Lecture 29

We now return to the study of acids and bases, two substances that are extremely common and are used in many facets of your lives. Some examples of things which you use or find on a daily basis which contain **acids** are tea, which contains tannic acid, and vinegar, which is mostly a dilute solution of acetic acid. The tartness in oranges and lemons and the bells of St. Clemens is primarily due to citric acid. Bleach is a dilute solution of hypochlorous acid. Some examples of **common basic substances** are Drano, which is mostly KOH, soaps and detergents, which are mild bases, and household cleansers some of which contain substantial amounts of ammonia. In addition, acids and bases are important because they are probably the most important group of homogeneous catalysts. There are many reactions whose rates are strongly dependent on the concentration of the hydronium ion, H_3O^+, or the hydroxide ion, OH^-.

We began our treatment of acids and bases when we discussed classes of reactions. However, at that time we treated only strong acids and strong bases, and dealt only quickly with the key definitions. I want to return to the various definitions of acids and bases, begin a treatment of weak acids and bases, which are only partially dissociated in solution, and talk about the reactions of acids and bases. Along the way, we'll pick up some important nomenclature as well.

The simplest and narrowest definitions of acids and bases are due to **Arrhenius**. According to Arrhenius, **an acid is a compound that produces hydronium ion, H_3O^+, when dissolved in water.** Examples of Arrhenius acids are hydrochloric acid, HCl; nitric acid, HNO_3; and acetic acid, CH_3COOH. Arrhenius acids produce hydronium ion according to the reaction,

$$HX + H_2O \rightleftharpoons X^- + H_3O^+,$$

where HX is any acid. In other words, **an acid creates H_3O^+ by transferring a proton to water.** X^- is the anion that remains when the acid loses its proton to water. Other examples of reactions in which hydronium ions are created in an aqueous solution of an acid are

$$HCl\ (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq),$$

and

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq).$$

The reaction by which acids react to form hydronium ion and an anion is called a **dissociation reaction**. The reason that an acid dissociates to a hydronium ion and an anion rather than a proton and an anion is that the highly electron deficient proton forms a coordinate covalent bond to the electron rich oxygen in water.

In the Arrhenius model, **a base is a substance that produces hydroxide ion when dissolved in water**. Typically an Arrhenius base actually contains OH^-, as in the case of compounds like NaOH, or $Al(OH)_3$. However, metal oxides are also Arrhenius bases. The reason is that the O^{2-} which forms when a metal oxide like K_2O dissolves in water, will react with a water molecule to form two hydroxyl radicals, i.e.,

$$O^{2-}(aq) + H_2O(l) \rightleftharpoons 2OH^-(aq).$$

The **Arrhenius model for acids and bases tends to be too narrow**. First, it applies only to aqueous solutions of acids and bases, yet acidic and basic behavior have been observed in many other solvents. Secondly, many substances that are bases do not contain OH- as part of their chemical makeup. Therefore, we need a more general model of acids and bases. We will discuss two, the Brønsted - Lowry model, and the Lewis model.

To deal with molecules like ammonia, which react as bases, but which don't fit in the Arrhenius scheme, Brønsted and Lowry proposed a new definition of acids and bases. **A Brønsted - Lowry acid is any compound which is capable of donating a proton to another species.** Here are some examples. A Brønsted - Lowry acid can be a neutral compound like HCl, when it donates a proton to H_20 in the reaction

$$HCl\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq).$$

A Brønsted Lowry acid can also be a cation like the hydronium ion when it donates a proton to ammonia in the reaction

$$H_3O^+(aq) + NH_3(aq) \rightleftharpoons H_2O(aq) + NH_4^+(aq).$$

It can also be an anion, as in the reaction

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^=(aq) + H_3O^+(aq).$$

A Brønsted Lowry base is any molecule that acts as a proton acceptor. The base can be neutral, as in the reaction between hydronium ion and ammonia, where the ammonia is acting as the base. It can also be an anion, as in the case of hydroxide ion, OH^-, in the reaction

$$HSO_4\text{-}(aq) + OH^-(aq) \rightleftharpoons SO_4^=(aq) + H_2O(l).$$

As another example, acetate ion acts as a base when it reacts with water in the reaction

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq).$$

Notice that **all of these reactions involve an acid, a compound that can donate a proton, reacting with a base, a compound that accepts a proton**. In the two examples we just mentioned, the HSO_4^-, which is acting as an acid, donates a proton to the OH^-, acting as a base, and the water, acting as an acid, donates a proton to the acetate ion, acting as a base.

Notice that we have written all of these reactions as equilibria. In the case of our reaction between hydronium ion and ammonia the forward reaction is,

$$H_3O^+ + NH_3 \rightarrow H_2O + NH_4^+.$$

In this reaction the H_3O^+ donates a proton so it is an acid. The NH_3 accepts a proton, so it is a base. IN THE REVERSE REACTION,

$$H_2O + NH_4^+ \rightarrow H_3O^+ + NH_3,$$

NH_4^+ DONATES A PROTON, SO WHAT IS IT? H_2O ACCEPTS A PROTON SO WHAT IS IT? So in our equilibrium, we start with an acid and a base, and end up with a new acid and a new base. The equilibrium will favor this side in which the acid and base are weaker. We will find that this is the case for all reactions of Brønsted - Lowry acids and bases.

It is useful to note that in our reaction the reactant acid is related to the product base by the transfer of a single proton. An acid and a base that differ only by a proton are called a **conjugate acid base pair**. In this case H_3O^+ and H_2O are a conjugate acid base pair. In such a pair we say that H_3O^+ is the conjugate acid for H_2O and that H_2O is the conjugate base for H_3O^+. Similarly, the base NH_3 and the acid NH_4^+ differ only by a single proton and are another conjugate acid base pair. Let's look at a couple more examples. **$HCN + OH^- \rightleftharpoons CN^- + H_2O$; $HNO_2 + NH_3 \rightleftharpoons NO_2^- + NH_4^+$.** [Have students identify product of acid base reaction, acids, bases, conjugate pair, partners.] **What is the conjugate acid of**

HS^-, the conjugate base of CH_3COOH, the conjugate base of HSO_4^-, the conjugate acid of $HCOO^-$?

It is useful at this point to bring up some additional **nomenclature involving acids and bases**. A **monoprotic acid** is an acid that has only one acidic proton. Examples are HCl and acetic acid, CH_3COOH. Note from this latter example that you can't just look at the number of hydrogen atoms in a molecule to decide if it is monoprotic. For now you'll just have to rely on memorization to determine whether an acid is monoprotic or not. **An acid that has more than one acidic proton is called a polyprotic acid.** Sulfuric acid is one example, generating two hydronium ions via the sequential reactions

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$$

and

$$HSO_4^- + H_2O \rightleftharpoons SO_4^= + H_30^+$$

yielding the overall reaction

$$H_2SO_4 + 2\ H_2O \rightleftharpoons SO_4^= + 2\ H_3O^+.$$

An **amphoteric** substance is one that can act either as an acid or a base. These substances are sometimes also called **amphiprotic**. An example is the ion HSO_4^-, which can act as an acid as above, or as a base in the reaction

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_2SO_4(aq) + OH^-.$$

The single most important amphoteric compound is water itself, as can be seen in the following reaction -

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq).$$

This reaction is called an **autoionization reaction**, since water reacts with itself to form the anion and cation. In this reaction, one water molecule acts as an acid, while the other acts as a base. The equilibrium established in this reaction dominates aqueous acid base chemistry and we will be devoting a substantial amount of attention to it shortly.

It will simplify our subsequent discussion if we learn a bit about **naming acids and bases. All neutral acids have a name which ends with "ic acid" or "ous acid".** Examples are H_2SO_4, sulfuric acid; HNO_3, nitric acid; H_2SO_3, sulfurous acid; CH_3COOH, acetic acid; and C_6H_5COOH, benzoic acid. We can make bases by removing the acidic protons from these acids. For example, SO_4^{-2}, NO_3^-, and CH_3COO^- are three bases made from the acids just mentioned. **We name these bases by cutting off the “ic acid” from the name of the acid and replacing it with “ate”**. For example in naming NO_3^- we cut off the “ic acid” from nitric acid and add “ate” to get nitrate. Similarly the SO_4^{-2} is called sulfate, CH_3COO^-, acetate, and $C_6H_5COO^-$, benzoate. If we make a metal salt of these bases, we just add the name of the metal to the base. For example, $NaNO_3$ is sodium nitrate. WHAT DO WE CALL $NaCH_3COO$, KC_6H_5COO? **If we remove a proton from an acid whose name ends with “ous acid”, we name the base by removing the “ous” and replacing it with “ite”**. For example, the SO_3^{-2} ion, which is obtained by removing two protons from sulfurous acid, is called the sulfite ion. The exception to these rules is when the anion produced is an atomic ion, like F-, fluoride, S^{2-}, sulfide, or O^{2-}, oxide. In this case we simply take the atomic name, remove the last few letters and replace them by “ide”.

Now let’s look at bases and their conjugate acids. Examples of bases are ammonia, NH_3; methylamine, CH_3NH_2, and diethylamine, $(C_2H_5)_2NH_2$. **To name the conjugate acid, remove the last vowels and replace them by “ium”**, so NH_4^+ is ammonium,

$CH_3NH_3^+$ is methylaminium, $(C_2H_5)_2NH_2^+$ is diethyl-aminium. **If we make a salt by adding an anion to a cation, we name the salt by adding the names of the cation and anion**. NH_4NO_3 is ammonium nitrate, CH_3NH_3Cl is methylaminium chloride. This nomenclature should help you identify conjugate acids and bases. IF I TALK ABOUT FORMATE ION, WHAT IS THE NAME OF THE CONJUGATE ACID? IF I TALK ABOUT ETHYLAMINIUM, WHAT IS THE CONJUGATE BASE?

Lecture 30

We tend to crudely classify acids by the extent to which the acid dissociates. We divide acids into strong and weak acids. A **strong acid** is one that completely dissociates. In other words, **the concentration of H_3O^+ in a solution of a strong monoprotic acid is the same as the nominal concentration of acid initially dissolved**. Examples of strong acids are hydrochloric acid and nitric acid. A more complete list of strong acids is found in your book. **A weak acid is one that is incompletely dissociated**. For example, aqueous acetic acid exists mostly as CH_3COOH and not CH_3COO^- and H_3O^+. HF exists mostly as HF and not as H_30^+ and F^-.

A strong base dissociates completely, e.g., NaOH will dissolve to form Na^+ and OH^-. Examples of strong bases are group one and two hydroxides, and group one and two oxides. For example, KOH, $Mg(OH)_2$ and CaO are all strong bases. **A weak base is either one that dissociates incompletely or one that binds protons only weakly.** As an example of the former, when NH_4OH, ammonium hydroxide, dissociates according to the reaction

$$NH_4OH \rightleftharpoons NH_4^+ + OH^{-,}$$

the equilibrium strongly favors the NH_4OH. As an example of the latter, Cl- is a very weak base. In the reaction

$$Cl^- + H_3O^+ \rightleftharpoons HCl + H_2O,$$

the equilibrium strongly favors the reactants, hydronium ion and chloride ion. So we see that there are two different ways in which we can have a weak base.

At this point we've talked about a lot of the qualitative properties of acids and bases. A useful question to ask is how we can **quantify these ideas of strong and weak acids and bases**. Furthermore, when we have an acidic or basic solution, we need a useful way to **quantify the acidity or basicity** of these solutions. We will concentrate on answering these questions for aqueous solutions, and as such will start with water self-ionization, since this is the only source of acid and base in a sample of pure water.

We've already mentioned **water self-ionization**. The water self ionization reaction is

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-.$$

The equilibrium constant for this reaction has the form $[H_3O^+][OH^-]$ and is called K_w. At 25°C $K_w = 1.000 \times 10^{-14}$. Let's figure out the concentration of H^+ and OH^- in pure H_2O using K_w. The only source of H_3O^+ and OH^- in pure water is the reaction $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$. Let's set up a concentration table for this reaction. Initially we have all water. WHAT ARE THE INITIALCONCENTRATIONS OF H_3O^+ AND OH^-? Now we let the reaction go to equilibrium. WHAT SHALL WE SAY THE CHANGE IN THE CONCENTRATION OF H_3O^+ IS? OF OH-? WHAT ARE THE FINAL CONCENTRATIONS OF H_3O^+ AND OH-? This means that $K_w = 1 \times 10^{-14} = x^2$. Thus, $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ M.

	Initial [ ] (M)	Change in [ ](M)	Final [ ] (M)
H_3O^+	0	x	x
OH^-	0	x	x

We can use K_w to calculate the concentration of OH^- in a solution where we know the [H_3O^+] or to calculate the [H_3O^+] in a solution where we know [OH-].

The case where the [H_3O^+] is easiest to find is the case of **solutions of strong acids**, like HCl or HNO_3. Strong acid solutions are completely dissociated. In other words, when we have a reaction like

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+ + Cl^-,$$

the equilibrium lies so far to the right that we don't even bother with equilibrium arrows> Because the equilibrium lies so far on the product side, equilibrium constants are not defined for strong acids. In these cases, the [H_3O^+] is equal to the concentration of the acid. Here are several examples. IN A 2M SOLUTION OF HCL, [H_3O^+] = ? WHAT ABOUT IN A 0.37M SOLUTION OF HNO_3, 2.9M HBR, 1.56 X 10^{-4}M $HClO_4$? The only exception to this is when the concentration of H3O+ added is comparable to the concentration generated by the autoionization of water. This is not a concern for acid concentrations greater than 10^{-6} M.

Similarly, it is very easy to find out the **concentration of OH^- in a solution of strong bases**. Here, the [OH^-] is just the concentration you get from completely dissolving your hydroxide, or twice the concentration you get from completely dissolving soluble oxides. FOR EXAMPLE WHAT ARE THE CONCENTRATIONS OF OH^- IN 1.4M NAOH, 0.35M $Ca(OH)_2$ OR 0.45 M Na_2O?

Let's **calculate the [OH^-] for the acid solutions** we've just mentioned. Remember that in aqueous solution the concentration of H_3O^+ and OH^- is governed by the equilibrium $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$, and is described by the equilibrium constant $K_w = [H_3O^+][OH^-]$. Therefore **any time we know the concentration of hydronium ion, we can calculate**

the concentration of hydroxide by $[OH^-] = \frac{K_w}{[H_3O^+]}$**.** So for a 2M HCl solution, [OH-]= $\frac{1.0x10^{-14}}{2.0}$ = 5.0×10^{-15}M. Let's do a few examples together. [.37M solution of HNO_3, 2.9M HBr, 1.56×10^{-4} M $HClO_4$] Similarly, **if we know the concentration of [OH-] in our solution, we can calculate $[H_3O^+]$ by** $[H_3O^+] = \frac{K_w}{[OH^-]}$. So for a 1.4 M NaOH solution, we have $[H_3O^+] = \frac{K_w}{[OH^-]}$ = $\frac{1.0x10^{-14}}{1.4}$ = 7.34×10^{-15}. WHAT IS THE $[H_3O^+]$ FOR A 0.35 M SOLUTION OF $Ca(OH)_2$?

Notice that when we deal with concentrations of hydronium ion and hydroxide ion in aqueous solution, the concentrations vary over many orders of magnitude, commonly running from about 15 M to 10^{-15} M. In order to create a less cumbersome way of dealing with this huge range of numbers, the **pH scale** was introduced. The pH is defined as

$$pH = -\log_{10}[H_3O^+].$$

The **pOH** has an analogous definition,

$$pOH = -\log_{10}[OH^-].$$

Note that your calculators will have two different log functions on them. One is usually abbreviated ln, and is a logarithm with base e. The log base 10, the one we use for pH and pOH calculations, is usually simply abbreviated on your calculators as log. Let's calculate the pH and pOH of our 2M HCl solution. $pH = -\log [H_3O^+] = -\log 2 = -.3$. $pOH = -\log_{10}[OH^-] = -\log_{10}[5.0 \times 10^{-15}] = 14.3$. Let's calculate the pH and pOH of neutral water. According to our definition $pH = -\log[H_3O^+] = -\log[1.0 \times 10^{-7}]= 7$. Calculating pOH for neutral water also yields a value of 7. Thus, **for aqueous solutions pH + pOH = 14**. This is an important fact that you will be able to use as a short cut in a lot of our acid-base problems. LET'S PRACTICE CALCULATING PH AND POH FOR A FEW OF THE EXAMPLES WE JUST WORKED OUT.

We can also calculate concentrations starting with pH values. Taking the antilog of our equation for pH yields

$$[H_3O^+] = 10^{-pH}$$

and similarly $$[OH^-] = 10^{-pOH}.$$

Let's try this a few times. Name a pH, any pH. [Also solicit values of pOH and calculate the [OH-].]

As we have said earlier, **weak bases and acids will not dissociate completely**, and this means that it is valuable to write an equilibrium expression for these reactions. For example, for the dissociation of acetic acid, the reaction is

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+.$$

Acid base reactions are so important that we define a **new equilibrium constant**

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}.$$

In general, for the reaction

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-,$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}.$$

WHEN WE DISSOLVE THE WEAK ACID HCO_3^- IN WATER, WHAT IS THE REACTION THAT OCCURS? WHAT IS THE EQUILIBRIUM CONSTANT EXPRESSION K_A FOR HCO_3^-?

We can write **an equilibrium expression for a weak base** as well. The classic example is NH_3. IF WE START OUT WITH NH_3, A BASE, AND WATER, WHAT ARE OUR PRODUCTS? The equilibrium constant, which we call K_b, is given by

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]},$$

for this reaction.

For a general reaction of a base with water,

$$B + H_2O \rightleftharpoons BH^+ + OH^-,$$

the equilibrium constant expression for K_b is given by

$$K_b = \frac{[BH^+][OH^-]}{[B]}.$$

For a conjugate acid-base pair in aqueous solution, $K_aK_b = K_w$. To see this consider the reactions

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Where NH_3 has $K_b = 1.8 \times 10^{-5}$ and

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+,$$

where NH_4^+ has $K_a = 5.6 \times 10^{-10}$. Their product, $K_b \times K_a = (1.8 \times 10^{-5})(5.6 \times 10^{-10}) = 1.0 \times 10^{-14}$. We can see why this is if we take the product of the equilibrium constant expressions.

$$K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} x \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-] = K_w$$

As another example, nitrous acid, HNO_2, has $K_a = 4.5 \times 10^{-4}$, its conjugate base, nitrite, NO_2^-, has $K_b = 2.2 \times 10^{-11}$, and once again, their product $K_a \times K_b = 1.0 \times 10^{-14}$. The advantage of this observation is that **if you know K_a you can calculate K_b for the**

conjugate base using $K_b = \frac{K_w}{K_a}$. Conversely, if you know K_b you can calculate K_a for the conjugate acid, using $K_a = \frac{K_w}{K_b}$. For hypochlorous acid, HOCl, $K_A = 3.1 \times 10^{-8}$. What is K_B for its conjugate base? For propionic acid, $K_A = 1.4 \times 10^{-5}$, what is K_B for its conjugate base? For hydrazine, $K_B = 1.7 \times 10^{-6}$, what is K_A for its conjugate acid? For pyridine, $K_B = 1.7 \times 10^{-9}$, what is K_A for its conjugate acid?

Practice calculations - lets calculate pH and pOH for all of the solutions below.

.20 M NaCl

.20 M HI

.20 M Lactic acid, $HC_3H_5O_3$, $K_A = 1.38 \times 10^{-4}$

.20 M aniline, $C_6H_5NH_2$, $K_B = 3.8 \times 10^{-10}$

.20 M KOH

.20 M CH_3NH_3Cl, K_B for $CH_3NH_2 = 3.7 \times 10^{-4}$

Now I'd like to turn to a slightly more complicated acid-base problem - **polyprotic acids**. As I've said earlier, these are **acids that can lose more than one proton**. Examples of polyprotic acids are H_3PO_4, phosphoric acid; $H_2C_6H_6O_6$, ascorbic acid; and, of course, H_2SO_4, sulfuric acid. I've already spoken to you of the biological significance of phosphoric acid. Ascorbic acid is another name for vitamin C. It is found in all fresh fruits and vegetables to some degree. It is named ascorbic acid, because it was found to be the cure for scurvy, a disease that plagued sailors who on long voyages were unable to maintain supplies of fresh fruits and vegetables. Does anyone know where the nickname Limey's for British sailors came from? The British navy discovered that eating limes cured scurvy, due as we now know to the presence of ascorbic acid, and that limes were easy to ship and didn't spoil over long voyages, so British sailors would suck on limes to prevent scurvy.

Ascorbic acid dissociates in two steps:

$$H_2C_6H_6O_6 + H_20 \rightleftharpoons H_3O^+ + HC_6H_6O_6^- \quad K_{a1} = 7.9 \text{ x } 10^{-5}$$

$$HC_6H_6O_6^- + H_20 \rightleftharpoons H_3O^+ + C_6H_6O_6^= \quad K_{a2} = 1.6 \text{ x } 10^{-12}$$

Let’s see how to calculate the equilibrium concentrations of $H_2C_6H_6O_6$, $HC_6H_5O_6$-, $C_6H_6O_6^=$, and H_3O^+ for a 0.2 M solution of ascorbic acid. The first step in a problem like this is to notice that since K_a is much larger for the first dissociation reaction, most of the H_3O^+ will be produced by the first reaction. This suggests that we should treat the two reactions one at a time. FOR THE FIRST REACTION, WHAT IS THE EQUILIBRIUM EXPRESSION?

$[K_{a1} = \frac{[HC_6H_6O_6^-][H_3O^+]}{[H_2C_6H_6O_6]}]$ WHAT IS THE CONCENTRATION TABLE FOR THIS REACTION?

	Initial [ ] (M)	Change in [ ] (M)	Equil. [ ] (M)
$H_2C_6H_6O_6$	.20	-x	.20-x ≈.20
$HC_6H_6O_6^-$	0	x	x
H_3O^+	0	x	x

We can simplify this problem by assuming that the concentration of the ascorbic acid remains essentially unchanged because of the small equilibrium constant. Plugging these values in our equilibrium expression gives

$$K_{a1} = 7.9 \text{ x } 10^{-5} = \frac{x^2}{.20}.$$

Therefore x = 4.0 x 10^{-3}. This tells us that $[H_2C_6H_6O_6]$ = .20 M, $[HC_6H_6O_6^-]$ = 4.0 x 10^{-3} M, and $[H_3O^+]$ = 4.0 x 10^{-3} M after our first reaction.

What is the equilibrium expression for the second reaction? [$K_{a2} = \frac{[C_6H_6O_6^{=}][H_3O^+]}{[HC_6H_6O_6^-]}$]. What is the concentration table for this reaction? Note that we use the results from our first equilibrium calculation as the initial concentrations in our second calculation.

	Initial [ ] (M)	Change in [ ] (M)	Equil. [ ] (M)
$HC_6H_6O_6^-$	4.0 x 10^{-3}	-x	4.0 x 10^{-3} - x ≈ 4.0 x 10^{-3}
$C_6H_6O_6^{=}$	0	x	x
H_3O^+	4.0 x 10^{-3}	x	4.0 x 10^{-3} + x ≈ 4.0 x 10^{-3}

Here we make that assumption that both the $HC_6H_6O_6^-$ and the H_3O^+ remain unchanged because of the small value of the equilibrium constant. Plugging the values from the table into our equilibrium expression yields K_{a2} = 1.6 x 10^{-12} = $\frac{4.0x10^{-3}x}{4.0x10^{-3}}$, and therefore x = 1.6 x 10^{-12} M. We can see that our assumptions were valid.

The procedure for calculating the concentrations of the various species for salts like Na_2SO_3, or K_3PO_4, where all the acidic protons have been replaced by metal ions, is very similar. Let's calculate the concentrations of ions in Na_2SO_3, given that K_{a1} for H_2SO_3 = 1.2 x 10^{-2}, and K_{a2} for $HS0_3^-$ is 6.2 x 10^{-8}.

Lecture 31

Let’s talk about the **relative strengths of acids and bases in conjugate acid-base pairs**.

Sulfurous acid is a moderately strong acid, with $K_a = 1.2 \times 10^{-2}$. WHAT IS K_B FOR THE CONJUGATE BASE? [8.3×10^{-13}]. IS THIS A STRONG BASE OR A WEAK BASE? So in this case we see that a relatively strong acid will have a weak conjugate base. This will always be true. **Strong acids have weak conjugate bases**. Let’s see what happens if we start out with a weak acid. Hydrogen cyanide, HCN, is a weak acid with $K_a = 4.0 \times 10^{-10.}$ What is the K_b of its conjugate base, CN^-? [2.5×10^{-5}]. Notice that this, while a weak base, is significantly stronger than the conjugate acid. So if we have a weak acid, the conjugate base will be stronger. In general, as a crude rule of thumb we can say that **a weak acid yields a strong conjugate base**. What if we start with a moderately strong base like NH_3, which has $K_b = 1.8 \times 10^{-5}$. WHAT WILL KA OF THE CONJUGATE ACID BE? IS THIS A WEAK ACID OR A STRONG ACID? So we see that our general rules of thumb will be as follows. Strong acids will have weak conjugate bases. Weak acids will have (relatively) strong conjugate bases. Strong bases will have weak conjugate acids. Weak bases will have (relatively) strong conjugate acids. We can make this more quantitative with the following statements. If an acid has $K_a > 1.0 \times 10^{-7}$, its conjugate base will be weaker. If an acid has $K_a < 1.0 \times 10^{-7}$, its conjugate base will be stronger. If a base has $K_b > 1.0 \times 10^{-7}$, its conjugate acid will be weaker, and if the base has $K_b < 1.0 \times 10^{-7}$, its conjugate acid will be stronger.

Notice that many of our K_a's and K_b's are very small numbers. In your book, the K_a's go as low as 1.3×10^{-13}, but some organic compounds have K_a's which are much smaller. To simplify the presentation of these small equilibrium constants, the **pK_a's and pK_b's** were introduced. The definitions are very similar and are analogous to the definition of pH.

$$pK_a \equiv -\log K_a$$

and

$$pK_b \equiv -\log K_b.$$

So for example, K_a for boric acid, H_3BO_3, is 7.3×10^{-10}. WHAT IS pK_A? [9.14] K_b for NH_3 is 1.8×10^{-5}. WHAT IS pK_B? [4.75]

I don't know if you've noticed this yet, but when we defined the Arrhenius acids, we also defined a characteristic **acid - base chemistry**. In the Arrhenius model, the chemistry is limited to two types of reactions. First, when an Arrhenius acid dissolves in water, it reacts with water to produce a hydronium ion,

$$HX(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + X^-(aq).$$

Second, when an Arrhenius acid and an Arrhenius base react, they form water and a salt,

$$HX(aq) + MOH(aq) \rightleftharpoons H_2O(l) + MX(aq),$$

the so called **neutralization reaction**. These neutralization reactions are most familiar when they are between strong acids and strong bases, as in the reaction

$$HNO_3 + KOH \rightleftharpoons H_2O + KNO_3.$$

However, they can also occur between a weak acid and a strong base. An example is the reaction

$$CH_3COOH + NaOH \rightleftharpoons H_2O + NaCH_3COO.$$

Note that as is the case for all neutralization reactions, one product is water. Note that in this case the other product is the salt of a weak base.

When we expanded our definitions of acids and bases with the Brønsted-Lowry definition, it expanded our range of acid-base reactions. In the Brønsted-Lowry system, an acid reacts by transferring a proton to a base to form a weaker acid and a weaker base. Notice that both of our Arrhenius reactions fit this definition, but that a growing number of reactions now fit the definition of acid base reactions as well. Note that these reactions now include bases other than hydroxide ion, and reactions where water is not one of the products. For example, one such reaction is

$$HNO_3 + NH_3 \rightleftharpoons NH_4^+ + NO_3^-.$$

If the water is evaporated from the aqueous solutions where these reactions occur, the result is a salt. One of the properties of these salts is high solubility. For example, the reaction between the strong acid hydrochloric acid and the weak base methylamine results in methylaminium chloride, the chloride salt of a weak acid, methylaminium.

$$CH_3NH_2 + HCl \rightleftharpoons CH_3NH_3Cl.$$

Notice that **in reactions of Brønsted Lowry acids and bases, the equilibrium always favors the side with the weakest acids and bases**. Thus in the case of the reaction between the nitric acid and the ammonia, the equilibrium favors the weak acid ammonium and the very weak base nitrate ion, while in the reaction between methylamine and HCl, the equilibrium favors the chloride ion and the weak acid methylaminium.

There is a third definition of acids and bases, which was proposed in 1923 by the Berkeley chemist G. N. Lewis, and which will further expand the number of reactions we recognize as acid base reactions. According to this definition **an acid is a substance which can accept electrons**, while **a base is any substance which can donate electrons**. Thus the Lewis definition is the most general definition of acids and bases, since it applies even to systems where protons are not transferred. In the Lewis formalism, the acid in an Arrhenius or Brønsted Lowry definition is the proton itself, since a proton, H^+, has no electrons, and is therefore an ideal electron acceptor. The hydroxide ion, OH^-, qualifies as a Lewis base. To see this, we draw the dot structure of OH-, and note that it has three electron lone pairs. It is the presence of these lone pairs that characterize hydroxide ion as a Lewis base. Other examples of Lewis bases that are also Brønsted Lowry bases are water, which has two electron lone pairs, or any of the amines, which have one. So you see, to identify a Lewis base, all you have to do is find those compounds whose Lewis dot structure reveals an electron lone pair.

The Lewis formalism is not just a way of reclassifying the acids and bases with which we are already familiar, but also identifies new compounds as acids and bases. For example, the dot structure of the compound BF_3 [draw] shows that it is two electrons short of an octet, and is therefore electron deficient and a Lewis acid. In addition, positively charged metal ions are potential Lewis acids, both because their positive charge attracts electrons and because all can accommodate at least one electron pair. For example, Fe^{+2} has six valence electrons. HOW MANY ELECTRONS DOES A TRANSITION METAL NEED TO FILL ITS VALENCE SHELL? This means that Fe^{+2} can accommodate up to six additional pairs of electrons, and is therefore a strong Lewis acid.

In the Lewis formalism, an acid base reaction is when a base provides a pair of electrons to share with an acid. The archetypal reaction would be that of BF_3 with

NH_3, in which a bond is formed between the two molecules, and both the electrons in this bond are donated by NH_3, the base. The product of such a reaction is called an **acid base adduct or complex**, and the bond is called either a **donor acceptor bond or a coordinate covalent bond**. Another example of these Lewis acid base reactions is the reaction of a proton with water to make H_3O^+. Here the electron poor proton reacts with the electron rich water. Finally, in a dramatic but not atypical case, Fe^{+2}, with its need for 12 electrons to fill its valence shell, will react with six molecules of CN-, a Lewis base, in the reaction

$$Fe^{+2}(aq) + 6\ CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq).$$

Much of the chemistry of transition metals is Lewis acid - base chemistry. As with other equilibrium reactions, it is useful to be able to characterize these Lewis acid-base reactions as favoring products or reactants at equilibrium. To do this we use equilibrium constants, which we call **formation constants**. For example, the reaction

$$Ag^+(aq) + 2\ Br^-(aq) \rightleftharpoons Ag(Br)_2^-(aq)$$

has the formation constant

$$K_f = \frac{[Ag(Br)_2^-]}{[Ag^+][Br^-]^2} = 1.3 \times 10^7.$$

The equilibrium constant for the reverse reaction,

$$Ag(Br)_2^-\ (aq) \rightleftharpoons Ag^+\ (aq) + 2\ Br^-(aq)$$

is called the **dissociation constant**. Your book only tabulates formation constants. HOW CAN WE FIND THE DISSOCIATION CONSTANT FOR THIS REACTION? Many formation constants are very large. In fact, these coordination complexes are often a route to the removal of free metal ions in solution. Let’s do an example.

Suppose that 0.1mol of $AgNO_3$ and 0.25 mol of NaBr are dissolved in a liter of water. Calculate the concentrations of Ag^+, Br^- and $AgBr_2^{--}$ at equilibrium. The reaction which occurs is the complex formation reaction above, with the equilibrium constant expression above. As usual, we just write out a concentration table. The challenge here is that if we work out our usual concentration table, we have a problem

	Initial [ ] (M)	Change (M)	Equil. [ ] (M)
Ag+	.100	-x	.100 - x
Br-	.250	-2x	.250 -2x
$AgBr_2^{--}$	0	x	x

Since the equilibrium constant for the reaction is so large, x should be large, and we can't apply our approximation. To simplify the solution of this problem we assume as our initial condition that all of our limiting reagent reacts. Which is the limiting reagent for this reaction? Thus if the Ag^+ was completely reacted, we would have a new set of initial concentrations,

	Initial [ ] (M)	Change (M)	Equil. [ ] (M)
Ag+	0	x	x
Br-	.050	2x	$.050 + 2x \approx .050$
$AgBr_2^-$	.100	-x	$.100 - x \approx .100$

Thus our equation for x becomes

$$K = \frac{.100}{.050x} = 1.3 \times 10^7,$$

and therefore $x = 1.54 \times 10^{-7}$. Our equilibrium concentrations are $[Ag^+] = 1.54 \times 10^{-7}$ M, [Br-] = .050 M, and $[AgBr_2^-] = .100$ M.

Lecture 32

I stated at the beginning of our study of acids and bases that one reason that acids and bases are important is that they are the most common form of homogeneous catalyst. Since the rates of reactions in which acids and bases appear as catalysts depend strongly upon the concentrations of hydronium ion or hydroxide, it seems apparent that it would be desirable to be able to control the pH of a reacting mixture. **Control of pH** is also important for studies of biochemical systems, since the activity of many enzymes is extremely dependent on pH. These are just two examples of systems for which pH control is extremely desirable.

Why is pH control a problem? Consider a 1 L aqueous biological system at pH 6.9. The concentration of hydronium ion is $10^{-6.9} = 1.26 \times 10^{-7}$ M. Addition of just 1.00×10^{-3} moles of HCl increases the hydronium ion concentration to 10^{-3}M = pH 3. This is a hostile pH for biological systems. What we need is a tool that will allow us to add small amounts of acid or base to a system without changing the pH significantly.

This is precisely the definition of a **buffer**. A **buffer is a solution that allows us to add small amounts of strong acid or strong base while keeping the pH change small**. Notice that buffers resist pH changes when either OH^- or H_3O^+ is added to them. Therefore, they must contain something which can react with OH^- and something which can react with H_3O^+. As such **they are made up of solutions of a weak acid and its conjugate base or a weak base and its conjugate acid.** A common example of the former would be a mixture of acetic acid and sodium acetate, CH_3COOH and $Na^+CH_3COO^-$. An example of the latter would be a mixture of ammonia and ammonium chloride, NH_3 and NH_4Cl. **Buffers**

control pH most effectively when the conjugate acid/conjugate base ratio [HA]/[A-] = 1:1, but buffers will control pH anytime that these ratios lie between 10:1 and 1:10.

Let's look at some specific examples. One example would be a mixture of 0.30 mol of benzoic acid, C_6H_5COOH, and 0.15 mol of sodium benzoate, NaC_6H_5COO in a 1 L aqueous solution. The K_a for benzoic acid is 6.5 x 10^{-5}. One feature of buffers is that **each buffer has a characteristic pH**. We can calculate these pH's easily. Let's do it for our benzoic acid-benzoate buffer. We begin by writing the equilibrium constant expression for the ionization of benzoic acid,

$$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+,$$

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}.$$

If we solve this equation for the $[H_3O^+]$, we get

$$[H_3O^+] = \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} K_a$$

Let's make an equilibrium table for this reaction.

	Initial [ ] (M)	Change in [ ] (M)	Equil [ ] (M)
C_6H_5COOH	.30	-x	$.30 - x \approx .30$
$C_6H_5COO^-$	.15	x	$.15 + x \approx .15$
H_3O^+	0	x	x

This means that $[H_3O^+] = \frac{.30}{.15} 6.5x10^{-5} = 1.3x10^{-4}\ M$. Therefore, the pH of this buffer is 3.89. Notice that in retrospect we did not need to bother with the concentration table for this example. We could merely have inserted our concentrations for acetate and acetic acid into the constant expression. This will be the case for all buffers in which the absolute concentrations of the conjugate base pairs are substantial, and for which the ratios of the conjugate acid/base pair is between 10:1 and 1:10.

An example of a basic buffer is a solution made up of methylamine, CH_3NH_2 and methylaminium chloride, $CH_3NH_3^+Cl^-$, $K_b = 3.7 \times 10^{-4}$. LET'S CALCULATE THE PH FOR THIS BUFFER, WHEN THE CONCENTRATION OF CH_3NH_2 IS 0.25 M AND THE CONCENTRATION OF $CH_3NH_3^+Cl^-$ IS 1.00 M.

Now let's see what happens when we add strong acid to a buffer. Let's calculate the result when we add 0.12 mol of HNO_3 to 1.00 L of a buffer which is 1M in both benzoic acid and benzoate, and which starts out with a pH of 4.19. We need to calculate this in two stages. First we have to realize that when we add 0.12 mol of nitric acid to a buffer solution, the strong acid will react almost completely with the base of the buffer. We can express this in a concentration table.

	Initial [ ] (M)	Change in [ ] (M)	Final [ ] (M)
C_6H_5COOH	1.00	.12	1.12
$C_6H_5COO^-$	1.00	-.12	.88
HNO_3	.12	-.12	0

These are the concentrations we now put into our buffer equation,

$$[H_3O^+] = K_a \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = 6.5 \times 10^{-5} \frac{1.12}{.88} = 8.27 \times 10^{-5} \text{ M.}$$

Therefore the pH = 4.08. In comparison, note that if we added 0.12 mol of HNO_3 to 1 L of an unbuffered aqueous solution which had an initial pH of 4.9, the effect would be far more dramatic. The initial $[H_3O^+]$ in this case is 6.5 x 10^{-5} M. Adding 0.12 mol of HNO_3 would yield a final concentration of 0.12 M, and a final pH of .75, a much larger change.

Let's see what happens if we add 0.12 mol of NaOH to the same benzoic acid benzoate buffer solution. Once again, we begin by recognizing that the strong base will effectively react completely with the buffer acid. The concentration table we get for addition of 0.12 Mol of NaOH to our buffer is

	Initial [ ] (M)	Change in [ ] (M)	Final [ ] (M)
C_6H_5COOH	1.00	-.12	.88
$C_6H_5COO^-$	1.00	.12	1.12
OH^-	.12	-.12	0

At this point we just use our buffer equation to obtain the new $[H_3O^+]$. Once again,

$$[H_3O^+] = K_a \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = 6.5 \times 10^{-5}\ \frac{.88}{1.12} = 5.11 \times 10^{-5}$$, and the new pH is 4.30.

We can see from this that a buffer resists changes in pH due to addition of strong acid or strong base.

How does a buffer work? When we add a strong acid to an unbuffered aqueous solution, every acid molecule increases the hydronium ion concentration. However, when we add the same amount of acid to a buffer, instead of reacting with the water, it reacts with the base in the buffer to form the conjugate acid. Since the acids in buffers are weaker acids than hydronium ion, this results in a lower pH change. Similarly, adding a strong base to water would just result in increase of OH-. When we add the base to the buffer however, it reacts instead with the acid to produce the conjugate base. Once again, since the conjugate base is a weak base, it contributes far less OH- to the solution than the strong base would, and the change in pH is smaller.

Now let's do a full buffer problem together. To 1L of a nitrous acid buffer consisting of 1 mol HNO_2 and 1 mol $NaNO_2$, and having an initial pH of 3.3, we add 0.06 L of 1 M HCl. K_a of nitrous acid is 4.5×10^{-4}. WHAT IS THE FINAL PH?

Our last subject in the chemistry of acids and bases is **titration**. **Titration is an analytic technique in which we measure the amount of a solution of one substance needed to react completely with a solution of another substance.** Generally, when we do this we know the concentration of one substance, and use the titration to determine the concentration of the other substance. Although we will be discussing titrations in terms of acids and bases, titrations can be done with any two substances that react with each other to produce a third substance, and which can be dissolved.

An important concept in titrations is the concept of the **equivalent**. For acids and bases, **an equivalent is the amount of a substance that produces or reacts with 1 mole of H_3O^+.** A mole of a monoprotic acid contains 1 equivalent of protons. A mole of a polyprotic acid contains two or more equivalents of protons, depending on how many acidic protons the polyprotic acid contains. HOW MANY EQUIVALENTS ARE THERE IN 1 MOL OF HCL, H_2SO_4, $CA(OH)_2$, KOH? 1 L OF 0.06M HNO_3, 1 L OF 0.06M H_3PO_4? We use equivalents to define a new unit of concentration called **normality**. **The normality of a solution is defined as the number of equivalents per mole of solution.** For example, a

1 M solution of HCl is a 1N solution, a 1 M H_2SO_4 solution is 2N, 1 M H_3PO_4 is 3N. WHAT IS THE NORMALITY OF 0.5M H_2SO_4? 0.03 M H_3AsO_4? 0.25 M HCL?

When we do a titration, we are trying to measure the amount of a solution it takes to reach the **equivalence point**. **The equivalence point of an acid base titration is the point at which one reactant has been exactly consumed by the addition of the other.** This will occur when the number of equivalents of the substance we add is exactly equal to the number of equivalents in the solution we are titrating. Let's look at some examples. If we have 1 L of 0.05 M HCl and titrate it with NaOH, we begin with 0.05 equivalents of HCl and therefore, we reach the equivalence point when we've added 0.05 mol, or .05 equivalents, of NaOH. Note that it is not the volumes of solution that are equal, but the number of equivalents. IF WE TITRATE 0.500 L OF .025 M CH_3COOH WITH KOH, HOW MANY EQUIVALENTS OF ACETIC ACID DO WE START OUT WITH? HOW MANY EQUIVALENTS OF KOH DO WE NEED TO ADD TO REACH THE EQUIVALENCE POINT? HOW MANY MOLES IS THIS?

Things are a little more complicated when we consider polyprotic acids. **With polyprotic acids we have more than one equivalent per mol of acid and therefore have more than one equivalence point.** For example for 1 L of 1M H_2SO_4, addition of 1 mol of NaOH gives the first equivalence point, which results in the conversion to HSO_4^-, while addition of the second mol of OH^- gives our second equivalence point, which leads to conversion to $SO_4^=$.

Usually when we do acid base titrations we determine the equivalence point by analyzing a **titration curve**. There are two basic types of titration curves that we will consider. The first is that of a strong acid with a strong base. The second is that of a weak acid with a strong base. The opposite types of curves, where the base is titrated by an acid, have the same general features, so we won't go over them. In general, all **titration curves are graphs of pH vs. volume of solution added**. In these cases, since we are titrating an acid with a base, the volume will be volume of base added.

Let’s draw the graphs of each of these types of titrations. For a titration of a strong acid with a strong base, we begin at the pH of our initial solution. Addition of base results in an immediate increase of pH, which has the appearance of a straight line until the solution nears the equivalence point. Then the pH rapidly increases until the equivalence point is passed. The pH at the equivalence point for a titration of strong acid by strong base is 7.

For the **titration of a weak acid with a strong base**, the appearance is somewhat different. We again begin at the pH of the initial solution. Addition of base initially leads to a rapid increase of pH, until 1/10 of the acid has been titrated. From this point until 9/10 of the acid has been titrated our solution acts like a buffer, and the pH changes only slowly. After we pass the **buffer region**, the pH increases rapidly until it passes the equivalence point. After the region of rapidly increasing pH is passed, the increase in pH slows again, but there will be little further increase in pH.

There are **three important points on this type of titration curve**, the initial point, the halfway point of the titration, when we are in the center of the buffer region, and the equivalence point. It is important to note that **for the titration of a weak acid with a strong base the pH at the equivalence point is not 7.** Let's calculate the pH at these three points for the titration of a strong acid by a strong base, and then for the titration of a weak acid by a strong base.

We'll begin with the former. Let's begin with the titration of 50 mL of 0.25 M HCl titrated with 0.1 M NaOH. What is the initial pH? How many moles of HCl do we begin with? How many equivalents is this? What volume of 0.1 M NaOH do we need to add to titrate 1/2 of this? What is the [HCl] at this point? What is the pH? What volume of 0.1 M NaOH do we need to reach the equivalence point? What is the [HCl] at this point?

Now let's look at the titration of 75 mL of 0.37 M CH_3COOH titrated with 0.13 M KOH. The K_a of acetic acid is 1.76 x 10^{-5}. What is the initial pH? How many moles of acetic acid do we begin with? How many equivalents is this? What volume of 0.13 M KOH do we need to add to titrate 1/2 of this? What is the [acetic acid] at this point? What steps do we follow to calculate the pH? What volume of 0.13 M NaOH do we need to reach the equivalence point? What is the [CH_3COOH] at this point? What about acetate ion? What steps do we follow to calculate the pH?

Our last acid - base topic is **indicators**. I don't really think we need to go over them in detail. In short, an indicator is a weak acid or weak base that changes color at a certain pH. For example, phenolphthalein, the indicator that you are most familiar with, turns pink when the pH goes higher than 8.7. The only other thing you need to know about indicators is that when you are doing a titration, if you use an indicator to show when you have reached your endpoint, you want to use the one which changes color as close to the pH of your endpoint as possible. So for example, we just calculated the pH at the equivalence point of our titration of acetic acid to be 8.87. If we look at a table of indicators, such as can be found in the CRC Handbook of Chemistry and Physics, we find that the best indicator for this titration is good old phenolphthalein.