Understanding Reactivity

Chemistry is the study of change. Up to this point, the molecular changes we have studied involved internal changes such as conformational rotation about single bonds of alkanes or ring flipping of cyclohexane. None of these changes involved the breaking and making of covalent bonds. The chemical change we will study from this point forward involves changes in electron configuration. Much of the language that was developed in previous lessons will apply to covalent bond changes. Our description of these changes will greatly benefit from the curved arrow notation that we began to study when we discussed resonance. The discussion of **intermediates** and **transition states** from the last lesson will be utilized as well.

Our goal in this course is to learn and understand the chemical transformations (i.e., *reactions*) common to molecular compounds. To achieve this goal, we will analyze reactions by breaking them down into a sequence of "**elementary steps**". This sequence of steps is called the ***reaction mechanism***. In order to write mechanisms, you will need a working knowledge of the electronic structure of molecules and the skill in writing curved arrow notation. This lesson will begin to put these skills to use as we learn to write the mechanism for a simple reaction - the proton transfer reaction.

Organizing chemistry around mechanisms allows the process of change to be **understood**, not just memorized. Once basic principles of reactivity are understood, you'll learn to **reason-by-analogy** to rationalize and predict outcomes of reactions that you've never previously seen.

"Elementary step"?

Elementary steps describe the process of change between ***adjoining*** minima on the MEP of an overall reaction. Many reactions have several minima (i.e., intermediates) located between starting and ending points. Thus, the overall reaction mechanism requires a sequence of elementary steps to describe the entire process.

Each elementary step has:

•A reaction arrow (→) connecting the starting and ending structures of that step

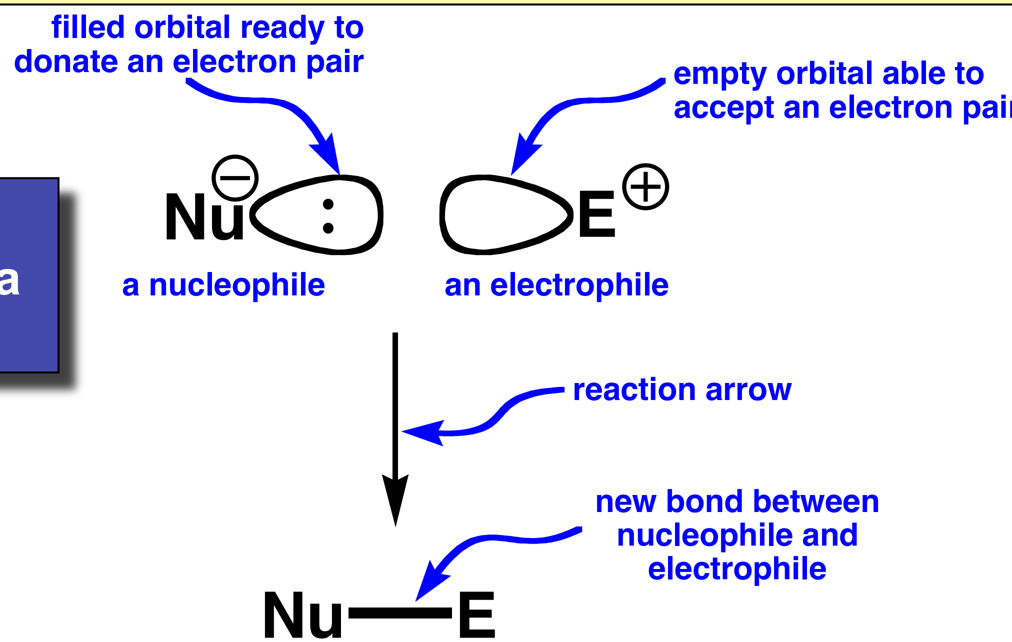
•Balanced charge

•Balanced stoichiometry

Nucleophiles and Electrophiles

We will expand the concept of acids and bases to a related classification scheme known as **electrophiles** and **nucleophiles**. The word *nucleophile* derives from the Greek *nucleo*, for "nucleus," and *philos*, for "loving." The word electrophile is derived from the Greek *electros*, "electron," and *philos*, "loving." Most elementary steps involve a nucleophile reacting with an electrophile. Electrophiles are electron deficient. They are characterized by partial or fully developed positive charges and by incomplete octets. Electrophiles have low-lying LUMOs. Nucleophiles are electron rich. They are characterized by partial or fully developed negative charges, and by electron lone pairs or pi bonds. Nucleophiles have high-lying HOMOs. It should not surprise you to learn that all acids are electrophiles, and all bases are nucleophiles.

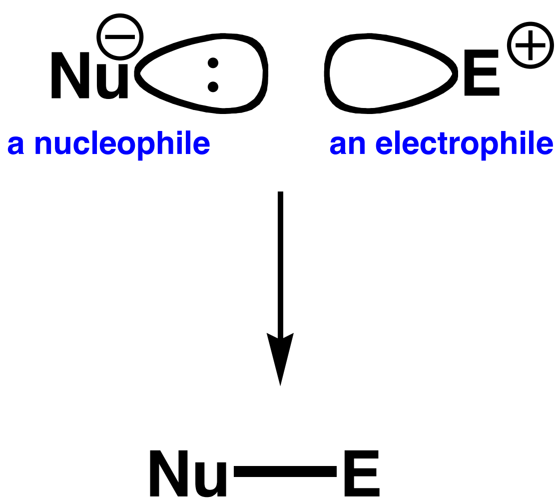
An elementary step between a generic nucleophile, Nu^-, and a generic electrophile, E^+



Notice that charge is balanced (the sum the formal charges on one side of the reaction arrow is the same as the sum of the charges on the other side)

Electron Reconfigurations - the Flow of Electrons - Usually Involve Electron Pairs

Covalent bond making and breaking are changes in electron configuration. Electron reconfiguration most often takes place as ***pairs*** of electrons, not as single electron entities. In fact, most all of the chemistry that we will study involves the "movement" of electrons in pairs. ***Heterolytic*** chemistry is the class of reactions that involves electrons moving in pairs, while ***homolytic*** chemistry describes the less common mode involving single electron reconfiguration. Organic chemists like to think of the "movement" of electrons as a "flow" of electron density from regions of high to regions of low electron density – that is – *from* ***nucleophiles*** *to* ***electrophiles***. The movement of electron pairs is represented by **curved arrows**.



The same process takes on a sense of "action" when curved arrows are used to illustrate electron flow