

Lecture Notes  
Chem 51A  
S. King

Chapter 2 Acids and Bases

I. Brønsted-Lowry Acids and Bases

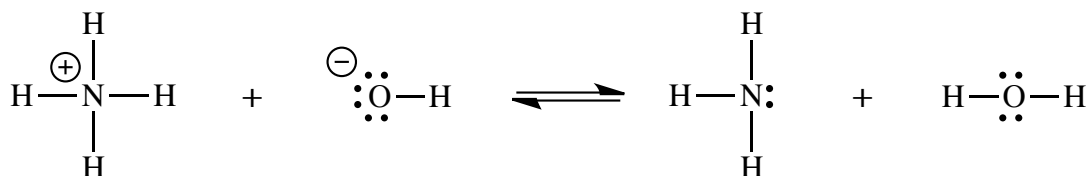
**Brønsted acid:** a species that donates a proton ( $\text{H}^+$ )

**Brønsted base:** a species that accepts a proton

A **Brønsted-Lowry acid** must contain a hydrogen atom. The symbol **HA** is used for a general Brønsted-Lowry acid.

A **Brønsted-Lowry base** must be able to form a bond to a proton. Because a proton has no electrons, a base must contain an available electron pair that can easily be donated to form a new bond. These include **lone pairs** or **electron pairs** in  $\pi$ -bonds. The symbol **B:** is used for a general Brønsted-Lowry base.

In a **Brønsted acid-base** reaction a proton is transferred from the acid to the base to give products that are the conjugate base and conjugate acid of the reactants.

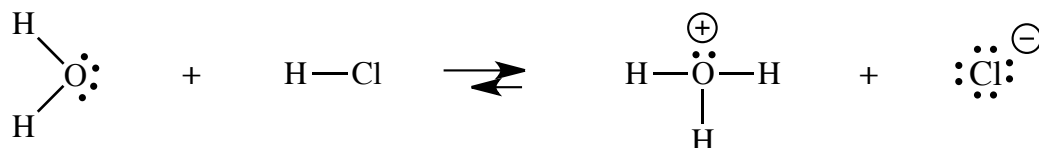


A *curved* arrow shows the movement of an **electron pair**.

The tail of the arrow always begins at an electron pair (such as non-bonding electrons or a covalent bond) and the head points to where that electron pair moves.

*This is an equilibrium process.*

**At equilibrium, the weaker acid and the weaker base are the major species found in the reaction mixture.**



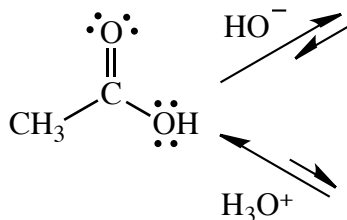
**\*\*STRONG ACIDS HAVE WEAK CONJUGATE BASES\*\***

**\*\*WEAK ACIDS HAVE STRONG CONJUGATE BASES\*\***

*Some compounds can act as both acids & bases. They are amphoteric compounds.*

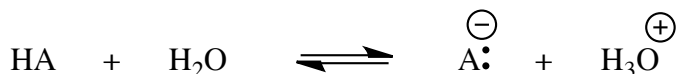
The most famous amphoteric compound is:

Another amphoteric compound is acetic acid:



### A. Organic Acids and Bases: $\text{pK}_a$

*General  
Acid/Base  
reaction:*



$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]} =$$

for dilute solutions,  $[\text{H}_2\text{O}]$  is constant

$$K_a = K_{\text{eq}}[\text{H}_2\text{O}] =$$

The larger the  $pK_a$  value, the weaker the acid

See Appendix A for a complete listing of  $pK_a$ 's.

very strong acids:

moderately strong acids:

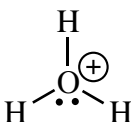
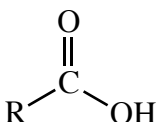
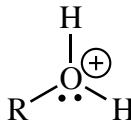
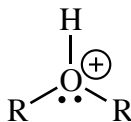
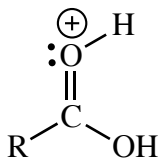
weak acids:

extremely weak acids:

Some examples of each are listed below, with  $pK_a$ 's rounded to the nearest 5:

Approximate  $pK_a$  values

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		$\text{RNH}_3^+$	ROH	$\text{CH}_4$
			$\text{H}_2\text{O}$	$\text{RCH}_3$
				
				

---

- Q.** We use  $pK_a$ 's to determine the strength of acids. How do we determine the strength of bases?
- A.** Some older books talk about  $pK_b$ 's, but it's really not necessary if you keep in mind the following rule of thumb:

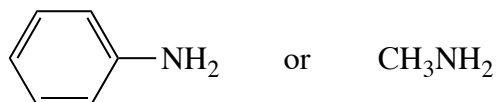
The stronger the acid, the weaker its conjugate base.

**Strong** bases have **weak** conjugate acids!

**Example 1:**  $\text{CH}_3\text{CH}_2^-$

*It is extremely difficult to remove a proton from an alkane!*

**Example 2:** Which is the strongest base?



## B. Equilibria in Acid Base Reactions

- Q.* How do we predict which way the equilibrium will lie in an acid-base reaction?
- A.* Acid-Base reactions are under equilibrium control. Reactions under equilibrium control always favor the formation of the most stable species.

**General Principle:**

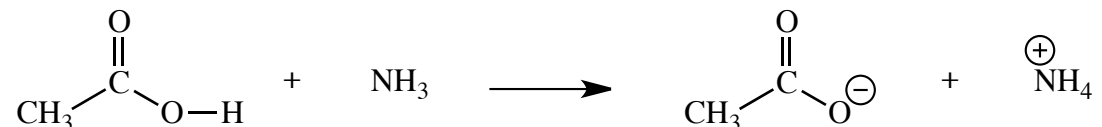
Acid-Base reactions always favor the formation of the weaker acid and the weaker base.

$\text{pK}_a$  values can be used to determine the direction of equilibrium, and can be used to approximate the ratio of reactants to products at equilibrium.

To determine the direction of equilibrium:

1. Identify the acid on each side of the arrow.
2. Assign  $pK_a$  values to each acid and compare. The equilibrium will be favored in the direction in which the weaker acid is formed.

**Example:** Predict the direction of equilibrium for the following reaction:



To determine the approximate ratio of reactants to products at equilibrium:

1. Determine the approximate  $pK_a$  difference,  $x$ , rounded to a whole number.
2. The approximate ratio of reactants to products will be:

$1 : 10^x$  if products are favored

*or*

$10^x : 1$  if reactants are favored

*Note:* If the ratio of *reactants:products* is 1:100 or greater, the reaction is said to have gone essentially to completion.

*For the above reaction:*

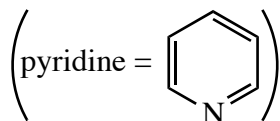
For exact  $K_{eq}$ :

**Q.** How can we know if a particular base is strong enough to deprotonate a given acid, so that the equilibrium lies to the right?

**A.** Consult a  $pK_a$  table. An acid can be deprotonated by the conjugate base of any acid having a higher  $pK_a$  (the  $pK_a$  difference should be greater than about 2.)

**Example:**

Which of the following bases is strong enough to deprotonate acetic acid,  $CH_3CO_2H$ ?  
 $H^-$ ,  $Cl^-$ , or pyridine?



### III. The Relationship Between Structure and Acidity

Structural differences in molecules can greatly affect acidity (remember: *structure determines reactivity!*) An understanding of how these structural differences affect acidity will allow us to estimate the acidity of compounds that we have never encountered (*ones that are not on any  $pK_a$  table!*) There is a general rule that will help in this process:

Anything that stabilizes a conjugate base  $A:^-$  makes the starting acid  $H-A$  more acidic

Four factors affect the acidity of  $H-A$ :

- A. The Element effect
- B. Inductive effects
- C. Resonance effects
- D. Hybridization effects

#### A. Periodic Trends: THE ELEMENT EFFECT

The most important factor determining the acidity of  $H-A$  is the *location of A in the periodic table*.

##### 1. Across a period (row):

Acidity increases as you move to the right across any period.

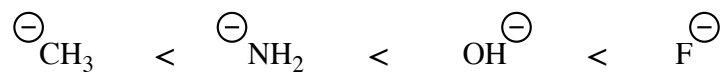


Why?

- ☛ Acid strength is determined by the stability of the conjugate base that is formed when the acid gives up its proton.

*The more stable the base, the stronger its conjugate acid*

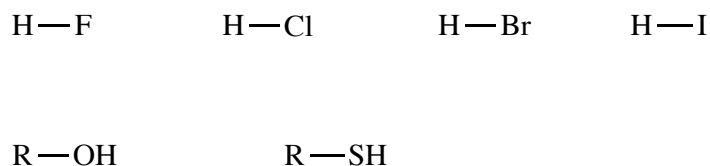
Look at the stability of the conjugate bases:



- ☛ Across a row in the periodic table, the acidity of H-A increases as the electronegativity of A increases

## 2. Down a column:

Acidity increases as we descend a vertical column.

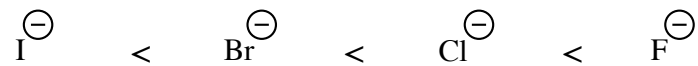


**Notice we see the opposite trend here!** Acidity & electronegativity increase in the opposite direction!

Why? When comparing atoms of **very** different size, the size of the atom is more important than its electronegativity in determining how well it bears its negative charge.

**Positive or negative charge is stabilized when it is spread over a larger volume.**





- ☛ *Down a column of the periodic table, the acidity of H–A increases as the size of A increases*

### **B. Inductive Effects**

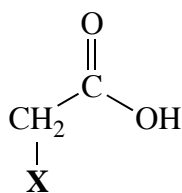
A second factor affecting the acidity of H–A is the presence of electronegative atoms.



Why? Electronegative groups such as halogens increase the acidity of nearby acids by stabilizing their conjugate bases.

Look at the conjugate bases:

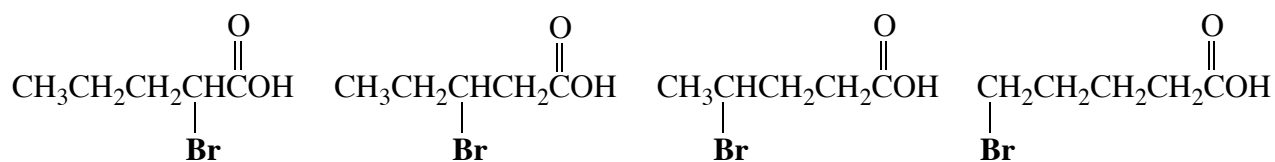
Look at Inductive Effects on Acetic Acid Derivatives:



<b>X</b>	<b>pK<sub>a</sub></b>	<b>Electronegativity</b>
H	4.76	2.1
I	3.17	2.4
Br	2.90	2.8
Cl	2.86	3.0
F	2.59	4.0
<hr/>		
OH	3.83	
CN	2.46	
NO <sub>2</sub>	1.68	
<hr/>		
CH <sub>3</sub>	4.87	

Electronegative atoms stabilize regions of high electron density by an electron-withdrawing inductive effect. An **inductive effect** is the pull of electron density through  $\sigma$ -bonds caused by electronegative atoms or groups.

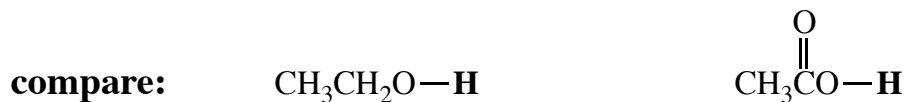
*Inductive effect decreases as the  $e^-$  withdrawing group gets further away:*



☛ *The acidity of H–A increases with the presence of electron-withdrawing groups in A. The more electronegative the atom, and the closer it is to the site of the negative charge, the greater the effect.*

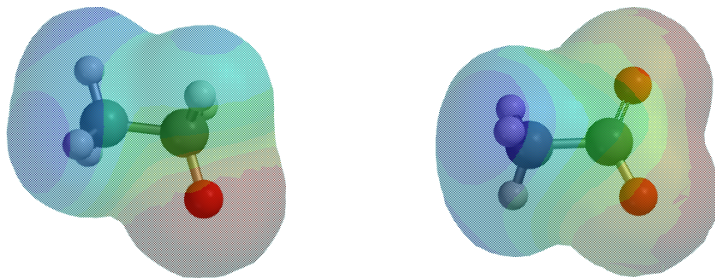
### C. Resonance Effects

A third factor affecting the acidity of H–A is resonance. Resonance effects can also stabilize conjugate bases. Any compound with delocalized electrons is more stable than it would be if all of its electrons were localized. The greater the delocalization of charge (indicated by the number and quality of contributing resonance structures), the more stable the conjugate base.

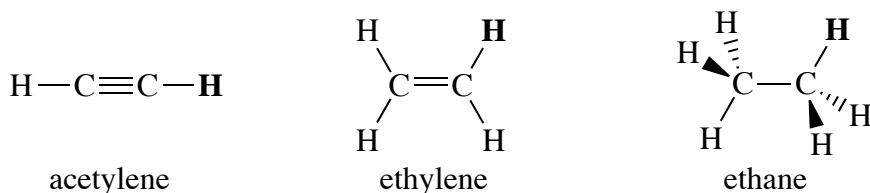


☛ *The acidity of H–A increases when the conjugate base, A:<sup>-</sup> is resonance stabilized.*

Look @ the electrostatic potential maps for ethoxide ion and carboxylate ion:

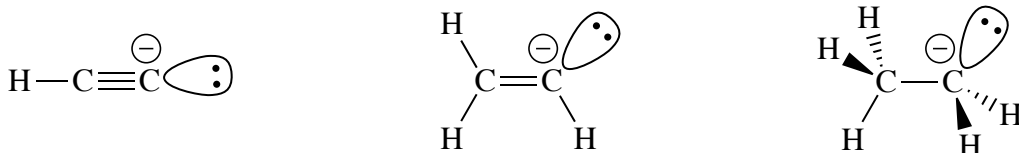


#### D. Hybridization Effects



*Why is acetylene so much more acidic than ethane?*

Look @ conjugate bases:



When carbon has more “*s character*”, the electrons are closer to the nucleus. In effect, C with more *s-character* is more electronegative - the electrons are pulled in toward the nucleus - they are lower in energy and less available for reaction.

Problem solving:

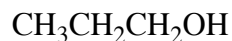
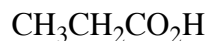
Element effects, inductive effects, resonance effects, and hybridization effects all need to be considered when determining the relative acidity of protons. The following steps make this process more manageable:

- Step 1:** Identify the atoms bound to the acidic hydrogens. If the H's are bound to different atoms, use periodic trends to assign relative acidity.
- Step 2:** If the two H's are bound to the same atom, draw the conjugate bases and look for other points of difference.
- Do electron withdrawing groups stabilize the conjugate base?
  - Is the conjugate base resonance stabilized?
  - Look at the hybridization of the conjugate base. Does increased "s" character stabilize the conjugate base?

**Example 1:** Rank the following compounds in order of increasing acidity:



**Example 2:** Rank the following compounds in order of increasing acidity:



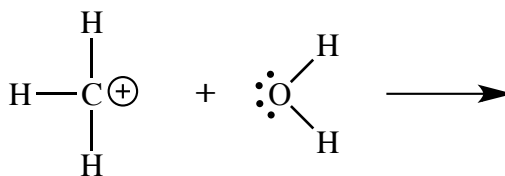
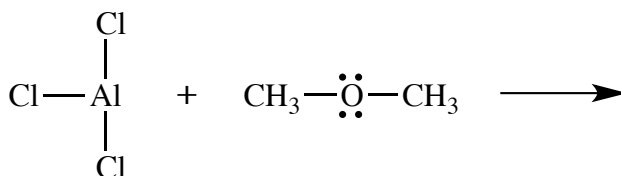
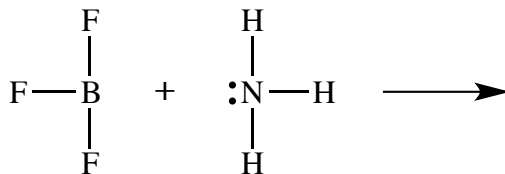
#### IV. Lewis Acid-Base Reactions

In 1923, a more general definition of acids & bases was introduced by G.N. Lewis:

- A **Lewis acid** is an *electron pair acceptor*
- A **Lewis base** is an *electron pair donor*

All Brønsted-Lowry acids and bases are also Lewis acids and bases, but this definition is more general because it is not limited to compounds that transfer protons. Open-shell compounds are also Lewis acids because they accept a pair of electrons from a Lewis base.

In the simplest Lewis acid-base reaction, one bond is formed and no bonds are broken:



- A Lewis acid is also called an **electrophile**.
- When a Lewis base reacts with an electrophile other than a proton, the Lewis base is called a **nucleophile**.

In some Lewis acid-base reactions, one bond is formed and one bond is broken. To draw products of this type of reaction, keep the following steps in mind:

1. Always identify the Lewis acid (*electrophile*) and Lewis base (*nucleophile*) first.
2. Draw a curved arrow from the electron pair of the Lewis Base to the electron-deficient atom of the acid.
3. Count electron pairs and break a bond when needed to keep the correct number of valence electrons.

**Example:**

