance Forms

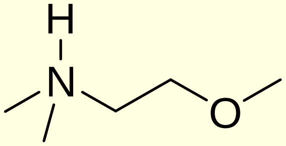


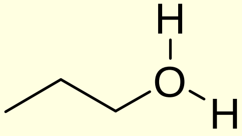


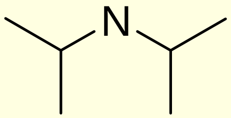
- Are any resonance structures degenerate?
- What is major resonance contributor?
- Can you draw any more resonance structures?

Formal Charge Problems

Provide formal charges for all heteroatoms (non carbon atoms).
Remember, all H's on heteroatoms must be (and are) drawn in structure.

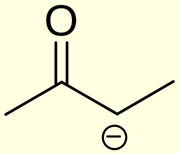


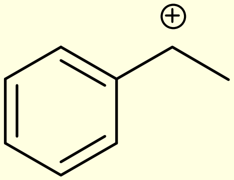


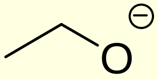


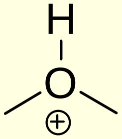
need to determine number of valence electrons to know how many lone pairs to add

For each compound below, provide all lone pairs and hydrogens required to be consistent with the given formal charges (again hydrogens are provided on heteroatoms along with any necessary charges).

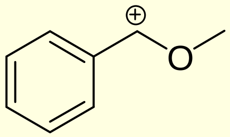


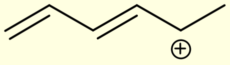


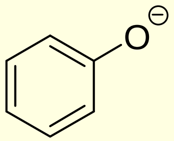


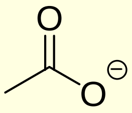


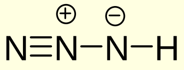
Resonance/Skeletal Problems







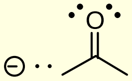


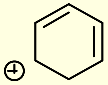


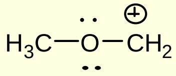
$N\equiv\overset{\oplus}{N}-\overset{\ominus}{N}-H$

Resonance Practice Problems

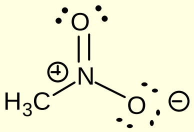
1. Draw the important resonance structures for each of the following molecules.

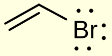


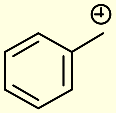


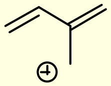


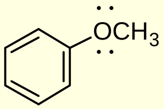
$H_3C-\ddot{O}-CH_2^{+}$

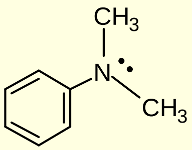


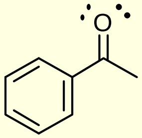


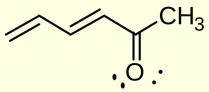










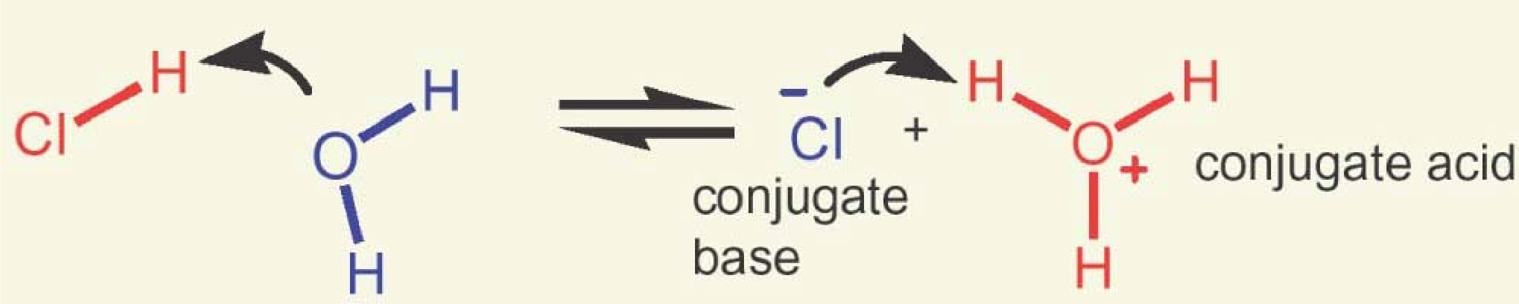


Put in answer keys to the previous slides

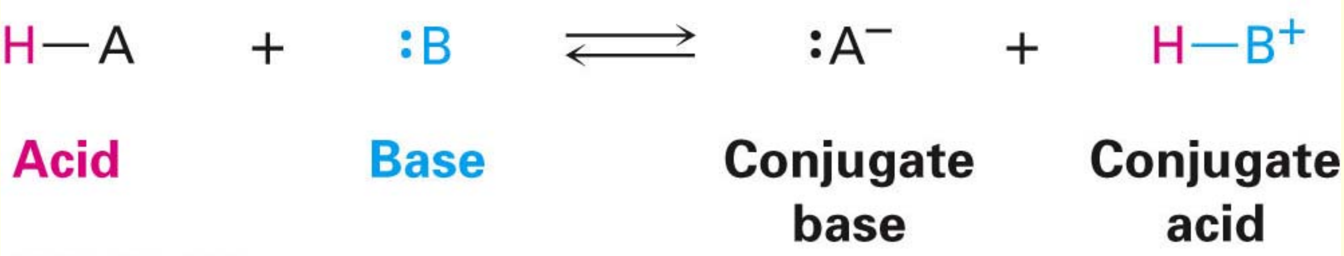
also put in slide about hydridization in resonance forms like pyrrole
if sp3 in one, sp2 in another must have sp2 hybrid for p orbital and not move other atoms

Brønsted Acids and Bases

- A **Brønsted acid** is a substance that donates a hydrogen ion (H^+)
- A **Brønsted base** is a substance that accepts the H^+



Acids are shown in red, bases in blue. Curved arrows go from bases to acids



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K_a – the Acidity Constant

- The concentration of water as a solvent does not change significantly when it is protonated
- The molecular weight of H_2O is 18 and one liter weighs 1000 grams, so the concentration is ~ 55.6 M at 25°
- The **acidity constant, K_a** for HA K_e times 55.6 M (leaving [water] out of the expression)
- K_a ranges from 10^{15} for the strongest acids to very small values (10^{-60}) for the weakest

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^-} + \mathrm{H_3O^+}$$

$$K_a = K_{eq}[\mathrm{H_2O}] = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

pK_a – the Acid Strength Scale

- pK_a = -log K_a
- The free energy in an equilibrium is related to –log of K_{eq} ($\Delta G = -RT \log K_{eq}$)
- A smaller value of pK_a indicates a stronger acid and is proportional to the energy difference between products and reactants
- The pK_a of water is 15.74

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad \text{and} \quad K_a = K_{eq} \times [H_2O] = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

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$$K_a = \frac{1.0 \times 10^{-14}}{55.6} = 1.80 \times 10^{-16} \quad \text{and} \quad pK_a = 15.74$$

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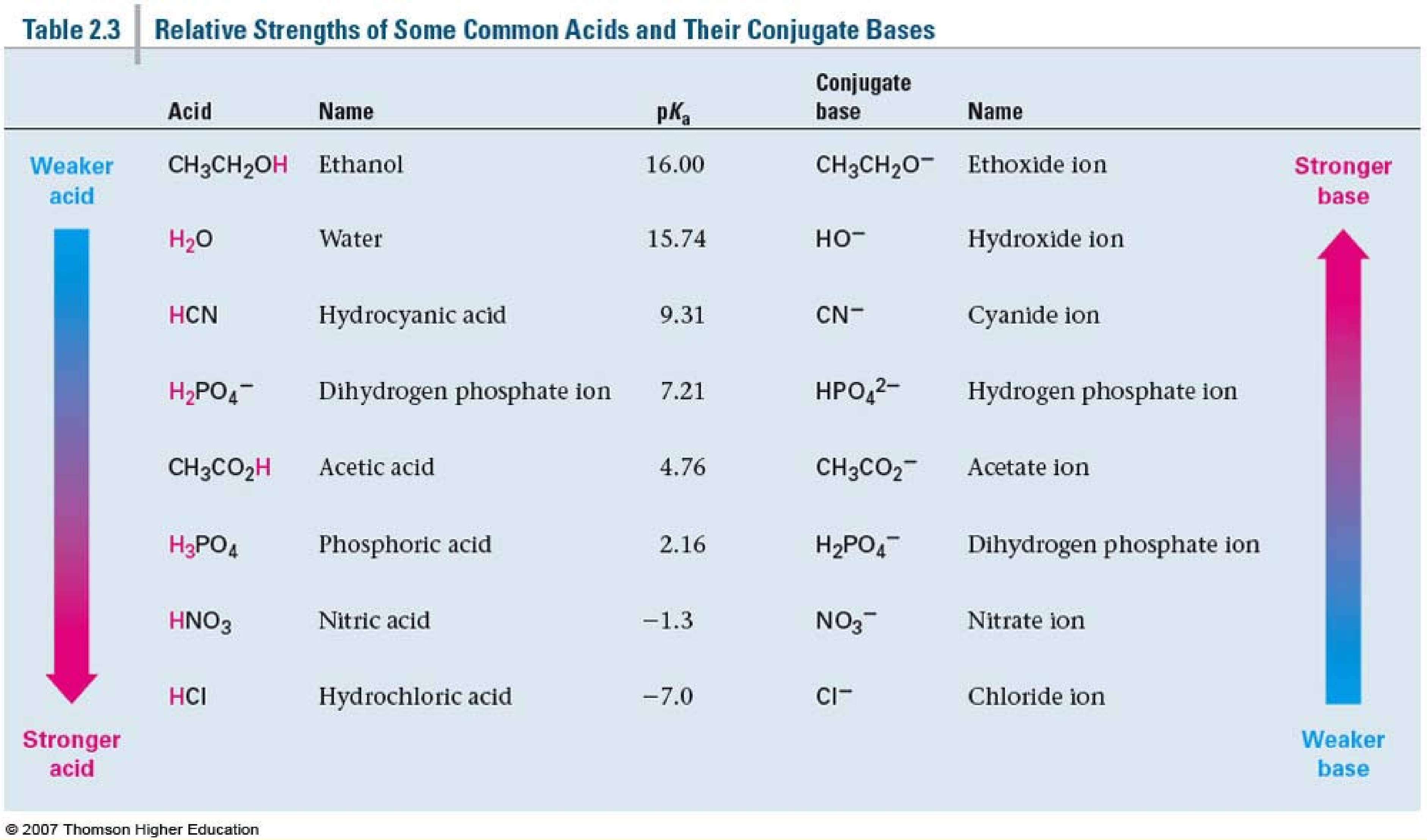


Table 2.3 Relative Strengths of Some Common Acids and Their Conjugate Bases

Weaker acid ↓ Stronger acid

Stronger base ↑ Weaker base

Acid	Name	pK_a	Conjugate base	Name
CH_3CH_2OH	Ethanol	16.00	$CH_3CH_2O^-$	Ethoxide ion
H_2O	Water	15.74	HO^-	Hydroxide ion
HCN	Hydrocyanic acid	9.31	CN^-	Cyanide ion
$H_2PO_4^-$	Dihydrogen phosphate ion	7.21	HPO_4^{2-}	Hydrogen phosphate ion
CH_3CO_2H	Acetic acid	4.76	$CH_3CO_2^-$	Acetate ion
H_3PO_4	Phosphoric acid	2.16	$H_2PO_4^-$	Dihydrogen phosphate ion
HNO_3	Nitric acid	−1.3	NO_3^-	Nitrate ion
HCl	Hydrochloric acid	−7.0	Cl^-	Chloride ion

Trends in Acidity: What makes a strong acid?

1. Strength of the H-A bond

The stronger this bond is, the less likely it will break to “give-up” an H+. For strong acids, this is a relatively weak bond. Important factor when comparing bonds between hydrogen and atoms within the same column (not row) of the periodic table

Why is HI a weaker bond than the others?

	H-I	>	H-Br	>	H-Cl	>	H-F
pKa =	-10		-9		-7		3.2

Trends in Acidity: What makes a strong acid?

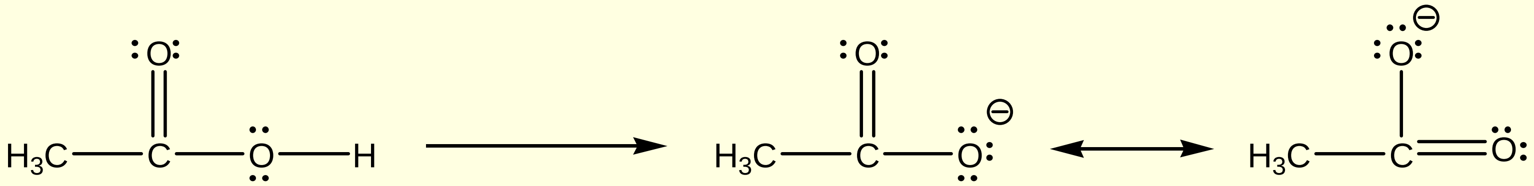
2. Stability of Conjugate Base, A^-
If the resulting anion from the dissociation is stabilized (A^-), it will be easier to form resulting in a stronger acid. Two major influences operate here:

A: Effect of Electronegativities. If the hydrogen is connected to a very electronegative atom the bond is polarized and the eventual breaking of the bond to form A^-, a stable anion since A is very electronegative, will become easier and result in a stronger acid (unless you are comparing atoms in the same column of the periodic table as in the above example where you must consider bond strength).

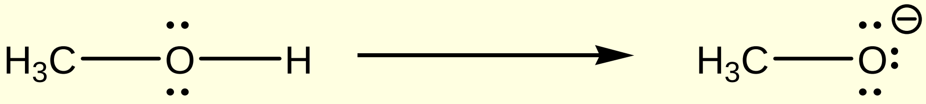
	H-F	>	H-OH	>	H-NH_2	>	H-CH_3
pKa =	3.2		15.7		38		49

Trends in Acidity: What makes a strong acid?

B: Resonance Effects. Delocalization of charge (through resonance showing the negative charge is located on more than one atom) will stabilize the anion, making it easier to form and result in a stronger acid.



pKa = 5



pKa = 16

H_2O versus HNO_3

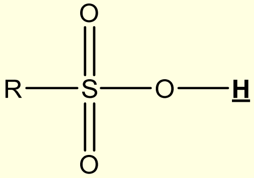
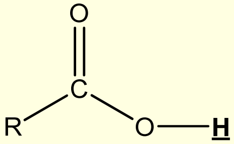
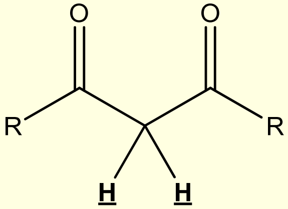
Trends in Acidity: What makes a strong acid?

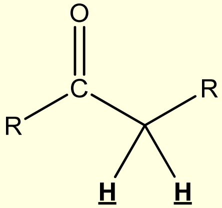
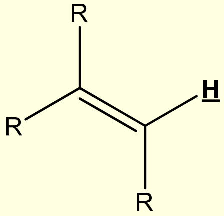
3. Inductive Effects

Electronegative groups can inductively “pull” electron density towards themselves. This can result in a net stabilization of the conjugate base, A-. This effect is much weaker than that of resonance noted above. An inductive effect rapidly decreases with distance.

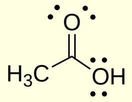
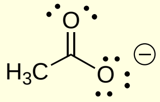
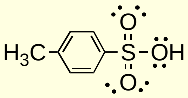
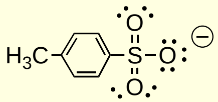
	$CF_3O\text{-}H$	>	$CH_2FO\text{-}H$	>	$CH_2FCH_2O\text{-}H$
pKa =	10		12		13

Some Common Organic Acids and their pKa’s

Functional Group		approx pKa
sulfonic acid	 $R-S(=O)_2-O-\underline{H}$	-1
carboxylic acid		5
thiol	$R-S-\underline{H}$	10
quaternary amine	$R-N\underline{H}_3^{\oplus}$	11
β-dicarbonyl		11

Functional Group		approx pKa
alcohol	$R-O-\underline{H}$	16
carbonyl		20
alkyne	$R-C\equiv C-\underline{H}$	25
amine	$R-N\underline{H}_2$	36
alkene		45
alkane	$R-\underline{H}$	50

pKa Table: Acidity and Basicity

	Acid		Conjugate Base	
Weak Acid	CH_4	49	$^{\ominus}{:}CH_3$	Strong Base
	NH_3	36	$^{\ominus}{:}NH_2$	
	$H-C\equiv C-H$	25	$H-C\equiv C{:}^{\ominus}$	
	H_3C-OH	16	$H_3C-O{:}^{\ominus}$	
	$H_2O{:}$	15.7	$^{\ominus}{:}OH$	
	H_3C-SH	11	$H_3C-S{:}^{\ominus}$	
	$^{\oplus}NH_4$	9.2	NH_3	
	$H-C\equiv N{:}$	9.1	$^{\ominus}{:}C\equiv N{:}$	
	$H_2S{:}$	7.0	$^{\ominus}{:}SH$	
		4.8		
	$H-N=\overset{\oplus}{N}=N{:}^{\ominus}$	4.7	$^{\ominus}{:}N=\overset{\oplus}{N}=N{:}^{\ominus}$	
	$H-F{:}$	3.2	$:F:^{\ominus}$	
	$H_3O^{\oplus}$	-1.7	$H_2O{:}$	
**	 p-toluene sulfonic acid	-6.5	 p-toluene sulfonate or Tosylate	**
	$H-Cl{:}$	-7.0	$:Cl:^{\ominus}$	
	$H-Br{:}$	-9.0	$:Br:^{\ominus}$	
Strong Acid	$H-I{:}$	-10.0	$:I:^{\ominus}$	Weak Base

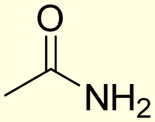
Increasing Nucleophilicty

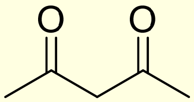
Increasing Leaving Group Capabilities

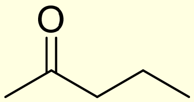
This chart will be VERY useful for sub-elim chemistry

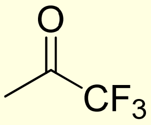
Predicting pKa Values

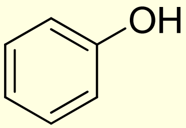
- Identify most acidic hydrogen and rank from most acidic (1) to least acidic (4)

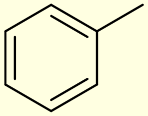


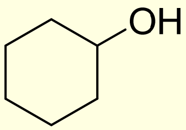


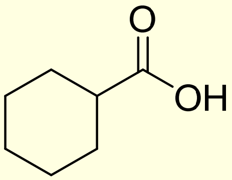












(rank by functional groups first, then compare like functional groups)

- The reactivity patterns of organic compounds often are acid-base combinations

Predicting Acid–Base Reactions from pK_a Values

For any given reaction involving an acid and a base, the equilibrium will be established such that it favors the weaker acid and weaker base:

$$\underset{\text{acid}}{\text{H-A}} \quad + \quad \underset{\text{base}}{\text{B}} \quad \rightleftharpoons \quad \underset{\text{conj base}}{\overset{\ominus}{\text{A}}} \quad + \quad \underset{\text{conj acid}}{\overset{\oplus}{\text{B-H}}}$$

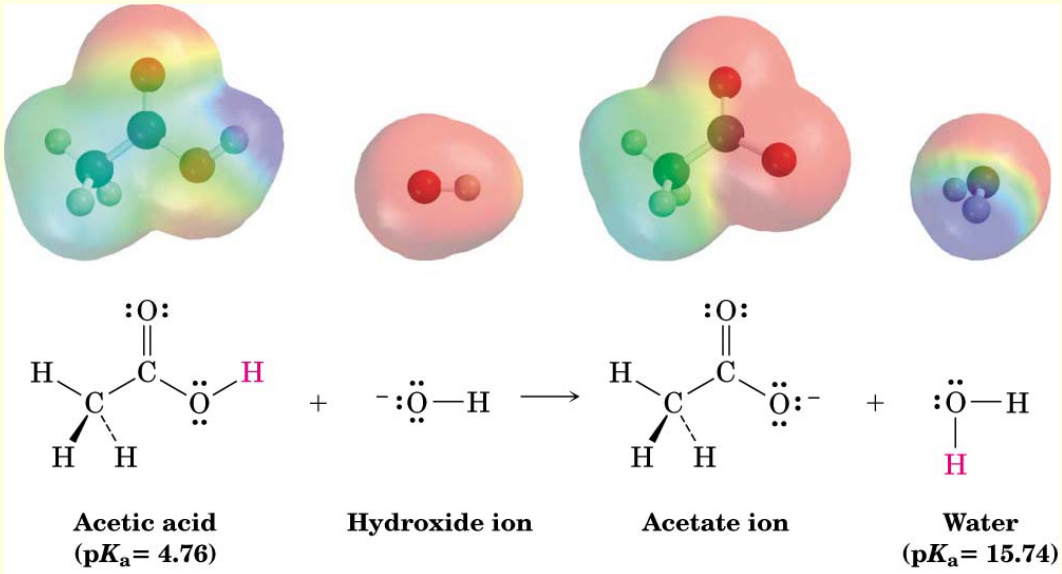
A new equilibrium expression can be written for this reaction which simplifies to the following:

$$K = \frac{\text{Ka reactant acid (HA)}}{\text{Ka product acid (HB)}} = 10^{-(\text{pKa HA} \ - \ \text{pKa HB})}$$

A simple inspection of this new equilibrium expression illustrates that if the reactant acid has a pKa value 2 units lower than the product conjugate acid then the equilibrium constant will be 10^2, or 100. This means that, as the reaction is written, the concentration of products to reactants will be approximately 100:1. Another way of stating this is that the reaction has gone to 99% completion (100/101).

Predicting Acid–Base Reactions from pK_a Values

- Which side of the following reaction is favored?
- What is K for this reaction?
- Does the reaction proceed from left to right?
- Draw in the curved arrows to show electron flow.



Acids and Bases: The Lewis Definition

- Lewis acids are electron pair acceptors
  (have + or δ+ charge, or unfilled octet)

  H^+, Li^+, $AlCl_3$, CH_3O-H

- Lewis bases are electron pair donors
  (have lone pairs to donate)

  H-O-H, CH_3-O-H, CH_3-NH_2

- no scale of strengths as in Brønsted definition of pK_a

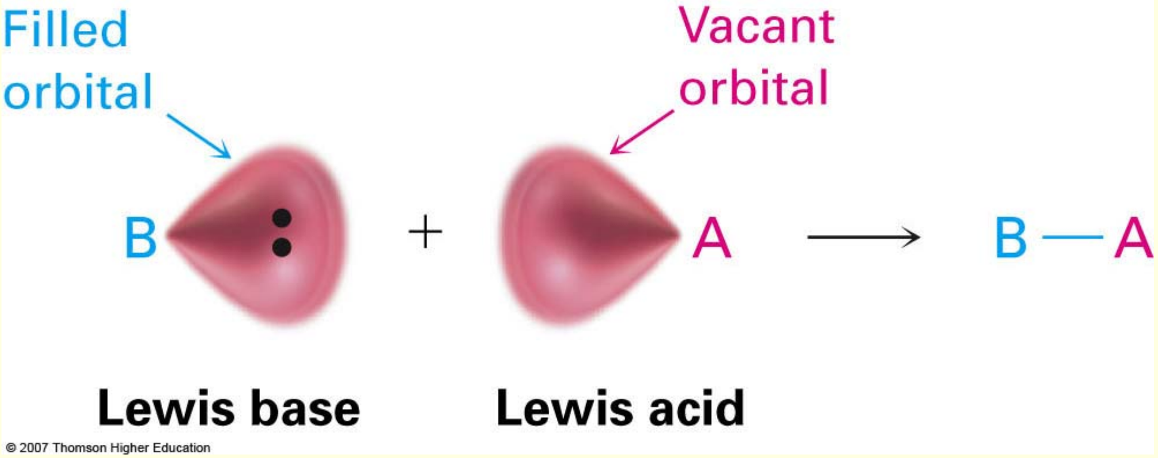
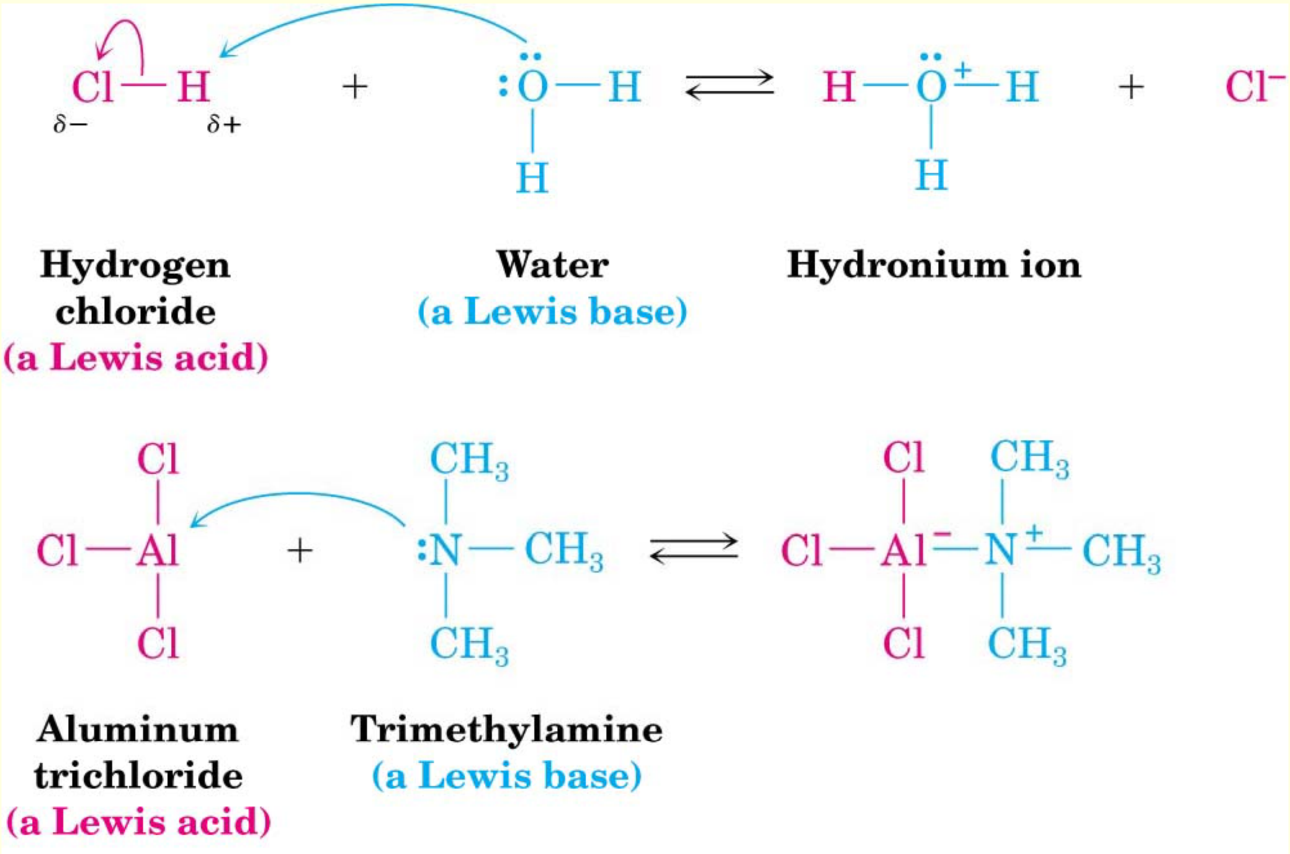


Illustration of Curved Arrows in Following Lewis Acid-Base Reactions

- The combination of a Lewis acid and a Lewis base can be shown with a curved arrow from base to acid



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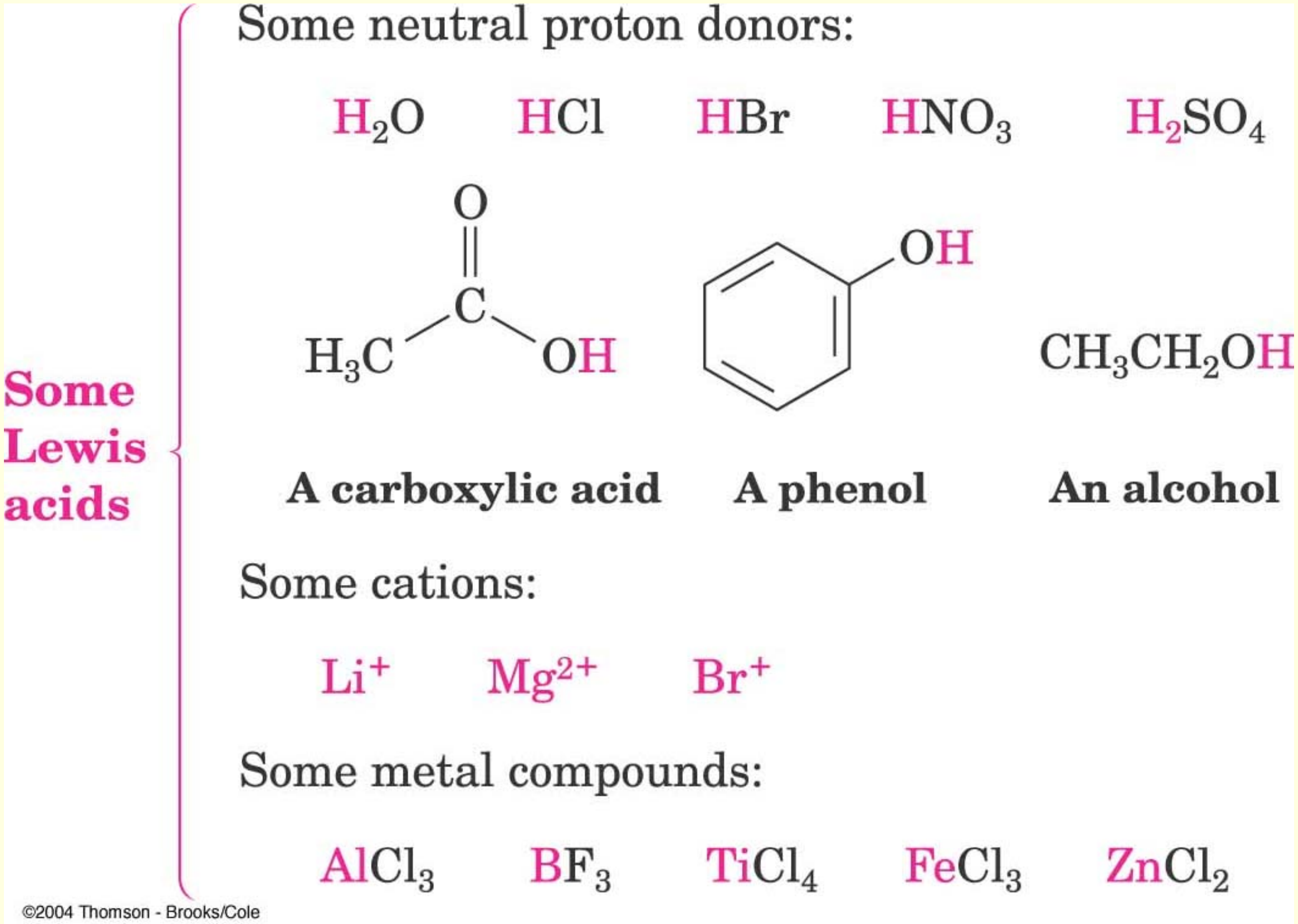
Lewis Acids



Some Lewis acids

Some neutral proton donors:

H_2O HCl HBr HNO_3 H_2SO_4

CH_3CH_2OH

A carboxylic acid **A phenol** **An alcohol**

Some cations:

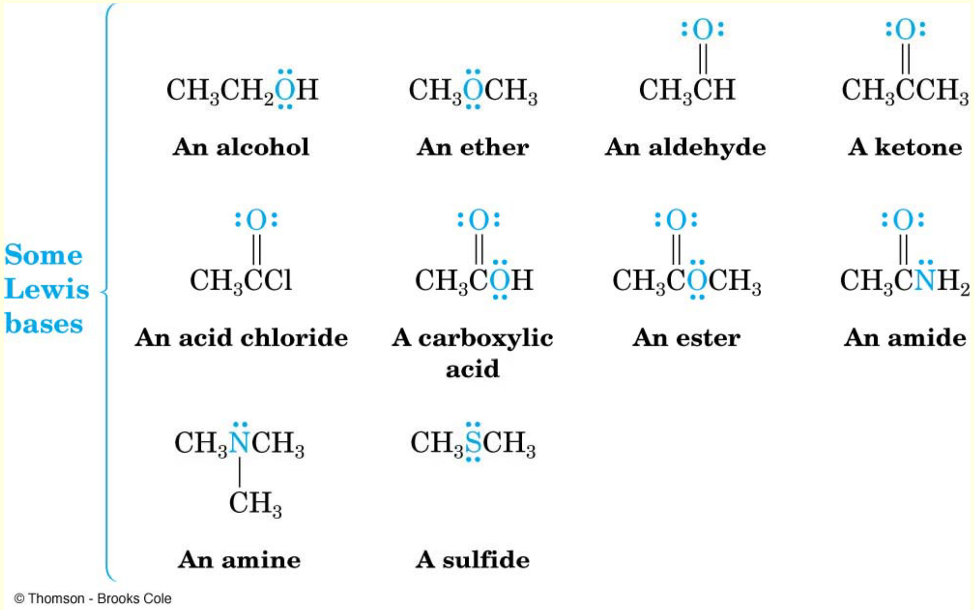
Li^+ Mg^{2+} Br^+

Some metal compounds:

$AlCl_3$ BF_3 $TiCl_4$ $FeCl_3$ $ZnCl_2$

Lewis Bases

- Lewis bases can accept protons as well as Lewis acids, therefore the definition encompasses that for Brønsted bases
- Most oxygen- and nitrogen-containing organic compounds are Lewis bases because they have lone pairs of electrons
- Some compounds can act as both acids and bases, depending on the reaction



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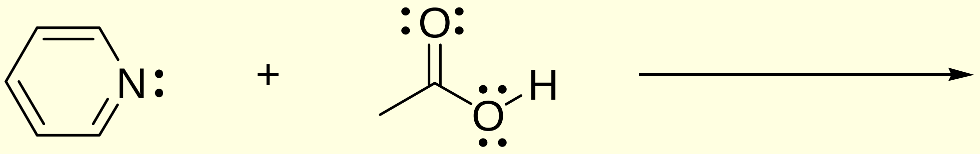
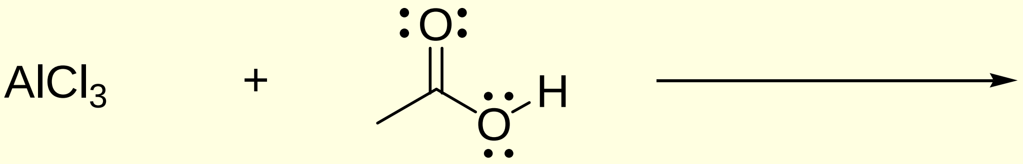
C=C π-bond will also act as a weak Lewis Base (chapter 6 & 7)

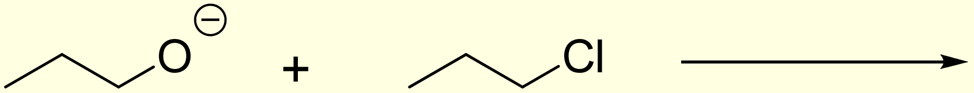
R-X not a Lewis base, but X^{-1} is

Predicting Reactions

Identify Lewis acids, Lewis bases, predict product, add curved arrows



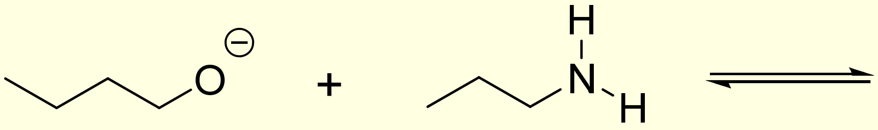




Sample Problems

1. Draw two additional resonance structures with curved arrows and identify major resonance contributor

2. Predict product if Bronsted-Lowry acid-base reaction occurs. Provide curved arrows. Which side is favored?



3. Predict Lewis acid-base product, with curved arrows, for the following reaction.