Objective 8

intro to Reactivity 2: identify polar bonds (δ+ and δ-),
nucleophiles (Lewis base, electron pair donor),
electrophiles (Lewis acid, electron pair acceptor).
Use curved arrows to predict product.
Identify common bond breaking and making processes.
Chem 12A Objectives
Predict the product of a reaction.

Methionine + Adenosine Triphosphate (ATP) → SAM
Chem 12A Objective
Explain how reactants form products with a mechanism.

Squalene → Lanosterol

Precursor to cholesterol
Roots Run Deep Winery

“Our label was designed to tell the story of how you can make an educated guess in winemaking, not to give you nightmares about your high school chemistry class. It shows you actual winemaking formulas that are either induced or naturally occur during a specific winemaking process.”

Educated Guess

× (NAPA VALLEY + 2007)

CHARDONNAY
Chem 12A Objective

How is an unsaturated fat made saturated?

How do you synthesize an organic compound? E.g., How would you synthesize 1,3-butadiene (precursor to rubber) from acetylene?

\[
\text{from } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{ } \quad \text{
Organic Reactions are classified as **Polar**, **Radical**, or **Pericyclic**.

1. **Polar** reactions – nucleophile (Lewis base) reacts with an electrophile (Lewis acid).
   - heterolytic bond breaking and making
     \[ C:C \rightarrow C: + C \]
   Use “Curved Arrows” From Nu:\(-\) to E\(+\) to Show Bonds Forming and Breaking (electron pairs move in the same direction)

   • **Most organic reactions are polar reactions and equilibrium reactions.**
   • Polar reaction: ID nucleophile and electrophile - see structure.
   • Best Nu:\(-\) reacts with best E\(+\).

2. Radical reactions - light (usually UV) is used to break chemical bonds
   - homolytic bond breaking and making
     \[ C:C \rightarrow C\cdot + C\cdot \]  
    radical = unpaired electron
   Curved arrows: one electron moves in opposite directions

3. pericyclic reactions - several pairs of electrons breaking/forming bonds in concert
4 Types of Organic Polar Reactions

- **Acid-Base**
  \[
  \text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water}
  \]

- **Addition**
  \[
  \text{Molecule} + \text{Additive} \rightarrow \text{Adduct}
  \]

- **Substitution**
  \[
  \text{Molecule} + \text{Nu}^+ \rightarrow \text{Nu-substituted Molecule} + \text{Leaving Group}
  \]

- **Elimination**
  \[
  \text{Molecule} + \text{Nu}^+ \rightarrow \text{Nu-eliminated Molecule} + \text{Leaving Group}
  \]

Identify the \text{Nu}^- and \text{E}^+ in each reaction.
**Structural Features** (functional groups) give you information about how organic compounds react.

a. Identify the most reactive nucleophile and electrophile to predict the most probable reaction partners.

b. Rank the relative reactivity of the common Nu:− and E+ (best to worst) by type and within each type. See Table 1 on Reactivity Principles and Trends (Course Info Handout, p. 5)

c. Draw a “curved arrow” from the nucleophile to the electrophile using a known bond breaking/making process. See Table 2 on Reactivity Principles and Trends

d. Many Organic Reactions occur at alpha carbon or H bonded to beta carbon.
Organic Reactions Involve

**Converting One Functional Group to Another**

Most organic reactions are **Polar Reactions**

Polar = look for (+) and (-) poles in molecule

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrophiles</strong></td>
<td><strong>Nucleophiles</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(+) pole</th>
<th>(-) pole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Sink</td>
<td>Electron Source</td>
</tr>
</tbody>
</table>

**Electrophile** | **Nucleophile**

<table>
<thead>
<tr>
<th>(+) charge</th>
<th>(-) charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid (Lewis)</td>
<td>Base (Lewis)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electron deficient species</th>
<th>Lone pair</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Less EN atom in polar bond</th>
<th>$\pi$ bond</th>
</tr>
</thead>
</table>

Table 1. Nucleophile (Electron Sources) and Electrophile (Electron Sinks) Classification

<table>
<thead>
<tr>
<th>Nucleophile Type</th>
<th>Example</th>
<th>Electrophile Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organometallics (see carbanions)</td>
<td>alkyl lithium (CH₃⁻)</td>
<td>Best</td>
<td>Electron deficient species</td>
</tr>
<tr>
<td>Group I hydrides (H:⁻)</td>
<td>NaH</td>
<td>Acids</td>
<td>HCl</td>
</tr>
<tr>
<td>Complex metal hydrides</td>
<td>NaBH₄</td>
<td>Single bonds between heteroatoms</td>
<td>C-O (C is the E⁺)</td>
</tr>
<tr>
<td>Active metals</td>
<td>Li metal</td>
<td>Leaving groups on sp³ carbons</td>
<td>CH₃I (I is the leaving group)</td>
</tr>
<tr>
<td>Lone pair nucleophiles, bases</td>
<td>ROH, RNH₂, OH</td>
<td>Carboxyl derivatives (sp²-bound L)</td>
<td>acyl halides, anhydrides, esters</td>
</tr>
<tr>
<td>Allylic sources</td>
<td>enolates, enamines</td>
<td>Heteroatom-carbon multiple bonds</td>
<td>aldehydes, ketones, nitriles, CO₂</td>
</tr>
<tr>
<td>Simple pi bonds</td>
<td>alkenes, alkynes, dienes</td>
<td>Conjugate acceptors</td>
<td>enones, acrylates</td>
</tr>
<tr>
<td>Aromatic rings</td>
<td>benzene</td>
<td>Worst</td>
<td>redox-active metals</td>
</tr>
</tbody>
</table>
Electronegativity tells us _______________.

Identify the polar bond(s). For each polar bond, show the atom with the partial positive charge ($\delta^+$) and the atom with the partial negative charge ($\delta^-$).

What *type of electrophile* is the $\delta^+$ atom?
Electronegativity tells us about bond polarity.

Intro to Reactivity and Structural Features:
An anion (nucleophile) can react with the:
1. carbon bonded to the Br (this C is called the alpha C and is an electrophile and is involved in substitution reactions),
2. H bonded to the carbon adjacent to the C bonded to Br (this C is called the beta carbon and is an electrophile and is involved in elimination reactions).

Explain using bond polarity.
**Polar Reactions Involve Nucleophiles and Electrophiles**

Fill in the table below.

Which functional group is the best Nu: -? E +?

Which reactant is the best Nu: -? E +?

Chem 12A Functional Groups and Reactants

<table>
<thead>
<tr>
<th>Functional Group/ Structural Feature</th>
<th>Nu: - or E +? Type?</th>
<th>Reactant</th>
<th>Nu: - or E +? Type?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>See radical rxns</td>
<td>OH -</td>
<td></td>
</tr>
<tr>
<td>Alkene/pi bond</td>
<td></td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>Alkyne/pi bond</td>
<td></td>
<td>HX</td>
<td></td>
</tr>
<tr>
<td>Alcohol/acidic H, basic O, alpha C</td>
<td></td>
<td>X -</td>
<td></td>
</tr>
<tr>
<td>Alkyl Halide/alpha C, H on beta C</td>
<td></td>
<td>X₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃O -</td>
<td></td>
</tr>
</tbody>
</table>

*Hint: see Table 1 on Reactivity Principles and Trends*
Explain or Predict the Major and Minor Reaction Products With a Reaction Mechanism

Experiment --> Rate law --> Reaction mechanism
Reaction mechanism: sequence by which bonds break and form going from reactants to intermediates to products. Rate determining step: slowest step in mechanism Stability of intermediate or product helps you determine product distribution.

Use “curved arrows” to show bonds breaking and forming in each elemental step.

For polar reactions:
Nu:− reacts with E+
Draw curved arrow from Nu:− to E+
4 Types of Organic Polar Reactions

**Acid-Base**

\[
\text{CH}_3\text{CO}_2\text{H} + \text{B}^- \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{B}^- \text{H}
\]

**Addition**

\[
\text{C} = \text{C} + \text{X}-\text{Y} \rightarrow \text{CH}_3\text{CH}=\text{Y}
\]

**Substitution**

\[
\text{Nu}^- + \text{H}_2\text{C}=\text{CH}-\text{H} \rightarrow \text{H}_2\text{C}=\text{CH}\text{Nu} + \text{H}_2\text{C}=\text{CH}^-
\]

**Elimination**

\[
\text{Nu}^- + \text{H}_2\text{C}=\text{CH}-\text{H} \rightarrow \text{H}_2\text{C}=\text{CH} + \text{Nu}^-\text{H} + \text{H}^-\text{C}=\text{CH}^-
\]

Identify the Nu:− and E+: in each reaction.
Polar Reactions:
1. Proton transfer

2. Ionization of a leaving group

3. Nucleophilic attack on:
   - Electron deficient species, e.g., C⁺
   - C bonded to leaving group (α-C)
   - H bonded to β C (C adjacent to C bonded to leaving group)
   - A polarized multiple bond, e.g., C=O

4. 1,2 rearrangement of a carbocation

Table 2. Known Bond Breaking and Making Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton transfer</td>
<td>1. Proton transfer</td>
</tr>
<tr>
<td>Ionization of a leaving group</td>
<td>2. Ionization of a leaving group</td>
</tr>
<tr>
<td>Nucleophilic attack</td>
<td>3. Nucleophilic attack on:</td>
</tr>
<tr>
<td></td>
<td>• Electron deficient species, e.g., C⁺</td>
</tr>
<tr>
<td></td>
<td>• C bonded to leaving group (α-C)</td>
</tr>
<tr>
<td></td>
<td>• H bonded to β C (C adjacent to C bonded to leaving group)</td>
</tr>
<tr>
<td></td>
<td>• A polarized multiple bond, e.g., C=O</td>
</tr>
<tr>
<td>1,2 rearrangement of a carbocation</td>
<td>4. 1,2 rearrangement of a carbocation</td>
</tr>
</tbody>
</table>
Identify the bond making/breaking process in each step. Use curved arrows to show bonds breaking/forming.

Step 1
\[
\text{CH}_3\text{OH} + \text{H-Cl} \rightarrow \text{CH}_3\text{OH}_2^+ + \text{Cl}^-
\]

Step 2
\[
\text{CH}_3\text{OH}_2^+ + \text{Cl}^- \rightarrow \text{CH}_3^+ + \text{Cl}^- + \text{H}_2\text{O}
\]

Step 3
\[
\text{CH}_3^+ + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}
\]

Choices: Proton transfer, ionization of LG, nucleophilic attack
Identify the bond making/breaking process in each step. Use curved arrows to show bonds breaking/forming.

More Practice Problems: Klein, Ch. 6.30

**Choices:** Proton transfer, ionization of LG, nucleophilic attack
Use curved arrows to show how each product is produced.

\[
\begin{array}{c}
\mathrm{Cl} \\
\mathrm{H}
\end{array}
+ \begin{array}{c}
\mathrm{O} \\
\mathrm{H}
\end{array} \rightarrow \begin{array}{c}
\mathrm{OH} \\
\mathrm{H}
\end{array} + \mathrm{Cl}^{-}
\]

The bond breaking/making process is a **nucleophilic attack**. What *type* of nucleophilic attack is this?

- Electron deficient species, e.g., C^+  
- C bonded to leaving group (α-C)  
- H bonded to β C (C adjacent to C bonded to leaving group)  
- A polarized multiple bond, e.g., C=O

What is the reaction type?

- Acid-base substitution  
- Elimination addition
Use curved arrows to show how each product is produced.

The bond breaking/making process is a nucleophilic attack. What type of nucleophilic attack is this?
- Electron deficient species, e.g., C\(^+\)
- C bonded to leaving group (\(\alpha\)-C)
- H bonded to \(\beta\) C (C adjacent to C bonded to leaving group)
- A polarized multiple bond, e.g., C=O

What is the reaction type?
- Acid-base substitution
- Elimination addition
Use curved arrows to show how each product is produced.

This reaction is an addition reaction.

What is the bond breaking/making process in the 1st step?

In the 2nd step, the bond breaking/making process is a nucleophilic attack.

What type of nucleophilic attack is this?

• Electron deficient species, e.g., C+
• C bonded to leaving group (α-C)
• H bonded to β C (C adjacent to C bonded to leaving group)
• A polarized multiple bond, e.g., C=O
**Objective**: Identify 3° or 2° or 1° Carbocations.
Rank Carbocations by stability: 3° > 2° > 1°

Classify the following carbocations as 3° or 2° or 1°. Which carbocation is the most stable? Least stable?

A

B

C
Objective: Identify how a Carbocation forms. Identify how a Carbanion forms.

Which reaction forms a Carbocation?

A

B

C

Hint: ID Nu: and E and reaction type.
1,2 rearrangement: If you see a 2° or 1° carbocation, see if a more stable C⁺ can form via hydride shift or alkyl shift on adjacent carbon.

Does this hydride (H⁻) shift make a more stable carbocation? If not, show a rearrangement that makes a more stable C⁺.
Carbocation Rearrangement Mechanism: Rearrangement proceeds through a protonated *mesomeric* cyclopropane intermediate (through computer simulations)

Which compound(s) will undergo a rearrangement? Use curved arrows to show the rearrangement.
(Klein, 6.18 a, c, and f)
A **Chemical Reaction** Occurs When **Reactants Collide** with _______ and __________ for Bonds to Break or Form.

Unstable, high energy substances

Stable, low energy substances

More reactive

Or

Less reactive?
A Reaction Occurs When Reactants Collide with Sufficient Energy and Correct Orientation for Bonds to Break or Form

**Sufficient Energy:**
high T or low T?

**Correct Orientation:**
Which path does blue take to red?
The “right” atoms in each reactant have to collide together. Alignment and access.
To Break a Bond \[\underline{\text{_____}}\] Energy
When a Bond Forms, Energy is \[\underline{\text{________}}\]

**Teflon**: A C-F bond is strong and is hard to break.
A lot of energy is \[\underline{\text{____}}\] when a C-F bond is formed.

**Dynamite and TNT**: A N-O is weak and is easy to break.
A \[\underline{\text{___}}\] of energy is \[\underline{\text{_____}}\] when a N-O bond is formed.
To Break a Bond **REQUIRES** Energy
When a Bond Forms, Energy is **RELEASED**

**Teflon**: A C-F bond is strong and is hard to break. A lot of energy is **RELEASED** when a C-F bond is formed.

**Dynamite and TNT**: A N-O is weak and is easy to break. A **LITTLE BIT** of energy is **RELEASED** when a N-O bond is formed.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta H$, kcal/mole</th>
<th>Bond</th>
<th>$\Delta H$, kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-F</td>
<td>116</td>
<td>C-H</td>
<td>109</td>
</tr>
<tr>
<td>C-Cl</td>
<td>81</td>
<td>N-H</td>
<td>101</td>
</tr>
<tr>
<td>C-Br</td>
<td>68</td>
<td>O-H</td>
<td>96</td>
</tr>
<tr>
<td>C-I</td>
<td>51</td>
<td>C-O</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N-O</td>
<td>48</td>
</tr>
</tbody>
</table>

Organic Chemists talk about “activating a C-H bond.” What does that mean?
General Reaction Principles are useful on paper (lecture) and in lab

(i) **Thermodynamics**
2 driving forces: enthalpy and entropy
What does structure tell you about stability?

Strong bonds don’t react (see Teflon with strong C-F bonds); Weak bonds do react (see weak N-O bonds in TNT). Bond dissociation energies can be used to estimate $\Delta H_{\text{rxn}}$ ("bonds broken minus bonds made") and give relative stabilities of reactants and products.

(ii) **Reaction rates**
3 factors: Temperature, concentration, and catalyst
What does structure tell you about reaction rate? Accessibility of reactant to reaction site.

(iii) **Equilibrium** (reversible reactions)
LeChatelier’s principle: stressing a reaction shifts the reaction in a direction that relieves the stress.
Stress: concentration, temperature, pressure (gases)
Teflon is stable and unreactive because of strong C-F bonds

\[
\left( \begin{array}{ccc}
F & F \\
F & F \\
\end{array} \right)_n
\]

http://en.wikipedia.org/wiki/Polytetrafluoroethylene#Properties

**Properties:** high m.p. (327°C)
Non-polar and Insolubility
High thermal stability
Low coefficient of friction
Low dielectric constant
Excellent weatherability
Flame resistant
Excellent toughness
Nitroglycerin is unstable and reactive because of weak N-O bonds.

\[ \text{O}_2\text{N} - \text{NO}_2 \quad \text{nitroglycerin} \]

Colorless liquid
\[ \Delta H_{\text{combustion}} = -1.53 \text{ MJ/mole} \]
Shock sensitivity = high
Friction sensitivity = high
Explosive velocity = 7700 m/sec

Since the 1860s, nitroglycerin has been used as an active ingredient in the manufacture of explosives, mostly dynamite. Nitroglycerin is also used medically as a vasodilator to treat heart conditions, such as angina and chronic heart failure

http://en.wikipedia.org/wiki/Nitroglycerin
Bond Strength Determines Reactivity.
What makes a bond strong or weak? What does d tell you?

<table>
<thead>
<tr>
<th>Bond</th>
<th>d, pm</th>
<th>( \Delta H ), kcal/mole</th>
<th>Bond</th>
<th>d, pm</th>
<th>( \Delta H ), kcal/mole</th>
<th>Bond</th>
<th>d, pm</th>
<th>( \Delta H ), kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>109</td>
<td>99</td>
<td>C-C</td>
<td>154</td>
<td>83</td>
<td>C-O</td>
<td>143</td>
<td>94</td>
</tr>
<tr>
<td>O-H</td>
<td>96</td>
<td>88</td>
<td>C=C</td>
<td>134</td>
<td>146</td>
<td>C=O</td>
<td>120</td>
<td>177</td>
</tr>
<tr>
<td>N-H</td>
<td>101</td>
<td>101</td>
<td>C≡C</td>
<td>120</td>
<td>201</td>
<td>C≡O</td>
<td>113</td>
<td>256</td>
</tr>
<tr>
<td>H-F</td>
<td>92</td>
<td>136</td>
<td>C-F</td>
<td>135</td>
<td>116</td>
<td>C-N</td>
<td>147</td>
<td>73</td>
</tr>
<tr>
<td>H-Cl</td>
<td>127</td>
<td>103</td>
<td>C-Cl</td>
<td>177</td>
<td>81</td>
<td>C=N</td>
<td>129</td>
<td>147</td>
</tr>
<tr>
<td>H-Br</td>
<td>141</td>
<td>87.5</td>
<td>C-Br</td>
<td>194</td>
<td>68</td>
<td>C≡N</td>
<td>116</td>
<td>212</td>
</tr>
<tr>
<td>H-I</td>
<td>161</td>
<td>71</td>
<td>C-I</td>
<td>214</td>
<td>51</td>
<td>N-O</td>
<td>140</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N=O</td>
<td>121</td>
<td>145</td>
</tr>
</tbody>
</table>

Note: Average bond energies. Some bonds show considerable variability.
### Table 1. Molecular Bond Dissociation Energies for RH → R + H: Experimental Bond Enthalpies and Radical Heats of Formation at 298 K

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_{298}$ (kcal mol$^{-1}$)</th>
<th>$\Delta H_{298}(R)$ (kcal mol$^{-1}$)</th>
<th>ref</th>
<th>$\Delta H_{298}$ (kcal mol$^{-1}$)</th>
<th>$\Delta H_{298}(R)$ (kcal mol$^{-1}$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>104.206 ± 0.003</td>
<td>52.103 ± 0.003</td>
<td>4</td>
<td>OH$^-$ → O$^-$ + H</td>
<td>110.21 ± 0.07</td>
<td>34</td>
</tr>
<tr>
<td>HF</td>
<td>136.25 ± 0.01</td>
<td>18.83 ± 0.17</td>
<td>6</td>
<td>OH$^+$ → O + H$^+$</td>
<td>115.2 ± 0.1</td>
<td>34</td>
</tr>
<tr>
<td>HCl</td>
<td>103.15 ± 0.03</td>
<td>29.03 ± 0.04</td>
<td>9</td>
<td>H$_2$S</td>
<td>91.2 ± 0.1</td>
<td>6</td>
</tr>
<tr>
<td>HBr</td>
<td>87.54 ± 0.05</td>
<td>28.62 ± 0.06</td>
<td>9</td>
<td>SH</td>
<td>84.1 ± 0.2</td>
<td>6</td>
</tr>
<tr>
<td>HI</td>
<td>71.32 ± 0.06</td>
<td>26.04 ± 0.08</td>
<td>9</td>
<td>H$^-$ → NO</td>
<td>49.5 ± 0.7</td>
<td>4</td>
</tr>
<tr>
<td>H-CN</td>
<td>126.3 ± 0.2</td>
<td>105.0 ± 0.7</td>
<td>6</td>
<td>H$^-$ → ONO (trans)</td>
<td>79.1 ± 0.2</td>
<td>4</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>107.6 ± 0.1</td>
<td>44.5 ± 0.1</td>
<td>6</td>
<td>SiH$_4$</td>
<td>91.7 ± 0.5</td>
<td>9</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>118.82 ± 0.07</td>
<td>8.86 ± 0.07</td>
<td>34</td>
<td>GeH$_4$</td>
<td>83 ± 2</td>
<td>9</td>
</tr>
<tr>
<td>OH</td>
<td>101.76 ± 0.07</td>
<td>59.55 ± 0.02</td>
<td>34</td>
<td>GeH$_4$</td>
<td>83 ± 2</td>
<td>9</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>104.99 ± 0.03</td>
<td>35.05 ± 0.07</td>
<td>31</td>
<td>CH$_3$CH=C$^-$H</td>
<td>110.7 ± 0.6</td>
<td>6</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>110.4 ± 0.2</td>
<td>93.3 ± 0.2</td>
<td>31</td>
<td>HCC=C$^-$H</td>
<td>133.32 ± 0.07</td>
<td>36</td>
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<tr>
<td>CH$_2$</td>
<td>101.3 ± 0.3</td>
<td>142.5 ± 0.2</td>
<td>9</td>
<td>CaH$_2$</td>
<td>112.9 ± 0.5</td>
<td>6</td>
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<tr>
<td>CH</td>
<td>80.9 ± 0.2</td>
<td>171.3 ± 0.1</td>
<td>9</td>
<td>CaH$_2$ → α CaH$_1$ + H</td>
<td>78 ± 3</td>
<td>37</td>
</tr>
<tr>
<td>CH$_3$C$^-$H = CH$_2$C$^-$H</td>
<td>101.1 ± 0.4</td>
<td>29.0 ± 0.4</td>
<td>10</td>
<td>CaH$_3$ → m CaH$_1$ + H</td>
<td>78 ± 3</td>
<td>106 ± 3</td>
</tr>
<tr>
<td>CH$_3$C$^-$H = CH$_2$C$^-$H</td>
<td>88.6 ± 0.4</td>
<td>21.5 ± 0.4</td>
<td>10</td>
<td>CaH$_3$ → m CaH$_1$ + H</td>
<td>78 ± 3</td>
<td>106 ± 3</td>
</tr>
<tr>
<td>CH$_3$C$^-$H = CH$_2$C$^-$H</td>
<td>98.2 ± 0.5</td>
<td>16.1 ± 0.5</td>
<td>10</td>
<td>CH$_3$CH$_2$H$^-$H</td>
<td>88.8 ± 0.4</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>96.5 ± 0.4</td>
<td>12.3 ± 0.4</td>
<td>10</td>
<td>CaH$_3$CH$_2$H$^-$H</td>
<td>88.8 ± 0.6</td>
<td>38</td>
</tr>
<tr>
<td>H$^-$CH$_2$OH</td>
<td>96.1 ± 0.2</td>
<td>-4.08 ± 0.2</td>
<td>16</td>
<td>CH$_3$CH$_2$O$^-$H</td>
<td>104.7 ± 0.8</td>
<td>6</td>
</tr>
<tr>
<td>CH$_3$O$^-$H</td>
<td>104.6 ± 0.7</td>
<td>4.3 ± 0.7</td>
<td>6</td>
<td>(CH$_3$)$_2$CHO$^-$H</td>
<td>105.7 ± 0.7</td>
<td>6</td>
</tr>
<tr>
<td>CH$_3$S$^-$H</td>
<td>87.4 ± 0.5</td>
<td>29.8 ± 0.4</td>
<td>39</td>
<td>(CH$_3$)$_2$CO$^-$H</td>
<td>106.3 ± 0.7</td>
<td>6</td>
</tr>
<tr>
<td>H$^-$CH$_2$SH</td>
<td>94 ± 2</td>
<td>36 ± 2</td>
<td>39</td>
<td>(CH$_3$)$_2$CO$^-$H</td>
<td>106.3 ± 0.7</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>87.8 ± 0.5</td>
<td>3.2 ± 0.5</td>
<td>14</td>
<td>CH$_3$CH$_3$COO$^-$H</td>
<td>85 ± 2</td>
<td>41</td>
</tr>
<tr>
<td>CH$_3$OO$^-$H</td>
<td>88 ± 1</td>
<td>4.8 ± 1.2</td>
<td>42</td>
<td>(CH$_3$)$_2$COO$^-$H</td>
<td>84 ± 2</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>98.144 ± 0.008</td>
<td>10.1 ± 0.1</td>
<td>6</td>
<td>H$^-$COOH is ≥</td>
<td>96 ± 1</td>
<td>45</td>
</tr>
<tr>
<td>CH$_3$C(O)$^-$H</td>
<td>89.4 ± 0.3</td>
<td>-2.4 ± 0.3</td>
<td>43</td>
<td>CH$_3$COO$^-$H</td>
<td>112 ± 3</td>
<td>44</td>
</tr>
<tr>
<td>H$^-$CH$_3$CHO</td>
<td>94 ± 2</td>
<td>2.5 ± 2.2</td>
<td>9</td>
<td>CaH$_3$COO$^-$H</td>
<td>111 ± 4</td>
<td>44</td>
</tr>
<tr>
<td>HCOO$^-$H</td>
<td>112 ± 3</td>
<td>-30 ± 3</td>
<td>44</td>
<td>CaH$_3$COO$^-$H</td>
<td>111 ± 4</td>
<td>44</td>
</tr>
</tbody>
</table>

Reference: [http://www.colorado.edu/chem/ellison/research/resThermo.html](http://www.colorado.edu/chem/ellison/research/resThermo.html)
Bigger Orbital Overlap Means Stronger Bond

• A ______ (stronger or weaker) bond will have _____ (more or less) s character in the bonding orbital.

• In general, a weak bond is _____ (more or less) reactive than a strong bond.

• A C-C single bond is unreactive.

• The $\pi$ bond in a C-C double bond or triple bond is reactive.
It is better to be spread out than concentrated.

Which compound is more stable? Why?

http://www.homocon.com/archives/2006/12/
http://danceswithfat.wordpress.com/2011/05/25/taking-up-space/crowded-subway/
General Reaction Principles are useful on paper (lecture) and in lab

(i) *Thermodynamics*
2 driving forces: enthalpy and entropy
What does structure tell you about stability?

(ii) *Reaction rates*
3 factors: Temperature, concentration, and catalyst
What does structure tell you about reaction rate? Accessibility of reactant to reaction site.

Which process occurs fastest? The fastest reactions produce the major product. E.g., proton transfer is very fast - often the first step in a reaction mechanism. But with weak organic acids and bases, proton transfer is slow enough to allow nucleophilic attack.

(iii) *Equilibrium* (reversible reactions)
LeChatelier’s principle: stressing a reaction shifts the reaction in a direction that relieves the stress.
Stress: concentration, temperature, pressure (gases)
Fill in the blanks:

A catalyst is used to ______ the reaction rate.

A catalyst ______ the activation energy of a reaction.

A catalyst ______ the equilibrium constant.

A catalyst ______ the reaction mechanism.

Increase     Decrease
Raises       Lowers
Changes      Does not change
**Kinetics:**
The rate law of a reaction is determined by Experiment

\[ A + B \rightarrow \text{products} \quad \text{rate} = k [A]^x [B]^y \]

*What information does x and y tell us?*

The rate law tells us the number of each reactant in the rate determining step in a **Reaction Mechanism**.

*What is a Reaction Mechanism?*

We can use a Reaction Mechanism to:
- explain product distribution.
- help us predict a product of a reaction.

The rate determining step is the ________ step of a mechanism.
A Reaction Energy Diagram tells you about THERMO and KINETICS

Progress of reaction

Label the following: reactants, products, intermediate, ΔH, $E_a$

Where is the thermo in this diagram?
Where is the kinetics in this diagram?
A Reaction Energy Diagram tells us about a Mechanism

How many steps in this mechanism?
Which step is the rate determining step?
If a catalyst is used, does the mechanism change?

Thermo: The stability of intermediates, such as $1^\circ$, $2^\circ$, $3^\circ$ carbocation, anions, radicals, can be used to choose between reasonable alternatives, e.g., Markovnikov’s rule. (see Reactivity Principles and Trends)
General Reaction Principles are useful on paper (lecture) and in lab

(i) **Thermodynamics**
2 driving forces: enthalpy and entropy
What does structure tell you about stability?

(ii) **Reaction rates**
3 factors: Temperature, concentration, and catalyst
What does structure tell you about reaction rate? Accessibility of reactant to reaction site.

(iii) **Equilibrium** (reversible reactions)
LeChatelier’s principle: stressing a reaction shifts the reaction in a direction that relieves the stress.
Stress: concentration, temperature, pressure (gases)
E.g., organic acid-base (proton transfer) reactions are equilibrium reactions and tend to form the weaker acid/base. See pK_a tables.
Most organic reactions are *exothermic* and *equilibrium* reactions.

In the **Organic Chemistry Lab**, you synthesize compounds:

\[
\text{Reactants} \rightleftharpoons \text{Products + heat}
\]

You choose the Reaction Conditions:
- Temperature, time, limiting reactant, excess reactant, …

What reaction conditions would you choose to **maximize product yield** and **minimize reaction time**?
Back to the Lab - Reaction conditions:

• High temperature or low temperature?

• What solvent to use if you reflux?

• Which reactant should be the excess reactant?

• How much excess reactant should you use?

• You can distill rather than reflux. Why would you want to distill your reaction mixture?

• Should you use a catalyst?