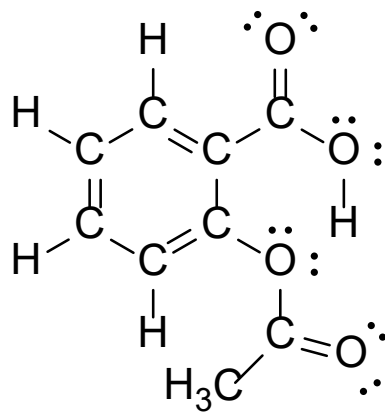


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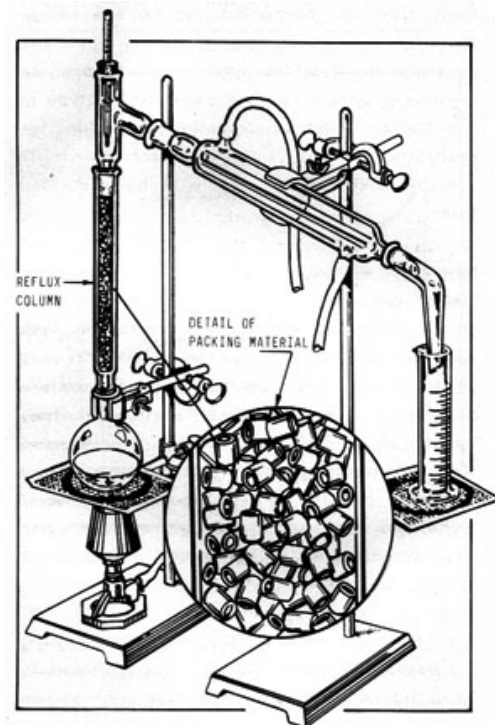
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CHEMISTRY 2000

Topic #3: Organic Chemistry
Fall 2020

Dr. Susan Findlay

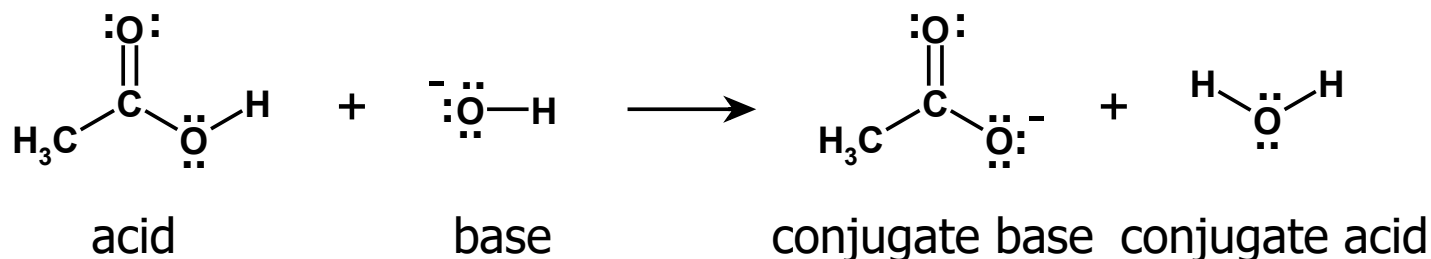
See Exercises in Topic 12



Measuring Strength of Acids

- When you hear the term “organic acid”, it usually refers to a carboxylic acid.

- Carboxylic acids are readily deprotonated by strong bases:



- This reaction is favoured in the forward direction because the products are lower in energy than the reactants.
 - In particular, the conjugate base (acetate; CH_3CO_2^-) is much more stable than the original base (hydroxide, OH^-).
 - Therefore, acetate is a weaker base than hydroxide.
 - Therefore, acetic acid is a stronger acid than water.



Measuring Strength of Acids

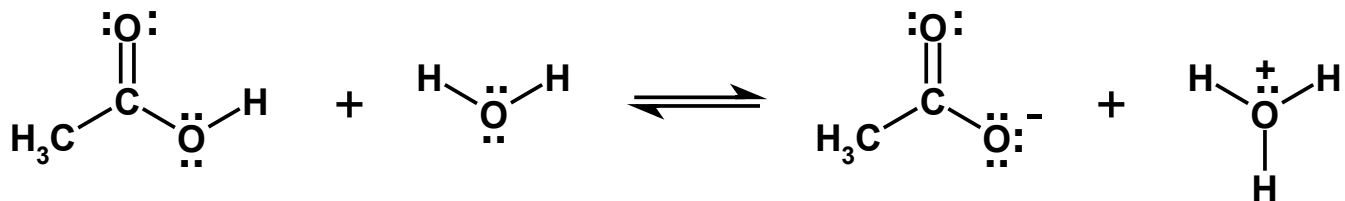
- An acid's strength depends on the stability of its conjugate base:
 - The conjugate base of HCl (a strong acid; $pK_a = -7$) is Cl^- (a very weak base)
 - The conjugate base of H_2O (a weak acid; $pK_a = 14$) is OH^- (a relatively strong base)

The strength of an acid can therefore be said to be inversely related to the strength of its conjugate base (*and vice versa*).

- Why is $CH_3CO_2^-$ more stable than OH^- ?

Measuring Strength of Acids-

- Consider the reaction below.
 - Identify the acid, base, conjugate acid and conjugate base.
 - Is this reaction product-favoured or reactant-favoured?
 - The pK_a of CH_3CO_2H is 5.
 - The pK_a of H_2O is 14.
 - The pK_a of H_3O^+ is 0.





Measuring Strength of Acids

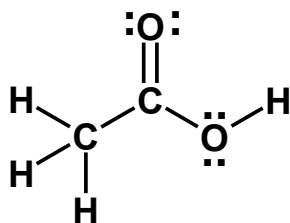
- The reaction on the previous page is equivalent to the acid dissociation equation for CH_3CO_2H (as long as the solution is sufficiently dilute that $X_{H_2O} \approx 1$):



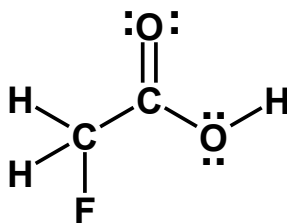
- Its equilibrium constant is therefore the K_a for CH_3CO_2H :
- Recall that we can relate the K_a and pK_a for an acid via the following equation:
- **An acid is stronger if it has a large K_a and a small pK_a .**

Factors Affecting Strength of Acids

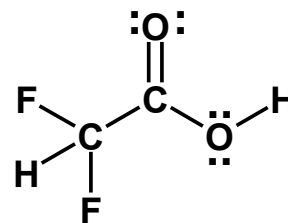
- We can increase the strength of an acid by adding electron-withdrawing groups, further stabilizing its conjugate base.
- To increase the acidity of acetic acid, replace one or more hydrogen atoms attached to carbon with halogens:



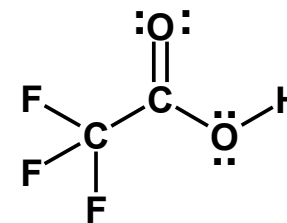
$\text{pK}_a = 4.74$



$\text{pK}_a = 2.66$



$\text{pK}_a = 1.24$



$\text{pK}_a = 0.23$

- This stabilization through σ bonds is called an **inductive effect**. Inductive effects are only meaningful when the electron withdrawing group is within a few bonds of the acidic hydrogen.



Factors Affecting Strength of Acids

- Carboxylic acids are among the most acidic organic molecules; however, a number of other functional groups contain acidic hydrogen atoms:
 - Alcohols are typically about as acidic as water. Most have pK_a values of $\sim 15-18$. (*Inductive effects can lower these values to ~ 12*)
 - Phenols are typically more acidic than alcohols. Most have pK_a values of $\sim 8-10$. (*The pK_a can go as low as 1 with the right groups attached to the aromatic ring*)
 - Thiols (R-SH) are also typically more acidic than alcohols. Most have pK_a values of $\sim 10-12$. (*Also subject to inductive effects*)
 - Amines are not acidic in water, but can be deprotonated by some **very** strong bases in unreactive solvents like alkanes or ethers. Their pK_a values are typically $\sim 35-40$!



Factors Affecting Strength of Acids

- Sulfur and nitrogen are both less electronegative than oxygen. Why are thiols more acidic than alcohols, but amines less acidic?



Factors Affecting Strength of Acids

- Phenol is “just an alcohol with a benzene ring”. Why is phenol more acidic than most non-aromatic alcohols?



Calculating pH of an Acidic Solution

- A strong acid ($pK_a < 0$) dissociates fully in water because it is a stronger acid than H_3O^+ ($pK_a = 0$) so reacts fully with H_2O to generate H_3O^+ and its conjugate base.

- This effect is known as **solvent leveling**.
 - No acid stronger than the conjugate acid of the solvent can exist in any solution.
 - No base stronger than the conjugate base of the solvent can exist in any solution. (*Hydroxide isn't the strongest base – not by a long shot! It's just the strongest base that can exist in water.*)



Calculating pH of an Acidic Solution

- Weak acids aren't subject to solvent leveling, so we must perform equilibrium calculations (ICE table) if we want to calculate pH of a solution of weak acid.
- We can often simplify the math by making assumptions:
 - If we have a relatively concentrated solution of a relatively weak acid, only a small percentage of the acid will dissociate so the equilibrium activity of HA will be very close to the initial activity. Assume this when $a_{HA} \gg K_a$.
 - You have likely been taught to treat the initial concentration of H^+ in water as zero. It's not. At 25 °C, it's $10^{-7} M$. You can often assume that the initial concentration of H^+ will be negligible – but not when working with very dilute solutions or very weak acids. You can assume that initial concentration of H^+ is negligible when $a_{HA} \cdot K_a \gg K_w$.
- **ALWAYS CHECK ASSUMPTIONS AFTER CALCULATING!!!**



Calculating pH of an Acidic Solution

- Calculate the pH of a 0.32 M solution of phenol ($pK_a = 9.95$) at $25\text{ }^\circ\text{C}$.



Calculating pH of an Acidic Solution



Calculating pH of an Acidic Solution

- Calculate the pH of a $4.2 \times 10^{-5} M$ solution of CH_3CO_2H ($pK_a = 4.74$) at $25\text{ }^\circ\text{C}$.



Calculating pH of an Acidic Solution



Distribution Curves

- We can also work backwards, using the K_a equation to work out the percent dissociation of an acid at a given pH .
- The pH tells us the activity (and therefore the concentration) of $H_{(aq)}^+$ so, as long as we know the K_a value for the acid, we're set.

$$K_a = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \quad \text{so} \quad \frac{K_a}{a_{H^+}} = \frac{a_{A^-}}{a_{HA}}$$

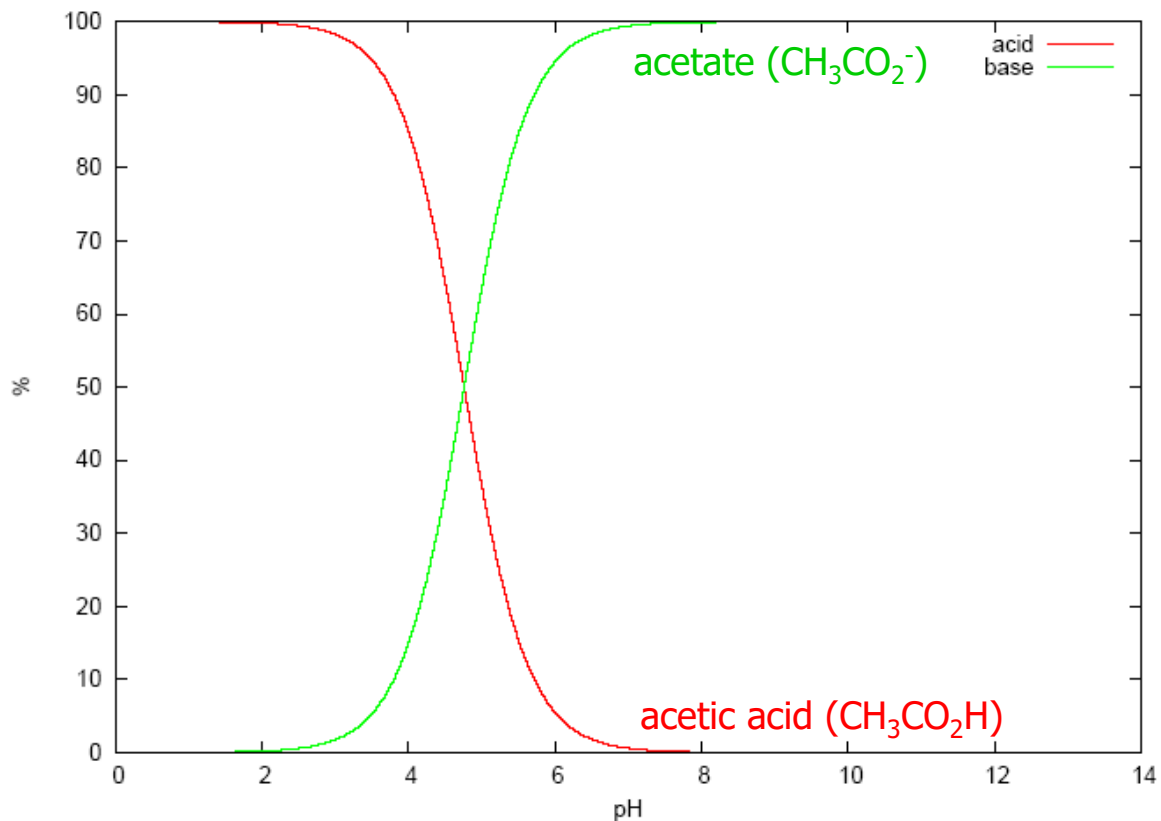


Distribution Curves

- Calculate the percent dissociation of acetic acid ($pK_a = 4.74$) at pH 4.00.

Distribution Curves

- If we repeat this calculation at a large number of different pH values, we generate what is known as a distribution curve:



Note that the two curves cross at the pK_a of the acid!

The pK_a of an acid is the pH at which it is exactly 50% dissociated. 18



Distribution Curves

- We can see why an acid will be 50% dissociated at its pK_a if we take the negative logarithm of both sides of the K_a expression:

$$-\log(K_a) = -\log\left(\frac{a_{H^+} \cdot a_{A^-}}{a_{HA}}\right)$$

$$-\log(K_a) = -\log(a_{H^+}) - \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

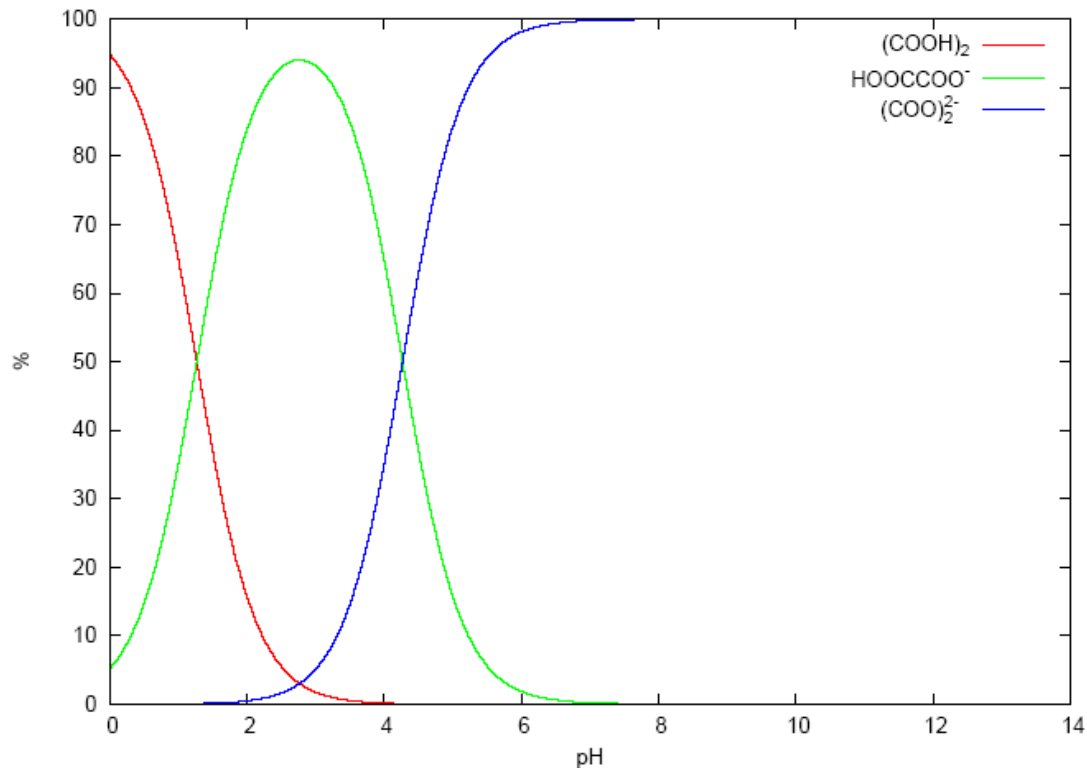
$$pK_a = pH - \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

$$pK_a + \log\left(\frac{a_{A^-}}{a_{HA}}\right) = pH$$

- This is the **Henderson-Hasselbalch equation**. We can see that if $\frac{a_{A^-}}{a_{HA}} = 1$ then $\log\left(\frac{a_{A^-}}{a_{HA}}\right) = 0$ and $pH = pK_a$. As the acid's percent dissociation rises, so does the pH and vice versa.

Distribution Curves for Polyprotic Acids

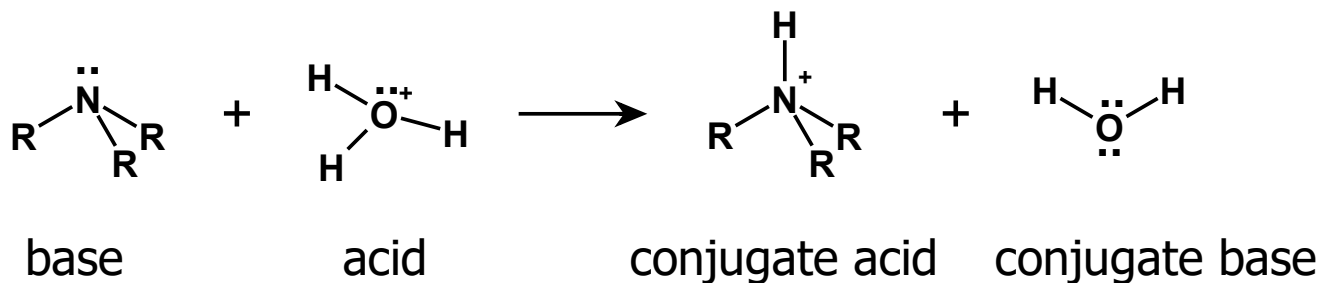
- If an acid has multiple acidic protons whose pK_a values are different by several units, the distribution curve will look like several monoprotic distribution curves superimposed:



If the pK_a values are too close, the distribution curve will become more complex.

Organic Bases (Amines)

- When you hear the term “organic base”, it’s generally referring to an amine.
- Amines are readily protonated by strong acids:



- The basicity of amines is due to the lone pair on the nitrogen atom which makes all amines (R = H, alkyl or combination) both Lewis bases and Brønsted bases.



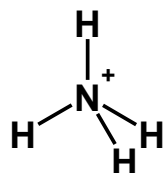
Organic Bases (Amines)

- We have seen one other functional group containing nitrogen. Why is an amine considered a good base, but an amide is not?

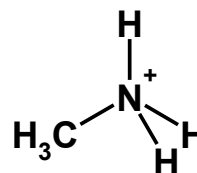
- The nitrogen atom of an amide is so weakly basic that the oxygen of the carbonyl group will be protonated over it!

Measuring Strength of Bases

- We can measure a base's strength using either of two measures:
 - We can refer to the K_a (or pK_a) of the conjugate acid. Since the strength of a base is inversely related to the strength of its conjugate acid, we can deduce the strength of a base from the strength of its conjugate acid.



$$pK_a = 9.3$$



$$pK_a = 10.6$$

Smaller pK_a for Conjugate Acid

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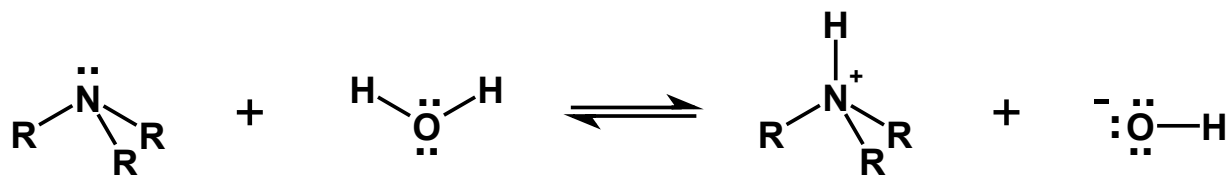
Stronger Conjugate Acid

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Weaker Base

Measuring Strength of Bases

- Alternatively, we can refer to the K_b (or pK_b) of the base itself. This is the equilibrium constant for reaction of the base with water:



Measuring Strength of Bases

- K_b is inversely proportional to K_a for the conjugate acid:

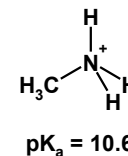
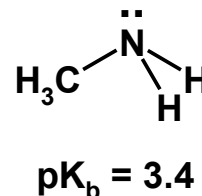
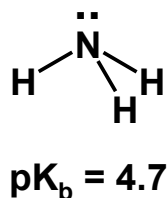
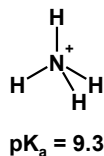
$$K_a = \frac{K_w}{K_b}$$

or

$$K_a \cdot K_b = K_w$$

where $K_w = 10^{-14}$ at 25 °C.

- We can also say that $pK_a + pK_b = pK_w$. At 25 °C, $pK_w = 14$.



Larger K_b = Smaller pK_b = Stronger Base



Calculating pH of a Basic Solution

- The pK_a of aniline ($C_6H_5NH_2$) is 28. The pK_a of $C_6H_5NH_3^+$ is 4. What are the K_b and pK_b values for aniline?



Calculating pH of a Basic Solution

- We can calculate the pH of a solution of weak base by:
 - Using the K_b expression and nominal solution concentration to calculate a_{OH^-} then
 - Using the K_w expression ($K_w = a_{H^+} \cdot a_{OH^-}$) to calculate a_{H^+} then
 - Using a_{H^+} to calculate pH .

Recall that, at 25 °C, $K_w = 10^{-14}$.



Calculating pH of a Basic Solution

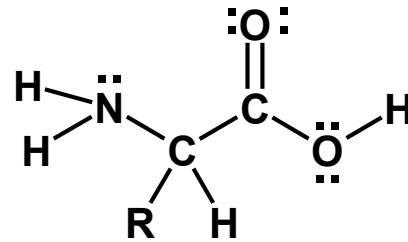
- Calculate the pH of a $0.71\ M$ aqueous solution of aniline at $25\ ^\circ\text{C}$.



Calculating pH of a Basic Solution

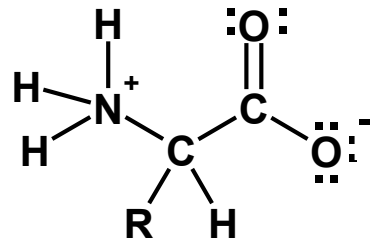
Amino Acids: Acid and Base

- Some textbooks present the structure of an amino acid as follows



in order to show that the name comes from having an **amine** group and a carboxylic **acid** group.

- This is not how an amino acid actually exists in biological systems (or other $pH \approx 7$ solution). Instead, it exists as the **zwitterion**:





Amino Acids: Acid and Base

- Why is this?
 - The pK_a for the $-CO_2H$ proton is typically ~ 2 (slightly lower than the standard 3-5 range for carboxylic acids).
 - The pK_a for the conjugate acid of the amine group (i.e. for the $-NH_3^+$ proton) is typically $\sim 9-10$.
- Use this data to sketch a distribution curve for the amino acid, labeling with the major species within each pH range.