Structure and Reactivity: Acidity and Basicity

In this section we will analyze how structure affects acidity and basicity. Acids and bases are vital to many chemical reactions and we need to understand what properties contribute to their strength. First we will begin by understanding how a reaction occurs. When two molecules collide with proper orientation and sufficient energy they can react with one another.

For example, in the self-ionization of water we see that two water molecules collide to react and form a hydroxide ion and a hydronium ion. Each reaction begins first by an **electrostatic attraction** between an electron rich and an electron poor region of the reactants. Hydrogen bonding occurs between the electron deficient hydrogen of one water molecule with the electron rich oxygen of another water molecule. The products form as the electron from one O-H bond becomes a lone pair on oxygen. Additionally the lone pair on the oxygen of another water molecule becomes shared in a new O-H covalent bond.

$$H_2O_{(l)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$
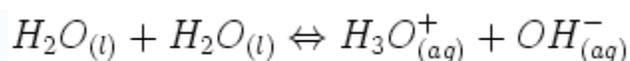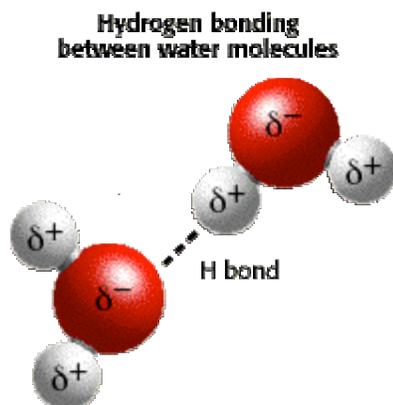
Reaction Mechanism: The **reaction mechanism** is a step by step account of bond and electron changes. Reaction mechanisms are very useful because they provide us with predictive power and organizational information. For example, based on the previous reaction, we can predict that any oxygen, and hence the alcohol functional group, can take away a hydrogen atom. The reaction mechanism also shows us where the electrons move to and what bonds they form giving us organizational power. In chemical reactions, we see that electrons move from regions of excess to regions where they are deficient. Now, we will introduce some terms that will illustrate this topic.

Electron Deficient Region: The electron deficient region serves as the electron acceptor in the reaction because it is electron poor. It may have a formal positive charge, a partial positive charge, or an open octet all of which illustrate electron deficiency. The species which gains a pair of electrons from another atom to form a new covalent bond is termed the **electrophile** ("electron loving"). Based on this definition this species can also be termed a

Lewis acid. It is important to note that a new covalent bond must be formed for the species to be considered an electrophile. You may remember from general chemistry that in a proton transfer reaction the species which donates the proton is termed acid. Therefore based on this definition a **Bronsted acid** is a proton donor.

Electron Rich Region: The electron rich region serves as the electron donor in the reaction because it is willing to share its electron density. The electron rich species can be identified based on a negative formal charge, a partial negative charge, a pi bond, or a lone pair. This species which shares a pair of electrons with another atom to form a new covalent bond is termed the **nucleophile**. Based on this definition this species can also be termed a **Lewis base**. In a proton transfer reaction this species is the proton acceptor and is termed the **Bronsted base**.

Nucleophile   Electrophile

Figure 1: Based on this definition we see that the flow of electrons is from the nucleophile to the electrophile. The **curved arrow** indicates the relocalization of electrons. The base of the arrow indicates the source of electrons and the head of the arrow indicates the destination of the electrons.

Position of Equilibrium: Every chemical process is in principle in equilibrium. In general chemistry we learned what an equilibrium reaction is, we will now learn to predict the position of the equilibrium and illustrate the reaction mechanism.

Figure 2:

In this reaction ammonia serves as the nucleophile because it has a lone pair which it uses to form a new N-H covalent bond. The water molecule serves as the electrophile because the electron deficient H atom accepts the lone pair to form a new covalent bond. The nitrogen atom loses one electron and thus goes from being neutral to now having a +1 formal charge. The oxygen molecule gains a lone pair, that it used to share as a covalent bond, and therefore acquires a -1 charge. Each reaction may have its equilibrium lying to the left, right, or in the

middle. In determining the **equilibrium constant** we take into account the concentration of the products and those of the reactants. The formula we use is the following:

$$K_{eq} = \frac{[\text{ Products }]}{[\text{Reactants}]}$$

In this particular reaction our K_{eq} can be calculated using:

$$K_{eq} = \frac{[NH_4^+]\,[OH^-]}{[H_2O]\,[NH_3]}$$

In addition we can set up an equation for the acidity constant K_a. We can use the expression $K_{eq}\,[H_2O] = K_a$. The **acidity constant** tells us the extent of ionization and reactivity of the acid. The greater the value of K_a, the stronger the acid and the greater is its tendency to give up a proton. The acidity constant essentially expresses the relative ratio of the ionized product to the unionized reactants. For convenience purposes, the strength of the acid is generally denoted by its pK_a value rather than its K_a value. The following equation can be used to interconvert between the two: **$pK_a = -\log K_a$**. This equation indicates that a more negative pK_a value represents a stronger acid. Additionally a pK_a change of one unit represents one order of magnitude in acidity. Generally very strong acids have a $pK_a < 1$, moderately strong acids fall between pK_a's of 1 and 5, and weak acids have $pK_a > 5$. It is important to distinguish between pK_a and pH. While the pH scale is used to describe the acidity of a solution, the pK_a is used to describe a particular compound.

Example 1: Use the information to compare the ionization of the compounds. The pK_a of hydroiodic acid is -10 and the pK_a of benzene is 43.
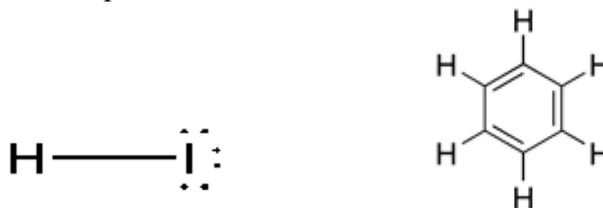
*We know that stronger acids have greater K_a values and more negative pK_a values. Therefore, we know that HI is the stronger acid in this case. This means that HI has a greater tendency to give up a proton. In a proton transfer equilibibrium essentially all of the HI will be deprotonated and the solution will be composed almost entirely of hydronium ion and conjugate base. The equilibrium will lie very far to the right in this reaction. HI can be classified as a strong acid because its pK_a is less than 1. On the other hand, based on pK_a we know that benzene is an extremely weak acid. Essentially, none of the benzene will deprotonate in a proton transfer reaction. The equilibrium will lie very far to the left in this reaction.

Using Structure to Predict pK_a

In this section we learn to use structure in analyzing the acidity and basicity of compounds. Instead of simply looking up pK_a values we will learn to use the conjugate base in predicting the strength of the acid. A fundamental principle concerning the strength of acids and bases is best exemplified through the **conjugate seesaw.** This principle states that the greater the strength of the acid the weaker is its conjugate base, and vice-versa.

Figure 3:
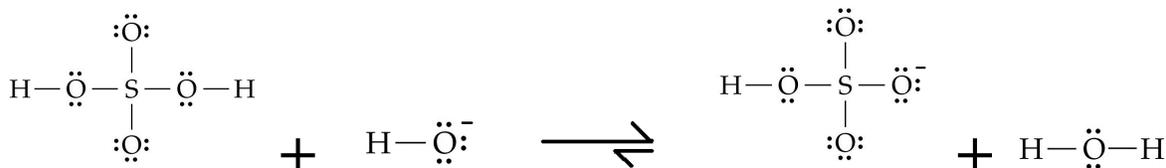
In an acid-base equilibrium, the reaction always favors the formation of the weakest acid and the weakest base due to their stability. The weakest acid and the weakest base must always be on the same side of the reaction. In this example the weakest base is the conjugate base of sulfuric acid HSO_4^- and the weakest acid is H_2O. Thus the equilibrium favors their formation as indicated by the single headed arrows. This proton transfer equilibrium represents a "tug of war" for the hydrogen as sulfuric acid and water both possess it at some time. In order to predict the favored side of the equilibrium one must first understand how to use structure in predicting basicity. We must predict who can most readily bond to H. Essentially which base has the greatest driving force to share electron density and form a covalent bond with a proton (the stronger base). Therefore we now understand the basis of a fundamental relationship:

Basicity _ Charge Density

The base with the greater charge concentration (electron density / unit surface area) wants to share its electron density more and thus is a stronger base.

Example 2: Which of the two acids is stronger?

phenol   cyclohexanol
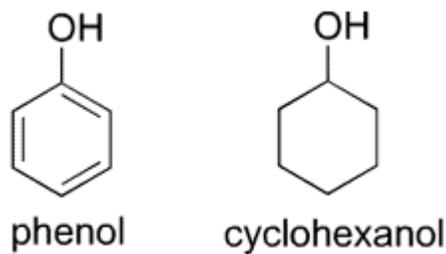
*To determine the strength of the acids we must analyze the strength of their conjugate bases. The strength of a base is proportional to charge density. The negative charge on the conjugate base of cyclohexanol cannot be delocalized because no significant resonance contributors. On the other hand, the conjugate base of phenol has four significant resonance contributors and this greatly delocalizes the electron density. As a result the conjugate base of phenol has less charge density which means more stability. Therefore it is the weaker base and phenol is the stronger acid.

Resonance Contributors:

phenol conjugate base
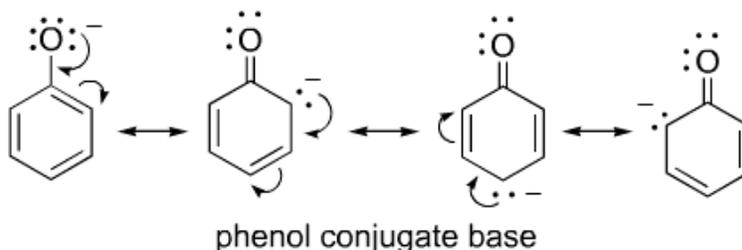
Factors Influencing Base Strength

The following four factors are discussed in order of importance.

<u>Resonance</u>: Anytime multiple Lewis structures can represent one compound it is said to have resonance. Resonance can either increase or decrease the electron density at the atom that will actually share electrons with the proton. Additionally, resonance delocalizes the electron density and thus leads to greater stabilization. Therefore reactions which increase resonance are favored because of the gain in stabilization. Additionally, reactions which lead to a decrease in resonance are inhibited due to this loss. In most cases, the presence of resonance leads to less basicity although this does not always hold true.

Example 3: Which of the following is the stronger acid: ethanol (CH_3CH_2OH) or acetic acid (CH_3CO_2H)?

*Again to compare the strengths of the acids we must look at the structure of their conjugate bases. The conjugate base of ethanol is the ethoxide ion. This ion has a negative charge localized on the oxygen atom and it has no resonance to delocalize this charge. On the other hand, the conjugate base of acetic acid (acetate ion) has two significant contributing structures which delocalize the negative charge and stabilize the base. As a result the acetate ion is a weaker base and its conjugate acid (acetic acid) is the stronger of the two acids.

CH₃CH₂ÖH (Ethanol) —remove proton→ CH₃CH₂Ö:⁻ (Ethoxide ion: no resonance)

Acetic acid —remove proton→ Acetate ion: two contributing structures
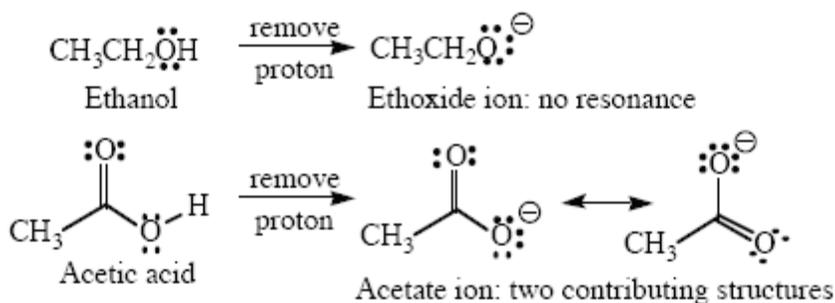
Atomic Size: As we already know basicity is proportional to charge density. When comparing atoms of equal formal charge the larger atom provides more space for the charge. Therefore, in a larger atom the negative charge is more dispersed and the charge density decreases. As a result negative charges prefer to rest on large atoms rather than being localized on a small atom (due to increase stability). Therefore smaller atoms have a greater driving force to share electron density because of increased charge concentration and are thereby stronger bases. It is important to understand that this principle applies when considering atoms in the same column of the period table (as size changes are significant). Because size does not greatly change across a period, this principle does not apply. When comparing atoms across a period, we consider electronegativity.

Figure 4:

Across the period: Atomic size changes are not significant factors in basicity

B	C	N	O	F
				Cl
				Br
				I

Down the family: Significant atomic radius effects on basicity
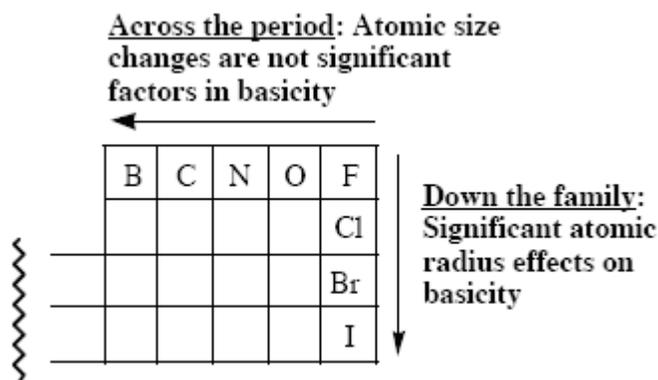
Example 4: Which of the following acids is strongest: HF, HCl, HBr, HI?

*In determining the strongest acids, again we should look at the conjugate bases. In each conjugate base, resonance does not apply, so we can rule resonance out as an influence of charge density and hence basicity. Thus, we must look at the size of the atoms on which the negative 1 formal charge lies. Since each atom lies in the same column, we know that size increases as you move down. Therefore, charge density decreases as you move down the column. The -1 formal charge is most concentrated on the smaller atom, making it most willing to share its electrons. As a result, F⁻ is the strongest base, so it will have the weakest conjugate acid. On the other hand, I- is the weakest base so its conjugate acid is strongest. The correct order of acid strength is: HI> HBr > HCl > HF.

Figure 5:

increasing stability
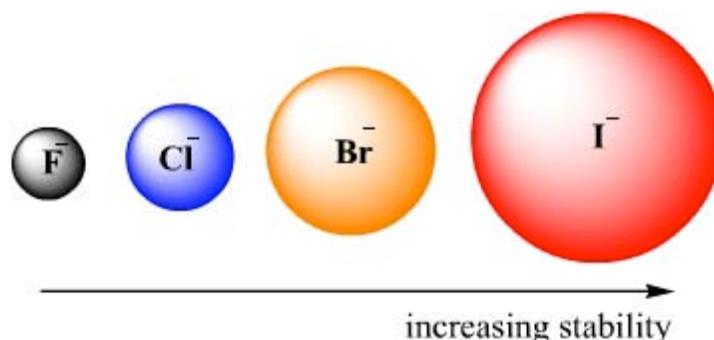
Electronegativity: Electronegativity is a measure of an atom's attraction for electrons. The greater the electronegativity of an atom the greater is its desire to withhold its electrons. Electronegativity increases as we go across a period and up a column in the period table. Bases donate electrons to form new covalent bonds; therefore if they have a greater attraction for electrons they are less likely to share them. As a result we see that electronegativity is related to basicity. The greater the electronegativity of an atom, the less it is willing to share its electrons. Electronegativity is important to consider when comparing atoms in the same row of the periodic table.

Example 5: Which is the strongest acid H_2O, NH_3, or CH_4?

increasing anion stability
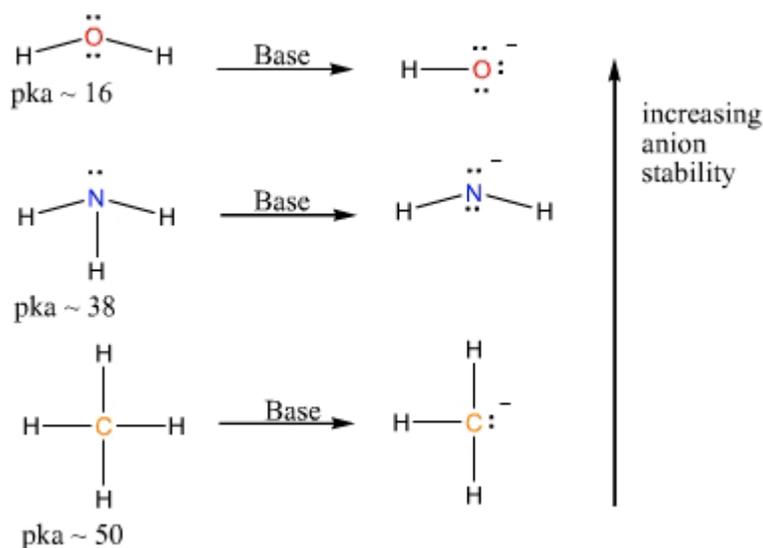
* In comparing the strengths of acids we must analyze the structure of their conjugate bases. Each of their conjugate bases has a -1 formal charge. In this example, none of the bases are stabilized by resonance. The negative charge lies on atoms in the same row (C, N, O) therefore size is not a factor in determining basicity. Finally, we resort to using electronegativity differences between the atoms. The atoms are all in the same period and electronegativity increases as we move to the right. The more electronegative the atom the less likely it is to

share electron density, and thus it is a weaker base. Oxygen is the most electronegative atom; this makes the hydroxide ion the weakest base. On the other hand, carbon is the least electronegative atom; therefore CH_3^- is the strongest base. We know that basicity and acidity are inversely related, therefore in order of acidity $H_2O>$ $NH_3 > CH_4$.

Inductive Effect: Nearby atoms may add to or detract from the electron density of the atom sharing electrons with the proton. This in turn influences its driving force to share electron density, and ultimately its basicity. In many cases, electronegative atoms near a molecule pull away the electron density and make it less basic because its driving force to share electron density is decreased. The inductive effect includes the affect of all the atoms other than the atom sharing electron density with the proton. This is the fourth most important factor influencing basicity and often times comes into play when the same functional groups are present on the molecules being compared. This is due to the fact that similar functional groups have similar resonance, atomic size, and electronegativity.

Example 6: Which of the following acids is more acidic?
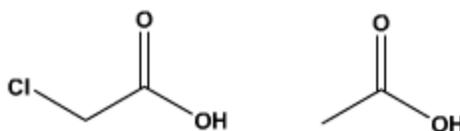
*In order to analyze the acidity of the compounds we analyze the structure of their conjugate bases. Both compounds have the same functional group (carboxylic acid) and therefore the resonance, atomic size, and electronegativity factors cannot be used to distinguish them. However, the atoms remote to each oxygen in the respective molecules differ. While acetic acid has a remote methyl group, one hydrogen is substituted for a chlorine atom in the other molecule. Chlorine is far more electronegative in comparison to hydrogen and therefore pulls away the electron density of the oxygen molecule. As a result, the base is weaker and its conjugate acid is thereby stronger.
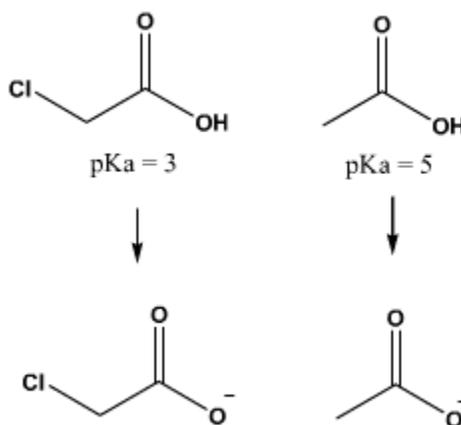
Two additional factors to consider:

Hybridization: Another important aspect to consider when determining acidity is the hybridization of the carbon. We know that s orbitals are closer to the nucleus than p orbitals. This tells us that the more s character a hybrid orbital has the closer are the electrons to the atom. Therefore, we see that there is a direct relationship between s character and electronegativity; the greater the s character of the hybrid orbital, the greater is the electronegativity of the atom. Such atoms are less willing to share their electron density and thereby have greater acidic character.

Figure 6: The greater the s character of the hybrid orbital, the greater the acidity of the acid.
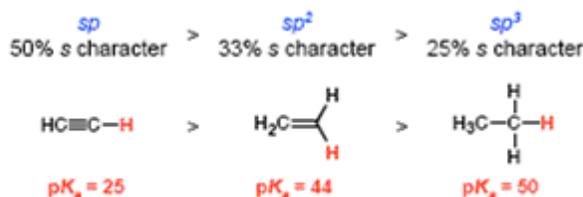
Charge: In general, a base with a negative formal charge has a greater driving force to share electron density then a neutral base. This relates to the initial principle introduced regarding charge density and basicity. The greater the electron density (in this case due to negative charge), the stronger the base and the weaker the conjugate acid. For example, in comparing the acidities of H_3O^+ and acetic acid we must first analyze the structure of their conjugate bases H_2O and acetate ion. At first it may seem that due to resonance, the basicity of acetate is below that of H_2O. However, the acetate ion also has a negative charge which H_2O lacks. Resonance delocalizes this negative charge onto two oxygen molecules which attain partial negative charges. In this case, charge has a greater influence on pK_a than resonance. As a result, H_2O is the weaker of the two bases and H_3O^+ is the stronger of the two acids.

Sources
- *Bettelheim, Brown, March, Introduction to General, Organic, and Biochemistry 6th edition, p. 197-201*
- *Atkins, Jones, Chemical Principles 3rd Edition, p. 374-370*
- *Bruice, Organic Chemistry 4th edition, p. 39-54, p. 250-252*
- *S. Hardinger PhD, Organic Molecular Structures and Interactions, p.84-89, p.314-342*
- *http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/text_images/CH15/FG15_00-04.JPG, September 9, 2006*
- *http://www.chemhelper.com/acidbase2.htm, September 10, 2006*
- *http://web.chem.ucla.edu/~harding/tutorials/acids_and_bases/mol_str.pdf, September 10, 2006-*
- *http://ocw.mit.edu/NR/rdonlyres/Chemistry/5-12Spring-2005/444A067C-4268-4CEA-873F26B25918CF0D/0/lecture02b_s05.pdf#search=%22hybridization%20and%20basicity%22, September 10, 2006*
- *http://www.biology.arizona.edu/biochemistry/tutorials/chemistry/graphics/water.gif&imgrefurl, September 10, 2006*
- *http://en.wikipedia.org/wiki/Self-ionization_of_water, September 9, 2006*