**Misunderstood Topics from CHM235**

**Arrow Pushing**

You will see arrow pushing everyday. Just to review some simple principles.

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; a bond is broken when the electrons are pushed towards an atom that is in the same 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.

Provide arrows:

a. \[ \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad + \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad \rightarrow \quad 2 \text{H}_2\text{O} \]

b. \[ \begin{array}{c}
\text{C} \\
\text{H}
\end{array} \quad + \quad \begin{array}{c}
\text{N} \\
\text{C}_2
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{N} \\
\text{O}_2
\end{array} \]

c. \[ \begin{array}{c}
\text{C} \\
\text{H}
\end{array} \quad + \quad \begin{array}{c}
\text{O} \\
\text{C}_3
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{C}
\end{array} \quad + \quad \text{H} \quad + \quad \begin{array}{c}
\text{O}
\end{array} \]

d. \[ \begin{array}{c}
\text{H} \\
\text{C}
\end{array} \quad + \quad \begin{array}{c}
\text{N} \\
\text{H}_3
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{N} \\
\text{H}_3
\end{array} \quad + \quad \begin{array}{c}
\text{N} \\
\text{H}_4
\end{array} \]

e. \[ \begin{array}{c}
\text{H} \\
\text{C}
\end{array} \quad + \quad \begin{array}{c}
\text{S} \\
\text{O}_2
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{O}
\end{array} \quad + \quad \text{S} \quad + \quad \text{S}_2 \quad + \quad \begin{array}{c}
\text{O}
\end{array} \]

Provide products:

f. \[ \begin{array}{c}
\text{H} \\
\text{C}
\end{array} \quad + \quad \begin{array}{c}
\text{Br}
\end{array} \]

\[ \begin{array}{c}
\text{H} \\
\text{C}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{C}
\end{array} \]

j. \[ \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \]

k. \[ \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \]

l. \[ \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \]

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

Another useful webpage:
http://www.chem.ucalgary.ca/courses/350/uccurlyarr.html
http://www.abdn.ac.uk/curly-arrows/chemistry/StudentCA.html
Acid/Base chemistry is based on acid dissociation: We talk about Ka and pKa.

Typical pKa's of these acids are approximately:
- C(sp³)-H: 50
- C(sp²)-H: 40
- C(sp)-H: 25
- C(alpha)-H: 20
- NH₃: 35
- H₂O: 15
- ROH: 15
- RCO₂H: 5

Strong-H < 0

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 states?

Unlikely acids

Most C-H acids are extremely weak.

\[ R_3C(sp³)-H \rightleftharpoons H^+ + R_3C(sp³)^- \quad Ka = pKa = \]

\[ R_3C(sp²)-H \rightleftharpoons H^+ + R_3C(sp²)^- \quad Ka = pKa = \]

\[ R_3C(sp)-H \rightleftharpoons H^+ + R_3C(sp)^- \quad Ka = pKa = \]

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.

\[
\begin{align*}
E & \\
R-H & \\
\text{rxn} & \\
R^-(sp³) & \\
R^-(sp²) & \\
R^-(sp) & \\
\downarrow & \quad Ka\cdot10^{35}
\end{align*}
\]

N-H:
What are some N-H acids?

pKa's of N-H:
- pKa's of N⁻-H

Even more acidic is O-H?

What are some O-H acids?

pKa's of O-H:
- pKa's of O⁻-H

Bases are classified based on pKa of their conjugate acid.
A strong base has a CA with pKa > 10. These bases usually lead E₂ products.

Classify these bases as strong or weak:
- OH⁻
- CH₃COO⁻
- N≡C⁻
- NH₂⁻
- NH₃
- Cl⁻
Equilibrium and predicting reaction

To calculate the extent of an acid base reaction is crucial. We can tell the direction and extent of any reaction given the pKas.

Given pKa(HCl) = -5 and pKa(H₂O) = 16 and pKa(NH₃) = 33. pKa(NH₄⁺) = 9. Make sure you understand why N-H can have more than one acid strength pKa.

**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 = \(10^{+ or - (pK_{a1} - pK_{a2})}\)

Left = -, Right = +. This can be derived algebraically. You're going to have to ask for it.

**Reactions.**

\[
\text{HO}^- + \text{H-Cl} \overset{\rightleftharpoons}{\text{H-OH} + \text{Cl}^-}
\]

Which direction will this reaction go and what will be the magnitude of the Keq?

\[
\text{H-C≡H} + \text{OH}^- \overset{\rightleftharpoons}{\text{H-OH} + \text{HC≡C}^-}
\]

Which direction will this reaction go and what will be the magnitude of the Keq?

\[
\text{H-C≡H} + \text{NH}_2^- \overset{\rightleftharpoons}{\text{H-NH}_2 + \text{HC≡C}^-}
\]

Which direction will this reaction go and what will be the magnitude of the Keq?

**Practice:**

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

(2) Given methanol CH₃OH 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.

**Spectroscopy**

**IR Spectroscopy:** What is IR good for?

<table>
<thead>
<tr>
<th>OH</th>
<th>CH(sp³)</th>
<th>CH(sp)</th>
<th>CH(sp²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>C=C</td>
<td>C-O</td>
<td></td>
</tr>
</tbody>
</table>

There are others: alkynes, aldehydes, nitriles, etc.

Back to basics. Assign OH, NH, CH(sp³), CH(sp²), C=C, C=O, C-O.
NMR

^1H NMR

NMR is really important because we can tell __________. There are 4 main points about NMR:
1. Integration = number of protons. Area under peaks. A ratio of number of protons.

2. Equivalence. Compare integration to the formula, if there is same number of protons as the formula, then all of the molecule is in the spectrum. If it is half, then you have half in the spectrum and must use symmetry to generate the rest.
To see equivalence, we can use symmetry and/or topology:
Symmetry depends on an axis or a plane (mirror) of symmetry.
Topology is a map: Place yourself on a proton and take a walk around the molecule. Is it the path the same or is it different?

3. Chemical shift
   0-2  H-C saturated
   2-3  H-C allyl
   3-4  H-C-EN (EN=N,O,F,Cl,Br,I)
   5-6  H-C vinyl
   6-8  H-C aromatic

You can have multiple effects. CH₃Cl CH₂Cl₂ CHCl₃
            3-4      5-6      7-8
Every Cl exerts about a 2 ppm shift. Assumes that a normal proton in a completely saturated environment is about 1 ppm. (0-2 ppm).

4. Splitting = n-1 nearest neighbors in a Pascal's triangle intensity pattern:
   0 neighbors = singlet
   1 neighbors = doublet
   2 neighbors = triplet
   3 neighbors = quartet

^13C NMR

Like proton NMR but different. ^13C NMR is based on 0 – 200 ppm. Since this is 20 times ^1H, just multiply by 20.
1. Chemical shifts are not as predictable as proton, but this is a guide.
   0-40  H-C saturated
   40-60  H-C allyl
   60-80  H-C-EN (EN=N,O,F,Cl,Br,I)
   100-120  H-C vinyl
   120-160  H-C aromatic
   with the bonus of C=O, around 180-200 ppm.

2. Integration = not used too much. It is difficult to integrate ^13C.
3. Splitting = we usually ignore splitting. We usually blast the splitting away with microwave energy.
   Most ^13C NMR spectra that you will see a forest of lines.

4. Equivalence. This is the main point of ^13C NMR. You can tell at a glance the number of unique carbons that are present in a molecule. This is very useful indeed.

Practice: The following spectra are based on simple alkyl bromides.
First, there is the pattern for C₂ Ethyl bromide, then C₃ – two types of propyl bromides, then on the next page, 4 types of butyl bromides.

Second are some ^13C NMR examples:

More practice is on the course web page.
Common $^1$H NMR Patterns: Match the groups and assign peaks. Ethyl, Propyl and Isopropyl: $\text{C}_9\text{H}_{12}$
More NMRs: Formula = C₄H₁₀O

Formula = C₈H₁₈ – best burning gasoline

Formula = C₅H₁₁Br
Using $^{13}$C NMR Patterns to determine structures. Here are aromatics substituted by two methyls. $\text{C}_8\text{H}_{10}$
Mass Spectrum and Degree of Unsaturation.

**Mass Spec** gives two bits of information. Most importantly, we get the exact mass of the molecule. This is usually the smallest peak because the molecule tends to fall apart once it becomes electrocuted and gains a charge. The second bit of info is how the molecule falls apart.

For example, let's consider the two propyl alcohol isomers. The mass spectrum of propyl alcohol would be $3\times12 + 8\times1 + 16 = 60$

![Mass Spectrum of Propyl Alcohol](image1)

Notice the 60 peak is there. The next peak is 17 less (OH) and a little more stable is less 18 (H₂O). This is from the elimination of water. However, the most stable species in the mass spec is at 31 – corresponding to loss of 29 = OH (17) + CH₂ (12). CH₂OH is equivalent to protonated formaldehyde.

Would loss of CH₂OH be easier from CH₃CH₂CH₂OH or (CH₃)₂CHOH?

The other isomer is shown here:

![Mass Spectrum of Secondary Propyl Alcohol](image2)

Here there is no 60 peak, but a 59 and the most stable species is 45. 45 is loss of 15. 15 usually corresponds to methyl (CH₃). That would leave CH₃CHOH (protonated acetaldehyde).

Would loss of CH₃ be easier from CH₃CH₂CH₂OH or (CH₃)₂CHOH?
Degree of Unsaturation is a little trick to tell how many double bonds or rings are in a molecule. If the molecule is completely saturated, we know the formula. So, we can reason from there.

You can use a formula, but there is no need. This is how to calculate the saturation number.

**Saturation #:**

**Completely saturated** = \( C_nH_{2n+2} \) If in doubt, draw ethane: \( CH_3CH_2CH_3 = C_3H_6 \)

Now put in a ring \( (CH_2)_3 \) \( C_3H_6 \)

Or a double bond. \( CH_3CH=CH_2 \) \( C_3H_6 \)

Notice that 2H are lost for one ring or double bond = 1° unsaturation.

Now put a double bond in the ring:

\[
\text{CH}_2 \text{CHCH} \]

Cyclopropene or 2 pi bonds \( HC\equiv C \equiv CH_3 \) propyne

Formula = \( C_3H_4 \).

We lost 2 more H and now have 2° of unsaturation.

In general use this chart:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Degree of unsaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_nH_{2n+2} )</td>
<td>0</td>
</tr>
<tr>
<td>( C_nH_{2n} )</td>
<td>1</td>
</tr>
<tr>
<td>( C_nH_{2n-2} )</td>
<td>2</td>
</tr>
<tr>
<td>( C_nH_{2n-4} )</td>
<td>3</td>
</tr>
</tbody>
</table>

And so on.

Helpful additions:

X=F,Cl,Br,I count as H.

O doesn’t count.

N takes away an H. \( CH_2NH_2 \) methyl amine is saturated. \( C_4H_{2(1)2} \)

See even if you forget how, just draw a simple molecule and you can see how it works.

Practice:

What is the degree of unsaturation of benzene \( C_6H_6 \)?

What is the degree of unsaturation of acetone \( CH_3C=OCH_3 \)?

What is the degree of unsaturation of allyl bromide \( CH_2=CHCH_2Br \)?

How could you tell the difference between a cyclic and an alkene?

How could you tell the difference between a alkyne and 2 alkenes?

How could you tell the difference between an unsaturated ether and a ketone?

How could you tell the difference between an aldehyde and a ketone?

**Summaries – CHM235 Review**

1. Arrow pushing 10% of course grade.
2. Acid base – determining what is the most acidic proton, determining the direction of a reaction, determining the base or acid strength of a molecule.
3. IR spectra indicate functional groups.
4. Proton NMR gives structural information and spin-spin splitting.
5. CNMR gives structural information mainly by equivalence.
6. Degree of unsaturation tells how many double bonds and/or rings.