**Useful Definitions:**

**Mechanism** – A scheme that illustrates all reaction intermediates, as well as the flow of electrons and movement of atoms during bond breaking and bond making processes. Remember that arrows are used only to indicate the movement of electrons. Movement of atoms is assumed, but not explicitly indicated, by the arrows.

**Nucleophile** – A molecule that contains an atom with a lone pair AND a full or partial negative charge.

**Electrophile** – A molecule that contains an atom with a full or partial positive charge AND can be attacked by a nucleophile without creating a non-viable species such as a pentavalent (five bonds) carbon.

**Brønsted-Lowry Base** – A molecule containing at least one atom with a lone pair that will accommodate binding to a proton during a proton transfer reaction.

**Lewis Base –** A molecule that can donate a lone pair in a bond-forming process.

**Brønsted-Lowry Acid** – A molecule that can donate a proton during a proton transfer reaction.

**Lewis Acid –** A molecule that can accept a lone pair in a bond-forming process.

**Leaving group** – A group that will be relatively stable when it departs, such as a small neutral species like H2O or N2, or a group such as a halide atom that departs as a relatively stable ion.

Mechanisms: The Basics

**A) The Correct Use of Arrows to Indicate Electron Movement**

The ability to write an organic reaction mechanism properly is key to success in organic chemistry classes. Organic chemists use a technique called **arrow pushing** to depict the flow or movement of electrons during chemical reactions. Arrow pushing helps chemists keep track of the way in which electrons and their associated atoms redistribute as bonds are made and broken. The first essential rule to keep in mind is the following:

***First rule:* Arrows are used to indicate movement of *electrons***

A regular arrow (double-sided arrowhead) is used to indicate the movement of two electrons, while a line with a single-sided arrowhead (sometimes called a “fish hook arrow”) is used for single electron movement involved with radical reactions that are first described in Chapter 8.



The great majority of reactions that will be discussed in this book involve movement of pairs of electrons, so they are represented by double-sided arrowheads.

***Second Rule:* Arrows are never used to indicate the movement of atoms directly. The arrows only show atom movement indirectly as a consequence of electron movement when covalent bonds are made and broken.**



A common mistake beginning students make is that they will erroneously write an arrow pointing *from* the H of the acetic acid *to* the O atom of the hydroxide anion. This is wrong, because such an arrow would be indicating the H *atom* movement directly, not *electron* movement!



***Third Rule:* Arrows always start at an electron source and end at an electron sink.**



An **electron** **source** is a bond or a lone pair of electrons. It is either a  bond or a lone pair on an atom of relatively high electron density in a molecule or ion, or a bond that must break during a reaction. An **electron sink** is an atom on a molecule or ion that can accept a new bond or lone pair of electrons.

***Fourth rule:* Breaking a bond will occur to avoid overfilling valence (hypervalence) on an atom serving as an electron sink.**

In these cases, the electron source for the arrow is the bond being broken, and the sink is an atom able to accommodate the electrons as a lone pair, generally an electronegative atom such as an O atom or a halogen. If an ion is created, that ion is often stabilized by resonance delocalization or other stabilizing interactions.



**Polar Reaction Mechanisms:** Polar reactions are most of what you will see in organic chemistry. There are only four different mechanistic elements that combine to make up the different steps of almost all the mechanisms you saw in CH320M/CH328M. Better yet, in CH320N the following four mechanistic elements are pretty much all you need to think about until we get to electrophilic aromatic substitution.

1. **Make a new bond between a nucleophile (source for an arrow) and an electrophile (sink for an arrow).** Use this element when there is a nucleophile present in the solution as well as an electrophile suitable for reaction to occur.
2. **Break a bond so that relatively stable molecules or ions are created**  Use this element when there is no suitable nucleophile-electrophile or proton transfer reaction, but breaking a bond can create neutral molecules or relatively stable ions, or both.
3. **Add a proton** Use this element when there is no suitable nucleophile-electrophile reaction, but the molecule has a strongly basic functional group or there is a strong acid present.
4. **Take a proton away** Use this element when there is no suitable nucleophile-electrophile reaction, but the molecule has a strongly acidic proton or there is a strong base present.

The situation is even simpler than you might expect because 1 and 2 are the functional reverse of each other, as are 3 and 4.

# Mechanism Summary

The following questions and mechanistic elements are described from the point of view of the carbon-containing reagent, written in the form of a flowchart.

Is there a strong acid present or is the carbon- containing reagent a strong base?

## YES

# Add a proton

## NO

Is there a strong base present or is the carbon- containing reagent a strong acid?

# YES Take a proton

**away**

## NO

Are there a nucleophile and electrophile present?

## NO

Can a bond be broken to create stable molecules or ions?

## NO

Think about alternative mechanistic elements (radical reaction, SN2, E2, etc.)

**YES**

# Make a bond

**YES**

# Break a bon