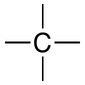
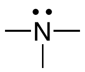
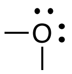
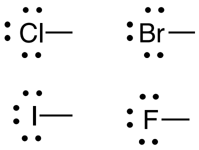
Normal Bonds (Sections 1.2-1.5)

Summary of **Normal, Ideal Bonding** (No Formal Charge)

	Valence Electrons	Valence Bonds	Lone Pairs
	4	4	0
	5	3	1
	6	2	2
H—	1	1	0
	7	1	3

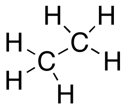
Rules for Drawing Lewis structures for organic molecules: (Sections 1.4-5)

1. Try to provide normal bonding for C, N, O atoms **if possible**. (Works > 95% of time)
2. Double or triple bonds will often be involved.
   - Double or triple bonds are often required to achieve normal bonding.
3. In any formula that has a charge, there will always be an atom with that formal charge.
4. In any formula that includes a metal, assume ionic bonding.
   - Assume positive charge for the metal,
   - Assume negative charge for the organic portion.
5. Do not draw bonds between nonmetals and metals, as if they were covalently bound.
6. Be sure to specify the formal charge on any atom that has formal charge.
7. Always be aware of how many lone pairs are on any atom
   - Note: We will often omit lone pairs. But you must know when they are there!

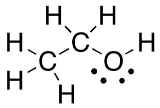
Lewis Structure Practice (Section 1-4,5)

1. Draw Lewis structures for the following formulas: (Include lone pairs or formal charges if necessary)

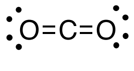
a. CH_3CH_3



b. CH_3CH_2OH



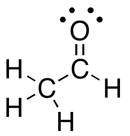
c. CO_2



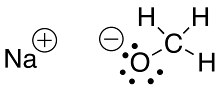
d. HCN

H−C≡N:

e. CH_3CHO



f. $NaOCH_3$



Formal Charge (Section 1-7): When an atom does not have it's normal bonding

- Atoms with formal charge dominate reactivity. Therefore the ability to recognize and identify atoms with formal charge is really important!

- **Skills**:
  1. Identify the formal charge for any atom that does not have normal bonding
  2. Identify the number of bonds and lone pairs associated with any atom whose formal charge is specified

- Note: Designation of formal charge is required. If you don't write the charge sign next to an atom that should have formal charge, you will lose test points!

Formal Charge Equations:

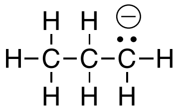
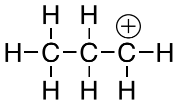
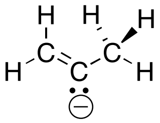
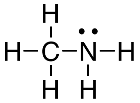
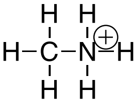
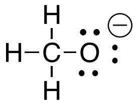
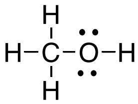
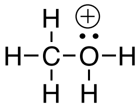
1. FC = group # - (bonds + unshared e's) (use to calculate FC)
2. Group # - FC = bonds + unshared electrons (given formal charge, use to find lone pairs)

Practical: (memorize)
C 4 bonds ⟷ neutral
3 bonds and zero lone pairs ⟷ cation +1
3 bonds and one lone pair ⟷ anion -1
N 4 bonds ⟷ cation +1
3 bonds and one lone pair ⟷ neutral
O 3 bonds and one lone pair ⟷ cation +1
2 bonds and 2 lone pairs ⟷ neutral
1 bond and three lone pairs ⟷ anion -1

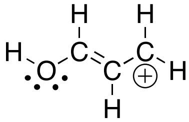
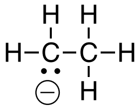
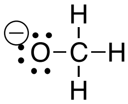
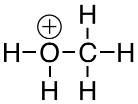
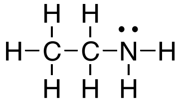
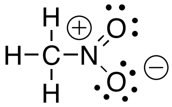
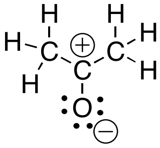
	FORMAL CHARGE			
# of bonds	C	N	O	F
4	0	+1	▨	▨
3	–1 or +1	0	+1	▨
2	▨	–1	0	▨
1	▨	▨	–1	0

Formal Charge Practice (Section 1-7)

1. Assign any **formal charges** to atoms that need them:

2. Fill in lone pairs on any atoms that need them (whether atoms with formal charge or neutral atoms):

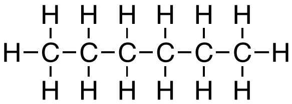
Notice: **With the exception of carbocations, all other C/N/O atoms end up with a combined total of four when you sum up their bonds and lone-pairs**. So apart from carbocations, if you know the number of bonds, you can fill in the correct number of lone pairs without even thinking much!

Structural Formulas (Section 1-10)

1. Full Structural Formulas
2. Condensed Formulas
3. Line-Angle Formulas

Since organic structures are large and complex, full Lewis structures are often a hassle. You'll need to be proficient in both condensed and line-angle formulas.

Full, Condensed, and Line-Angle Structures for Hexane, C_6H_{14}



$$\begin{array}{ccccccccccccccc} & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & \end{array}$$

A

Full

$CH_3CH_2CH_2CH_2CH_2CH_3$ **B**

or

$CH_3(CH_2)_4CH_3$ **C**

Condensed

D

Line-Angle

Condensed Formulas: Central atoms are shown with attached atoms, essentially in sequence

- Challenges:
    1. Handling parentheses
    2. Handling double and triple bonds
    3. Handling branches
    4. Handling ketones/aldehydes/esters/amides/carboxylic acids
    5. In general, recognizing when an oxygen is double-bonded off a carbon, and when it is single bonded both to carbon and to something else.

Line-Angle Formulas:

1. Each vertex represents a carbon
2. C-H bonds are often omitted: assume enough H's to give four bonds or the appropriate formal charge
3. Oxygen and Nitrogen atoms must be specified, and O-H and N-H bonds are **not** omitted

- Line-angle formulas are routinely the fastest and cleanest to draw.
- Line-angle is essential and optimal for showing 3-dimensional organic shape.

Formula Practice (Section 1-10)

3. Time race: Draw as many copies of C_6H_{14} hexane as you can in 20 seconds:

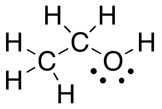
Full:

Condensed:

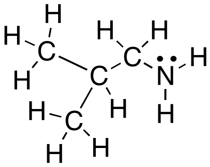
Line-Angle:

4. Draw the full structure, given the condensed structure. (Note:

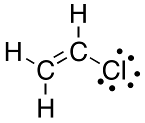
CH_3CH_2OH



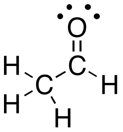
$(CH_3)_2CHCH_2NH_2$



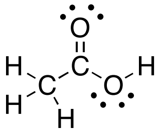
CH_2CHCl



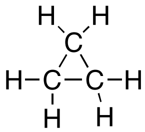
CH_3CHO

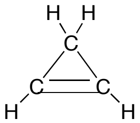


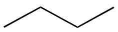
CH_3CO_2H

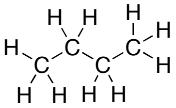


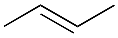
5. Fill in the full structure, including attached hydrogens and attached lone pairs, for the following line-angle structures. If given a condensed structure, convert it to a line-angle.

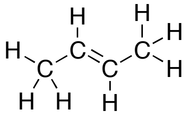


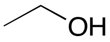


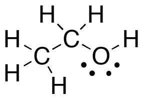


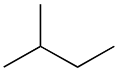


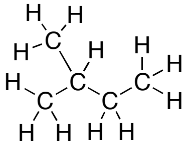


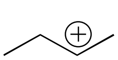


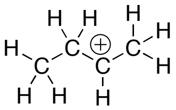


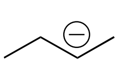


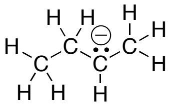


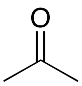


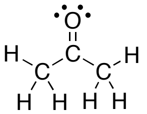




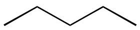




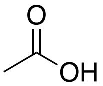




$CH_3CH_2CH_2CH_2CH_3$



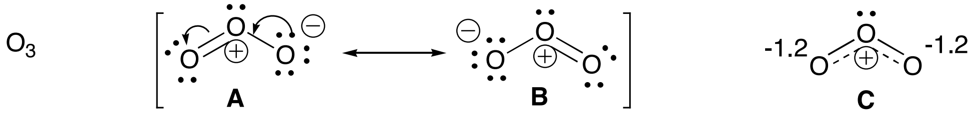
CH_3CO_2H



Resonance Structures (Section 1-9)

Sometimes a single Lewis structure does not provide an adequate picture.

Example: O_3 (ozone)



2 Resonance Forms

Actual Species Is a
Hybrid of the Resonance Forms

Notes/observations:

1. Neither form **A** nor **B** can avoid formal charges.
    - The majority of resonance situations have some formal charge involvement
2. The real molecule is hybrid: see picture **C**
    - The central oxygen has + charge
    - Each of the outside oxygens is -1/2
    - Both of the bonds to the outside oxygens are equal in length/strength
    - The actual length/strength of the oxygen-oxygen bonds reflect 1.5 bonds (shorter and stronger than single bonds; longer and weaker than double bonds)
3. Why not just draw the hybrid?
    - Hard to do, without first working through resonance structures first.
    - Hard to keep track of the electrons, which is essential for understanding reactivity
4. When are Two Structures related as Resonance Structures?
    - Atoms must be connected in exactly the same way. Resonance forms differ **only in the placement of electrons.**
    - If two Lewis structures have the same atomic connectivity, but differ **only** in the placement of some electrons, they are related as resonance structures.
    - If the placement/connectivity of atoms differ, then the two structures are not resonance structures (they may perhaps be related as "isomers", see later.)
    - KEY: FOR RESONANCE STRUCTURES, ELECTRONS MOVE BUT ATOMS DO NOT MOVE. IF ATOMS MOVE, YOU DON'T HAVE RESONANCE STRUCTURES
    - Note: The real molecule is represented by the hybrid, and electrons are not actually jumping back and forth.
5. Resonance, when it exists, involves the **delocalization** of electrons and charge
    - In ozone, instead of one of the outside oxygens getting stuck with a full negative charge, that negative charge is shared with the other outside oxygen, and both have a more manageable -1/2 charge
    - This delocalization of electrons/charge is stabilizing.
    - **KEY: RESONANCE IS STABILIZING**
6. Resonance, when it exists, always involves electrons in double bonds and/or lone pairs (π electrons)
7. One of the most frequent resonance situations we'll see is when you a charged atom attached to a double bonded atom ("allylic" situation")
8. When resonance structures are equal in stability, the hybrid is the average of the resonance forms
9. When resonance structures are unequal, the more stable structure dominates the hybrid
    - Ranking Stability:
    - More bonds → more stable (but don't exceed octet rule!). (Priority rule)
    - Bonds being equal (tiebreaker rule): **negative charge** is better on **more electronegative atom**; **positive charge** is better on **less electronegative atom**

Resonance Problems

1. Which of the following are related as resonance structures?

Yes, no atoms moved

No, an H-atom moved

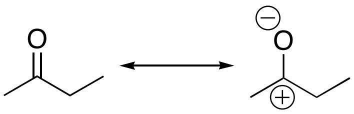
Yes, no atoms moved

No, an H-atom moved

Yes, no atoms moved

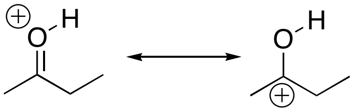
2. Which Resonance Structure is Better and would make a more than 50% contribution to the actual hybrid? Why, bonds or electronegativity?

a.



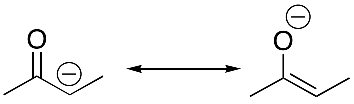
Left, extra bond

b.



Left, extra bond. More bonds is more important than electronegativity.

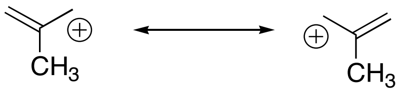
c.



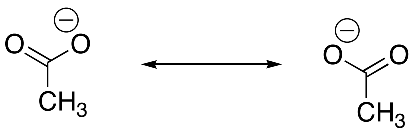
Right, both have same bonds. But electronegativity favors oxygen with negative charge

3. Draw a resonance structure for the following

a.

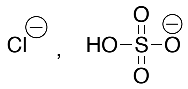
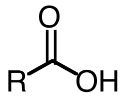
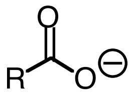
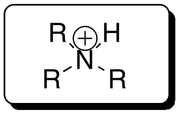
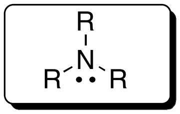
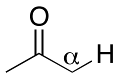
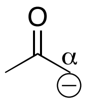


b.



Acid-Base Chemistry (Section 1-12-14)

Acidity/Basicity Table

Entry	Class	Structure	Ka	Acid Strength	Base	Base Strength
1	Strong Acids	H-Cl, H_2SO_4	10^2	Most acidic	 Cl^- , $HO-SO_3^-$	Least basic
2	Hydronium	H_3O^+, ROH^+ cationic	10^0		H_2O, HOR neutral	
3	Carboxylic Acid		10^{-5}			
4	Ammonium Ion (Charged)	 Charged, but only weakly acidic!	10^{-12}		 Neutral, but basic!	
5	Water	HOH	10^{-16}		HO^-	
6	Alcohol	ROH	10^{-17}		RO^-	
7	Ketones and Aldehydes		10^{-20}			
8	Amine (N-H)	$(iPr)_2N-H$	10^{-33}		$(iPr)_2N^-Li^+$	
9	Alkane (C-H)	RCH_3	10^{-50}	Least Acidic	RCH_2^-	Most basic

Quick Checklist of Acid/Base Factors

1. Charge
2. **Electronegativity**
3. **Resonance/Conjugation**
4. Hybridization
5. Impact of Electron Donors/Withdrawers
6. Amines/Ammoniums

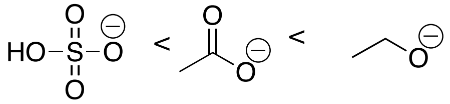
- **When a neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.**

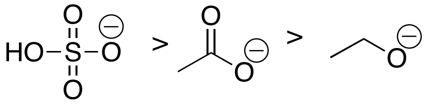
More Detailed Discussion of Acid/Base Patterns/Factors to remember

1. Charge: all else equal, cations are more acidic than neutrals, and anions more basic than neutrals.

2. Electronegativity:
   - Acidity: H-X (halogen) > H-O > H-N > H-C
   - Basicity: $X^{\ominus} < O^{\ominus} < N^{\ominus} < C^{\ominus}$
   - Anion Stability: $X^{\ominus} > O^{\ominus} > N^{\ominus} > C^{\ominus}$
   - Why: **The more stable the anion Z^- that forms, the more acidic the parent H-Z will be**. All acids H-Z must give up H^+. The better off the resulting anion Z^- is, the more willing H-Z will be to sacrifice H^+.
   - **The anion stability directly correlates the love for electrons.**
   - Notice three things:
     - ANION STABILITY and the ACIDITY OF A NEUTRAL ACID PRECURSOR ARE DIRECTLY RELATED.
     - ANION STABILITY and the BASICITY OF THE ANION ARE INVERSELY RELATED (more stable anion, less basic anion)
     - ANION BASICITY AND THE ACIDITY OF THE CONJUGATE ACID ARE INVERSELY RELATED (the stronger the acidity of the parent acid, the weaker the basicity of the conjugate anion)
   - KEY: WHEN THINKING ABOUT ACIDITY AND BASICITY, FOCUS ON THE ANION. THE STABILITY OF THE ANION DETERMINES ACID/BASE BEHAVIOR.

3. Resonance/Conjugation: Since anion resonance is stabilizing, **an acid that gives a resonance-stabilized anion is more acidic.** And an anion that forms with resonance will be more stable and less basic.
   - Oxygen Series Examples:
     Acidity: sulfuric acid > carboxylic acid > water or alcohol

     Anion Basicity: 

     Anion Stability: 
   - Note: Resonance is often useful as a tiebreaker (for example, molecules in which both have O-H bonds and both have equal charge, so that neither the charge factor nor the electronegativity factor could predict acidity/basicity)
   - NOTE: Resonance can sometimes (not always) trump electronegativity or even charge.
     - Example of resonance versus charge: A carboxylate anion, with serious resonance stabilization, ends up being so stabilized that it is even less basic than a neutral, uncharged amine! A hydrogen sulfate anion from sulfuric acid is less basic than not only neutral amines but also neutral oxygen (water, etc.)

4. Hybridization: For lone-pair basicity, (all else being equal), $sp^3 > sp^2 > sp > p$

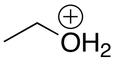
5. Electron donating/electron withdrawing substituents:
    - Electron withdrawing substituents stabilize anions, so they increase neutral acidity and decrease anion basicity
    - Electron donating substituents will destabilize anions, so they decrease neutral acidity and increase anion basicity.

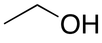
6. Ammonium Cations as Acids and Neutral Amines as Bases
    - Neutral amines are more basic than any neutral oxygen (electronegativity factor), and more basic than some resonance-stabilized oxygen anions.
    - Ammonium cations are more acidic than neutral nitrogen compounds or most neutral oxygen compounds, but less acidic than oxygens that give resonance-stabilized anions. (In this case, resonance factor trumps the charge factor).

Acid/Base Problems

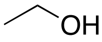
Choose the More Acidic for Each of the Following Pairs: Single Variable Problems

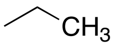
1. NH_3 $\oplus NH_4$ **Charge**, second one

2. 

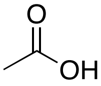


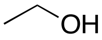
First one, **charge**

3. 

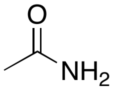


O-H most, N-H second, C-H least. **Electronegativity** and conjugate anion stability

4. 

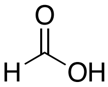


First one more acidic. Gives a **resonance stabilized** oxygen anion

5. 

First one more acidic. Gives a **resonance stabilized** anion

6. Rank the Acidity from 1 → 5, 1 being most acidic. (Think Anion! And Draw Anion!)

HF	H_2O	CH_3NH_2	 	CH_4
1	3	4	2	5

7. For the anions drawn in problem 6, rank them from 1 → 5 in terms of **basicity**.

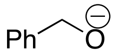
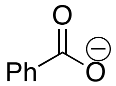
5	3	2	4	1

Choose the More **Basic** for Each of the Following Pairs (Single Variable)

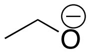
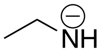
1. NH_3 **$NaNH_2$** Charge. (Na is cation, Nitrogen is anion)

2. **NaOH** H_2O Charge. (Na is cation, oxygen is anion)

3. **NH_3** H_2O **Electronegativity**. Oxygen, being more electronegative, is less willing to share a lone pair, and less willing to take on formal positive charge.

4.  

First one is more basic, because it's **less stable**. The second has **resonance**, and thus is more stable and less basic.

5.  

Nitrogen anion is more basic, because it's less stable, based on **electronegativity** factor.

Predicting Acid/Base Equilibria: Any acid base equilibrium favors the side that has the more stable, less reactive base

6. Draw arrow to show whether equilibrium favors products or reactants. (Why?)

a. $H_2O + {}^{\ominus}NH_2 \qquad {}^{\ominus}OH + NH_3$

Favors product side (right), because of **electronegativity**. Favors the more stable oxygen anion over the less stable nitrogen anion.

b. 

Favors reactant side (left) because of **resonance**. Resonance-stabilized oxygen anion on the left is more stable than the one on the right. More stable anion is preferred.

Generic acid/base reaction, with anionic base and neutral acid:

$$HA + B^{\ominus} \rightleftharpoons A^{\ominus} + BH$$

Stronger acid → weaker conjugate base
Weaker acid → stronger conjugate base

- Acid-base reactions always favor formation of the weaker acid and weaker base
- The weaker acid and weaker base are always on the same side
- The more stable anion is the weaker base

THEREFORE:

- The equilibrium will always favor the WEAKER, MORE STABLE ANION
- **IF YOU CAN IDENTIFY WHICH ANION IS MORE STABLE, YOU CAN PREDICT THE DIRECTION THE REACTION WILL GO**.
- This logic can be used to predict whether an anion can successfully deprotonate a neutral species.

7. Can $H_3C^{\ominus}$ deprotonate H_2O?

Yes, taking a proton from water results in formation of an oxygen anion. Which is more stable than the original carbon anion. Making a superior anion from a less stable one is favorable.

Some Arrow-Pushing Guidelines (Section 1.14)

1. Arrows follow electron movement.

2. Some rules for the appearance of arrows
   - The arrow must begin from the electron source. There are two sources:
     a. An atom (which must have a lone pair to give)
     b. A bond pair (an old bond that breaks)
   - An arrow must always point directly to an atom, because when electrons move, they always go to some new atom.

3. Ignore any Spectator Atoms. Any metal atom is always a "spectator"
   - When you have a metal spectator atom, realize that the non-metal next to it must have negative charge

4. Draw all H's on any Atom Whose Bonding Changes

5. Draw all lone-pairs on any Atom whose bonding changes

6. **KEY ON BOND CHANGES**. Any two-electron bond that changes (either made or broken) must have an arrow to illustrate:
   - where it came from (new bond made) or
   - an arrow showing where it goes to (old bond broken)

7. **Watch for Formal Charges and Changes in Formal Charge**
   - If an atom's charge gets more positive ⇒ it's donating/losing an electron pair ⇒ arrow must emanate from that atom or one of it's associated bonds. There are two "more positive" transactions:
     - When an anion becomes neutral. In this case, an arrow will emanate from the atom. The atom has donated a lone pair which becomes a bond pair.
     - When a neutral atom becomes cationic. In this case, the atom will be losing a bond pair, so the arrow should emanate from the bond rather than from the atom.

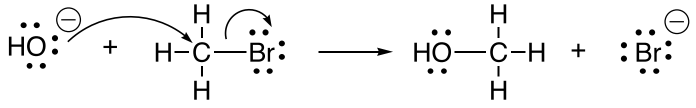
   - If an atom's charge gets more negative ⇒ it's accepting an electron pair ⇒ an arrow must point to that atom. Ordinarily the arrow will have started from a bond and will point to the atom.

8. **When bonds change, but Formal Charge Doesn't Change, A "Substitution" is Involved**
   - Often an atom gives up an old bond and replaces it with a new bond. This is "substitution".
   - In this case, there will be an incoming arrow pointing directly at the atom (to illustrate formation of the new bond), and an outgoing arrow emanating from the old bond that breaks

Examples of "Arrow Pushing" and "Mechanism" (Section 1-14)

Reaction: $HO^{\ominus} + CH_3Br \longrightarrow HOCH_3 + Br^{\ominus}$

Mechanism, with arrows to show how electrons move, how the new bond forms, and how an old bond breaks:

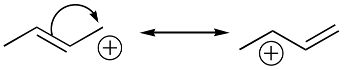


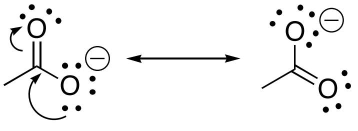
Notes:

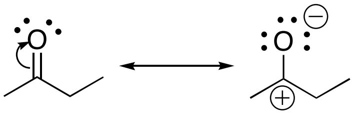
- Arrows are drawn to show how electron pairs are moving as new bonds form or old bonds break.
- Mechanisms help us to understand and generalize when and why bonds make or break, so that we can understand when and why reactions will occur and what products will form.
- Each arrow always goes from an electron source (either an atom with a lone pair or else a bond pair) to an acceptor atom
- **Terms:**
  a. "**Nucleophile**" = source of electon pair ("Lewis base")
  b. "**Electrophile**" = acceptor ("Lewis acid")

c. An arrow always proceeds from a nucleophile and points toward an electrophile.
d. Arrow-pushing is very helpful in relating two resonance structures

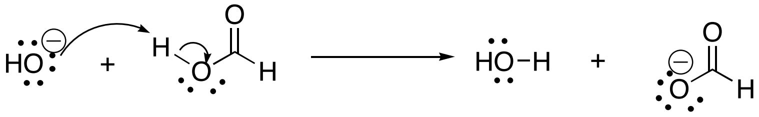
1. Use arrows to show how the electrons "move" from the first to the second resonance structures:

a. 

b. 

c. 

2. Use arrows to show the mechanism for the following acid-base reaction.



3. Use arrows to show the mechanism for the following two-step reaction. For the first step, identify the "nucleophile" and the "electrophile".