Acids and Bases

Centuries ago, certain substances were recognized for:

Sour taste	Turned vegetable blues to red	Solvent power	Ability to neutralize alkalies to form salts

These were called "acids" from "ac" which means sharp, as in *acetum*.

Other substances were recognized for:

Soapiness	Cutting grease	Having the reverse effect of acids

These were called "alkalies" which is from Arabic for plant ashes. They are also called bases.

Most Significant Properties

1) Their effect on acid/base indicators.
The table, below, summarizes the acid and base forms of 6 different acid/base indicators:

Acid Form (color)	Indicator	Base Form (color)
Red	**Litmus**	**Blue**
Clear	**Phenolphthalein**	**Pink**
Yellow	**Bromocresol green**	**Green**
Yellow	**Phenol red**	**Red**
Red	**Methyl red**	**Yellow**
Yellow	**Bromocresol purple**	**Purple**

2) Their ability to react with each other to produce salts.
3) Their catalytic action.
4) Their ability to displace weaker acids or bases.
5) Aqueous solutions conduct an electrical current.

Definitions of Acids and Bases

There are at least 4 definitions of acids and bases.

Arrhenius Definition of Acids and Bases

The first definitions are those of Arrhenius. By this set of definitions, an acid is a substance that dissociates in water to yield a proton (hydrogen ion). A base is a substance that dissociates in water to yield hydroxide ions. Examples of these sorts of reactions are summarized in the table, below:

Acid Name	Acids	Base Name	Bases
Hydrochloric	$HCl \rightarrow H^+ + Cl^-$	Sodium hydroxide	$NaOH \rightarrow Na^+ + OH^-$
Sulfuric	$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$	Potassium hydroxide	$KOH \rightarrow K^+ + OH^-$
Nitric	$HNO_3 \rightarrow H^+ + NO_3^-$	Magnesium hydroxide	$Mg(OH)_2 \rightarrow Mg^{2+} + 2\ OH^-$
Phosphoric	$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$	Barium hydroxide	$Ba(OH)_2 \rightarrow Ba^{2+} + 2\ OH^-$
Perchloric	$HClO_4 \rightarrow H^+ + ClO_4^-$	Aluminum hydroxide	$Al(OH)_3 \rightarrow Al^{3+} + 3\ OH^-$
Carbonic	$H_2CO_3 \rightarrow 2H^+ + CO_3^{2-}$	Tin (IV) hydroxide	$Sn(OH)_4 \rightarrow Sn^{4+} + 4OH^-$

Brønsted-Lowry Definition of Acids and Bases

By this set of definitions, an acid is a proton donor and a base is a proton acceptor when they dissociate in water. Representative reactions are summarized in the table, below:

Acid dissociation in water	Reaction of Hydroxide with an Acid
$HCl + H_2O \rightarrow H_3O^+ + Cl^-$	$HCl + OH^- \rightarrow H_2O + Cl^-$
$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$	$HNO_3 + OH^- \rightarrow H_2O + NO_3^-$
$HClO_4 + H_2O \rightarrow H_3O+ + ClO_4^-$	$H_2SO_4 + OH^- \rightarrow 2H_2O + SO_4^{2-}$

Species/substances that may either gain or lose protons (the hydrogen ion) are called amphipathic or amphiprotic or ampholytes. Examples are shown, below:

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Where RED indicates the acid and BLUE indicates the base form of each molecule.

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
$$H_3O^+ + HCO_3^- \rightarrow H_2CO_3 + H_2O$$

Where RED indicates the acid and BLUE indicates the base form of each molecule.

When a reaction is written in the following form,

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-,$$

the nitric acid is the acid and the water is the base. Once they react, a NEW acid and a NEW base are formed. The new acid is the H_3O^+ and the new base is the nitrate ion (NO_3^-). The nitric acid and the nitrate ion make up a conjugate acid-base pair, respectively. The water and the hydronium ion (H_3O^+) make up a conjugate base-acid pair, respectively. Two more examples of reactions that produce conjugate acid-base pairs follow:

$$H_2SO_4 + 2H_2O \rightarrow 2\ H_3O^+ + SO_4^{2-}$$
$$HOCl + H_2O \rightarrow H_3O^+ + OCl^-$$

H_2SO_4 and SO_4^{2-} are one conjugate acid-base pair in the first reaction. What is the other? HOCl and OCl^- is one of the conjugate acid-base pairs in the second reaction. What is the other?

The table, below summarizes a few acids with their conjugate bases:

Acid	Conjugate Base
Nitric (HNO_3)	Nitrate ion (NO_3^-)
Acetic ($HC_2H_3O_2$ or HOAc)	Acetate ion ($C_2H_3O_2^-$ or OAc^-)
Water (H_2O)	Hydroxide ion (OH^-)
Phosphoric (H_3PO_4)	Dihydrogen phosphate ion ($H_2PO_4^-$)

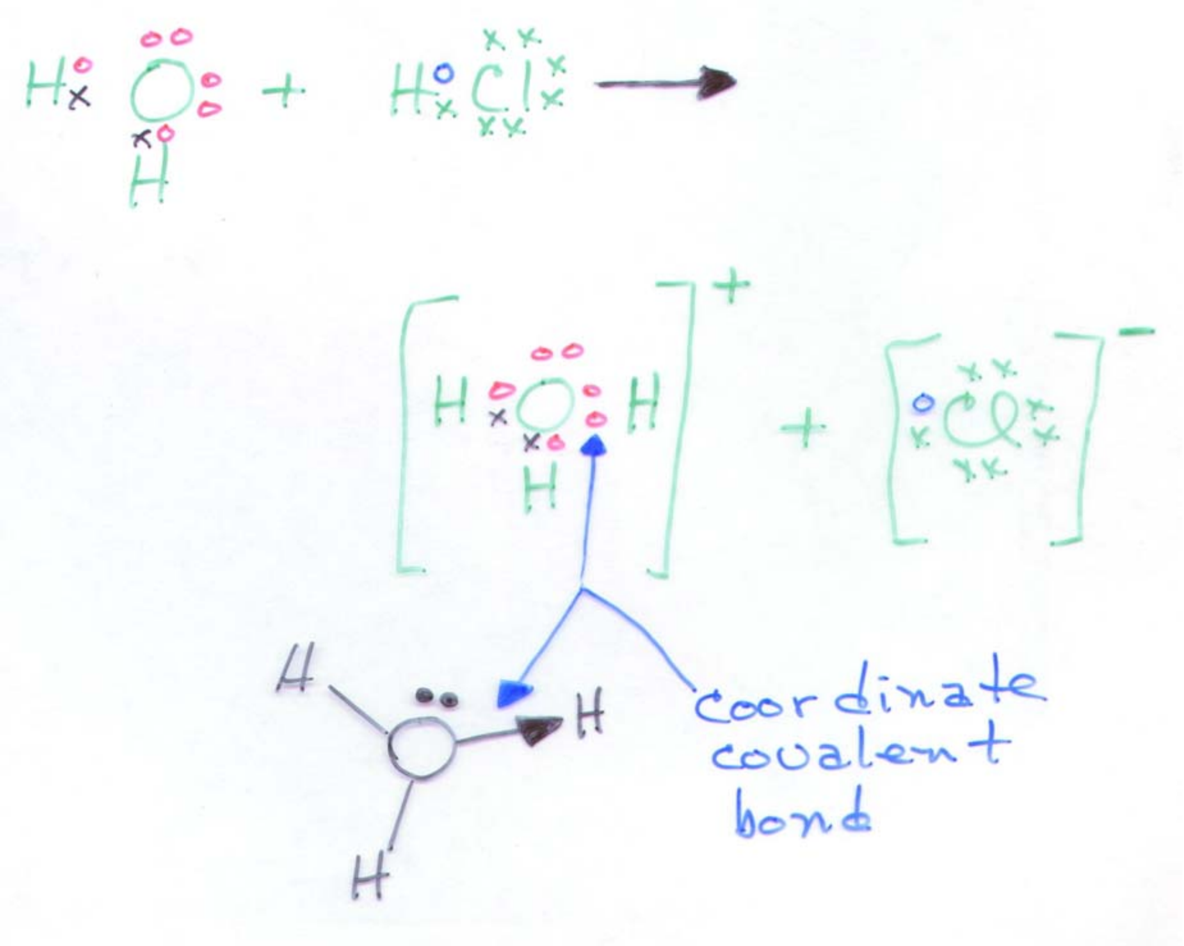
- In general, a strong acid gives a weak conjugate base; a weak acid gives a strong conjugate base; a strong base gives a weak conjugate acid; a weak base gives a strong conjugate acid.
  - Strong acids are those that dissociate 100% in water.
  - Examples include perchloric, sulfuric, hydrochloric and nitric acids.
  - Weak acids are those that ionize less than fully in water.
  - Examples include ammonia, water and carbonic acids.
- Strong bases are those that, like the acids, dissociate 100% in water.
  - Examples include sodium hydroxide.
  - Weak bases are those that, like the acids, dissociate less than fully in water.
  - Examples include the perchlorate ion, the iodide ion and the bromide ion.

Lewis Definition of Acids and Bases

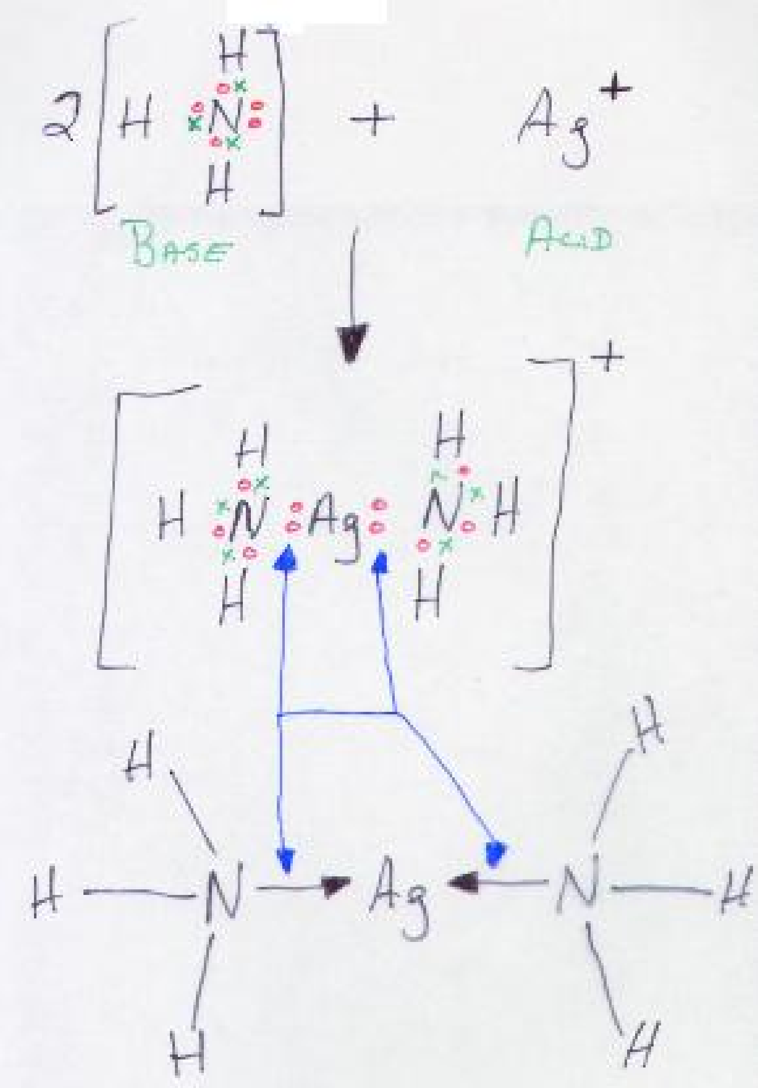
By this definition, acids are a molecule or ion which can accept a pair of electrons.

A base is a molecule or ion which can donate a pair of electrons.

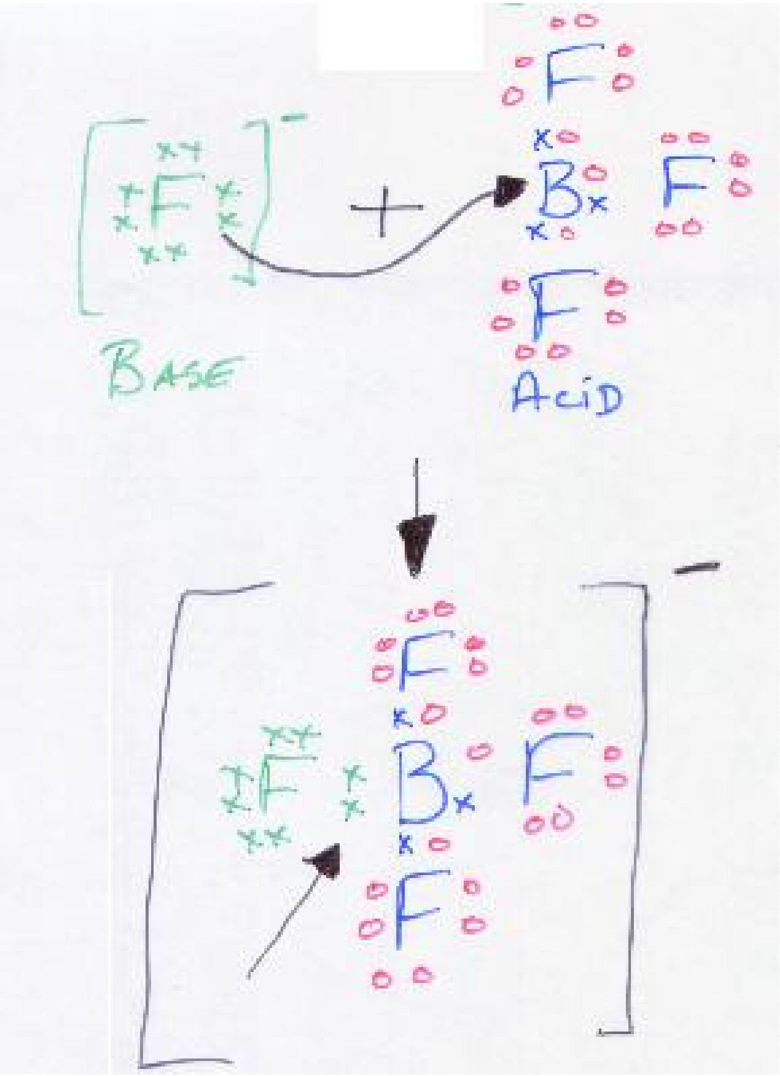
Example 1



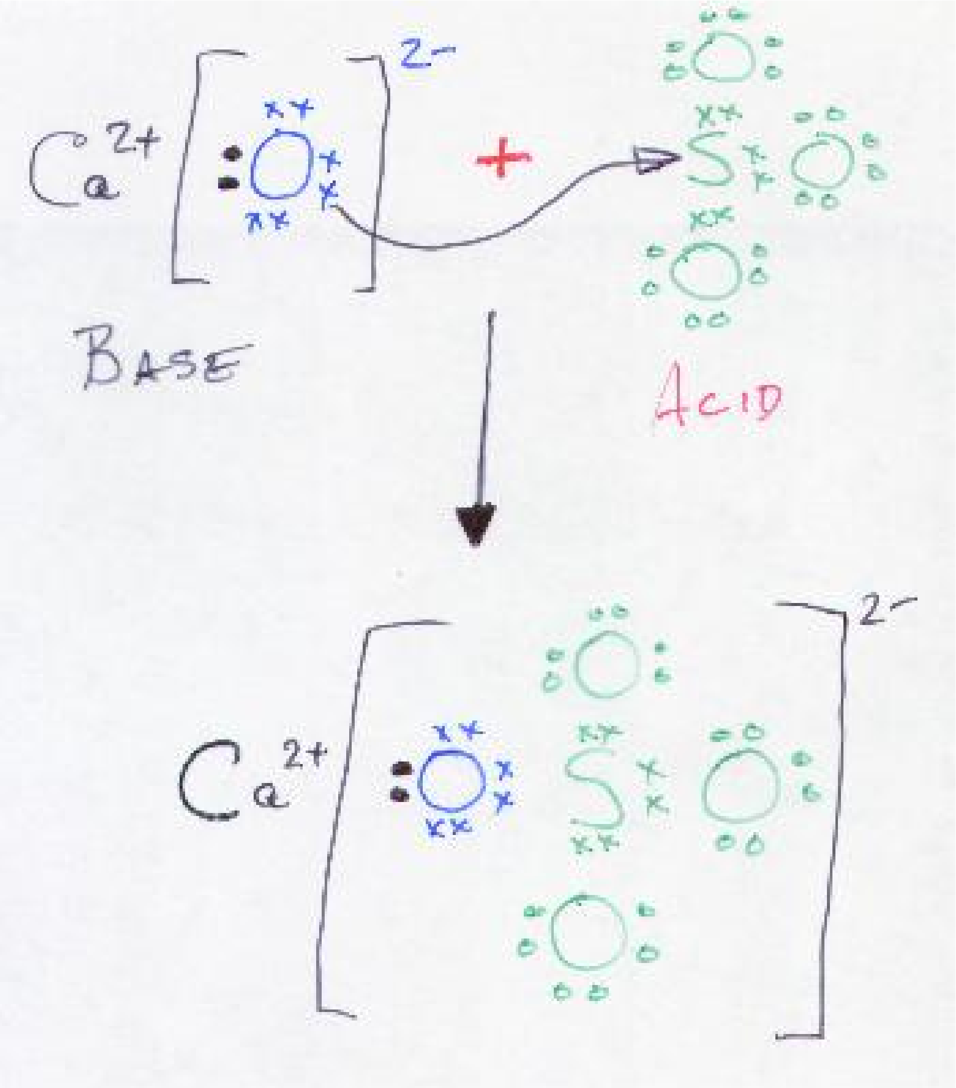
Example 2



Example 3



Example 4



Solvent Systems Concept of Acids and Bases

An acid is any material which gives a cation characteristic of the solvent.
A base is any material which gives an anion characteristic of the solvent.
Neutralization is a reaction between solvent cations and solvent anions to provide the solvent.
Examples of this system are summarized in the table, below, along with the reactions of solvation:

Protonic Solvent	**Solvated form**	**Unsolvated form**
Water	$H_2O + H_2O \rightarrow (H{\bullet}H_2O)^+ + OH^-$	$H^+ + OH^-$
Liquid Ammonia	$NH_3 + NH_3 \rightarrow (H{\bullet}NH_3)^+ + NH_2^-$	$H^+ + NH_2^-$
Non-Protonic Solvent		
Liquid Phosgene	$COCl_2 + COCl_2 \rightarrow (COCl{\bullet}COCl_2)^+ + Cl^-$	$COCl^+ + Cl^-$

Acid Formation and Dissociation

The formation of protonic acids may occur by 6 different mechanisms. These mechanisms and examples are summarized in the table, below:

Acid Formation Mechanism	Representative Reactions
Direct union of elements	$H_2 + Cl_2 \rightarrow 2\ HCl$ $H_2 + S \rightarrow H_2S$ $H_2 + Br_2 \rightarrow 2\ HBr$ $H_2 + F_2 \rightarrow 2HF$ $H_2 + I_2 \rightarrow 2HI$
Action of water on non-metal oxides	$CO_2 + H_2O \rightarrow H_2CO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$ $P_4O_{10} + 6\ H_2O \rightarrow 4H_3PO_4$ $SO_2 + H_2O \rightarrow H_2SO_3$
Heating salts of volatile acids with NON-volatile or SLIGHTLY volatile acids	$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow$ $NaBr + H_3PO_4 \rightarrow NaH_2PO_4 + HBr\uparrow$
By the action of salts with other acids producing a precipitate	$H^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl + H^+ + NO_3^-$ $2H^+ + SO_4^{2-} + Ba^{2+} + 2ClO_3^- \rightarrow BaSO_4 + 2H^+ + 2ClO_3^-$
By hydrolysis	$PBr_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HBr$ $PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl$
By oxidation-reduction reactions	$H_2S + I_2 \rightarrow 2HI + S$ $2HNO_3 + 2SO_2 + H_2O \rightarrow 2H_2SO_4 + NO\uparrow + NO_2\uparrow$

•If the acid has one ionizable proton, it is called a mono-protic acid.

•If it has 2, a di-protic acid.

•If it has three ionizable protons, it is called a triprotic acid.

•The significance has to with eventually using this information in reaction-type calculations.

•Each proton has its own dissociative step, i.e., the protons don't just "fall off" the acids all at once.

•They are removed a proton at a time.

Monoprotic Dissociation -- 1 H^+	Diprotic Dissociation -- 2 H^+	Triprotic Dissociation -- 3H^+
$HCl + H_2O \rightarrow H_3O^+ + Cl^-$	$H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$ $HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$	$H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$ $H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$ $HPO_4^{2-} + H_2O \rightarrow H_3O^+ + PO_4^{3-}$
$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$	$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$	
$HCN + H_2O \rightarrow H_3O^+ + CN^-$		

Base Formation

There are 5 mechanisms by which hydroxides are formed.
These mechanisms and representative reactions are summarized
in the table, below:

Base Mechanism	**Representative Reaction**
Alkali metals or alkaline earth metals react with water	$2\ K + 2\ H_2O \rightarrow 2\ K^+ + 2\ OH^- + H_2\uparrow$ $Ca + 2\ H_2O \rightarrow Ca^{2+} + 2\ OH^- + H_2\uparrow$ $2\ Na + 2\ H_2O \rightarrow 2\ Na^+ + 2\ OH^- + H_2\uparrow$
Water reacting with oxides of alkali/alkaline earth metals	$Na_2O + H_2O \rightarrow 2\ Na^+ + 2\ OH^-$ $CaO + H_2O \rightarrow Ca^{2+} + 2\ OH^-$ $MgO + H_2O \rightarrow Mg^{2+} + 2\ OH^-$
Salts with other bases with a resulting precipitate	$2\ Na^+ + CO_3^{2-} + Ca^{2+} + 2\ OH^- \rightarrow CaCO_3\downarrow + 2\ Na^+ + 2\ OH^-$
Electrolysis	$2\ Na^+ + 2\ Cl^- + 2\ H_2O + \text{Electrolysis} \rightarrow 2\ Na^+ + 2\ OH^- + H_2\uparrow + Cl_2\uparrow$
Dissolving NH_3 in water	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Normality and Buffers

In reactions, we need to express units in terms of protons, hydroxide ions or charges. When we do this we use a unit called EQUIVALENTS.

By definition, an equivalent (Eq) of base is that amount of base that contributes or provides 1 mol of hydroxide ion (OH^-):

$NaOH \rightarrow$ 1 mol OH^- which is 1 Eq

$Ba(OH)_2 \rightarrow$ 2 mol OH^- which is 2 Eq

$Al(OH)_3 \rightarrow$ 3 mol OH^- which is 3 Eq

By definition, an equivalent (Eq) of acid is that amount of acid that contributes or provides 1 mol of hydronium (H_3O^+) or hydrogen (H^+) ion:

$HCl \rightarrow$ 1 mol H^+ which is 1 Eq

$H_2SO_4 \rightarrow$ 2 mol H^+ which is 2 Eq

$H_3PO_4 \rightarrow$ 3 mol H^+ which is 3 Eq

By definition, an equivalent (Eq) of salt is that amount of salt that will contribute or provide 1 mol of positive (OR negative) charges when dissolved or dissociated:

$KCl \rightarrow K^+ + Cl^-$ which gives 1 Eq

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$ which gives 2 Eq

$AlCl_3 \rightarrow Al^{3+} + 3Cl^-$ which gives 3 Eq

Remember that we can calculate Molecular Weight by dividing the mass of X mol of substance (in grams) by the number of mols ("X") to get molecular weight in g/mol.

Using equivalents, we can calculate EQUIVALENT WEIGHT, as well: Let's calculate the equivalent weight of $AlCl_3$ -- this has a molecular weight of 133.5 g/mol

$$\frac{133.5\,g}{mol} * \frac{1\,mol\ AlCl_3}{3\,Eq} = \frac{44.5\,g}{Eq}$$

Notice that we used the total number of positive charges (OR negative charges: 3 * 1 = 3) for our equivalents.

Let's calculate the equivalent weight of sulfuric acid:

$$\frac{98\,g\,H_2SO_4}{mol} * \frac{1mol\,H_2SO_4}{2\,Eq} = \frac{49\,g}{Eq}$$

Let's calculate the equivalent weight of LiCl:

$$\frac{42.5\,g\,LiCl}{mol} * \frac{1mol\,LiCl}{1Eq} = \frac{42.5\,g}{Eq}$$

Let's calculate the equivalent weight (Eq Wt) of $Mg(OH)_2$

$$\frac{58.3\,g\,Mg(OH)_2}{mol} * \frac{1mol\,Mg(OH)_2}{2\,Eq} = \frac{29.15\,g}{Eq}$$

Clinically, the unit milli-equivalent is used (mEq) when measuring serum concentrations of electrolytes, e.g., sodium and potassium ions.

When we first learned about the mole, we extended our knowledge by studying a concentration term called molarity (M). This is a unit that expresses how many mols of a substance are dissolved in one liter of solution.

We can use equivalents to do a similar concentration term: normality (N).

Normality is defined as the number of equivalents of a substance that is dissolved in one liter of solution (Eq/L).

Let's begin by calculating the normality of a solution that has 40 g NaOH dissolved in 1 L of water:

$$(40\,g\,NaOH)*\frac{1\,mol}{40\,g\,NaOH}*\frac{1\,Eq}{1\,mol}*\frac{1}{1\,liter}=1\,N=1\frac{Eq}{L}$$

Notice how the units cancel out.

Let's calculate the normality of a solution of 29.15 g $Mg(OH)_2$ that is dissolved in 500 mL of water.

$$(29.15\,g\,Mg(OH)_2*\frac{1\,mol}{58.3\,g\,Mg(OH)_2}*\frac{2\,Eq}{1\,mol}*\frac{1}{0.5\,L}=2\,N=2\frac{Eq}{L}$$

Buffers

Buffers are solutions of salts that resist changes in pH, i.e., they maintain a relatively constant pH.

One example of a buffer pair is the HOAc/OAc- pair:

$$OAc^- + H^+ \Leftrightarrow HOAc$$

$$HOAc + OH^- \Leftrightarrow OAc^- + H_2O$$

Note that BOTH the hydrogen ion and the hydroxide ion react with the acetate ion.

The BUFFER CAPACITY is defined as the amount of hydrogen ion or hydroxide ion "absorbed" by a buffer without causing a significant change in the pH of the system.

One system of significance to all humans is the blood. In the blood, the following reactions occur very rapidly and continuously:

$$H_2O + CO_2 \Leftrightarrow H_2CO_3$$

$$HCO_3^{-} + H^{+} \Leftrightarrow H_2CO_3$$

$$H_2CO_3 + OH^{-} \Leftrightarrow HCO_3^{-} + H_2O$$

It is this particular reaction that plays the most significant role in acid-base balance in the human body -- as you will learn in A&P.

Auto-ionization of Water

Let's for a moment forget about acids and bases and focus on water. Water auto-ionizes in itself:

$$2H_2O \rightarrow H_3O^+ + OH^-$$

The reaction is NOT favored as written, although the ratio of protons to hydroxide ions is unity.

At 25° C, the concentration of both ionic species is $1*10^{-7}$ M.

Now, let's go back to the acids and bases.

H_3O^+ is acidic.

OH^- is alkaline.

In ACIDIC solutions, the molar concentration of H_3O^+ ($[H_3O^+]$) is greater than the molar concentration of OH^- ($[OH^-]$.

In NEUTRAL solutions, they are equal to each other.

In ALKALINE solutions, $[OH^-]$ is greater than $[H_3O^+]$.

In any dilute solution of water, the product of the hydronium ion concentration and hydroxide ion concentration is a constant, regardless of the solute.

This constant is called the dissociation constant of water and is represented by K_w.

We can determine the K_w based off of the equilibrium expression for the dissociation of water as follows:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Note that the coefficient "2" in the equilibrium reaction became the exponent "2" in the equilibrium expression.
By rearranging, the equation takes on a slightly different look:

$$K\,[H_2O]^2 = [H_3O^+] * [OH^-]$$

The molar concentration of water is around 55 M -- compared to the small amount that ionizes, it doesn't really change. Since it doesn't really change to any significance, the product of the constant, K, and the square of the $[H_2O]$ are equal to the K_w and the equation takes on the following look:

$$K_w = [H_3O^+] * [OH^-]$$

At 25° C, the K_w is equal to the square of $1*10^{-7}$, or $1*10^{-14}$.

Application Example 1:

Find $[H^+]$ and $[OH^-]$ in 0.02 M HCl.
Solution: HCl is a strong acid and is approximately 100% ionized in water. Hence $[H^+] \sim [HCl] = 0.02$ M.
Solution, part 2: $[H^+][OH^-] = K_w$, rearranging:

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1*10^{-14}}{2*10^{-2}} = 5*10^{-13}\ M$$

Application Example 2:

Determine the hydrogen ion and hydroxide ion concentrations in a mixture of 1 drop 6 M NaOH and 14 gtts water.
Solution: NaOH is a strong base, but the concentration in this solution changes from 6 M to some other concentration:

$$[OH^-] = [NaOH] = (6\,M)\left(\frac{1\,gtt\ NaOH}{1+14\ gtts\ total}\right) = 6*\frac{1}{15} = 0.4\,M$$

and,

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1*10^{-14}}{4*10^{-1}} = 2.5*10^{-14}\ M$$

The pH Scale -- Review

$$pH = -\log[H^+] or -\log[H_3O^+]$$

$$and$$

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

Common pitfalls with these relationships may be overcome by remembering the following:

pH drops with increasing H^+
pH increases with decreasing H^+

Also keep in mind that pH values are LOG values, e.g., a change in pH from 3 to 4 means that the hydrogen ion concentration changed from 0.001 M to 0.0001 M.

Example 1:
Determine the pH of a solution that has a [H+] of 0.00047 M.
Solution: pH = -log (0.00047) = 3.33

Example 2:
What is the hydrogen ion concentration of a solution with a pH of 5.72?
Solution:

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

$$[H^+] = 10^{-5.72}$$

$$[H^+] = 1.9 * 10^{-6}$$

Other useful "p" terms include the following:
pOH = - log [OH$^-$]
pK$_x$ = - log K$_x$, where "x" = a, b, eq, sp, d, i, ad nauseum.

How do we use this information to determine the acidity or alkalinity of a solution?
From:

$K_w = [H_3O^+] * [OH^-]$, we substitute the numerical values:

$$1*10^{-14} = (1*10^{-7}) * (1*10^{-7})$$

Next, we take the logs of each side:

$$\log (1*10^{-14}) = \log[(1*10^{-7}) * (1*10^{-7})]$$

which rearranges to:

$$\log (1*10^{-14}) = \log (1*10^{-7}) + \log (1*10^{-7})$$

This gives us:

$$-14 = -7 + -7$$

Take the negative of both sides and we get:

$$14 = 7 + 7$$

Taking the negative log (-log) of this equation may be re-written as "p":

$$pK_w = pH + pOH$$

or:

$14 = pH + pOH$, where $[H^+] = [H_3O^+]$

Another way to look at this is that:

$$[H_3O^+] = 1*10^{-pH}$$

At neutrality where the hydronium and hydroxide ion concentrations are equal, the pH is 7 ($-\log[1*10^{-7}]$).

When the pH is less than 7, the solution is acidic.
When pH equals 7, is neutral.
When the pH is greater than 7, the solution is alkaline or basic.

Acids and Bases Dissociate in Water

Fortunately for us, acids and bases dissociate in water:

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

Where HA is any acid and A^- is the anion left behind after the proton has separated from the acid.

We may determine the acid dissociation constant (like we did for water) as follows:

$$K = \frac{[H_3O^+]*[OH^-]}{[HA]*[H_2O]}$$

The water concentration doesn't change as we saw in the K_w determination, so we'll rearrange the equation as follows:

$$K*[H_2O] = K_a = \frac{[H_3O^+]*[A^-]}{[HA]}$$

Where K_a is the acid dissociation constant.

The K_a is equal to the arithmetic relationship between the undissociated and dissociated acid:

$HA \Leftrightarrow H^+ + A^-$

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

and notice that the K_a is directly proportional to $[H^+]$ -- more on this later.

Note that in all cases, these equilibrium expressions are the quotient of the product concentrations and the reactant concentrations.

Acids and bases like H_2A, H_3A, $M(OH)_2$ and $M(OH)_3$ have multiple dissociation steps.

Each step is represented by its own K_a or K_b:

$$H_2A \Leftrightarrow HA^- + H^+$$

$$HA^- \Leftrightarrow A^- + H^+$$

where

$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]}$$

and

$$K_{a2} = \frac{[A^-][H^+]}{[HA^-]}$$

The total K_a for this reaction is equal to the product of the two dissociation constants:

$$K_{a1} \bullet K_{a2} = \frac{[HA^-][H^+][A^-][H^+]}{[H_2A][HA^-]}$$

and

$$K_{a-TOTAL} = \frac{[H^+]^2[A^-]}{[H_2A]}$$

A tri-protic acid has three dissociations, hence the total K_a is equal to the products of the three dissociation constants.
Likewise, the K_b's for bases are calculable in the same manner; an exception for bases is that you are focusing on the OH-'s instead of the protons.

We can do the same for a base:

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

The equilibrium expression is as follows:

$$K = \frac{[NH_4^{\ +}]*[OH^-]}{[NH_3]*[H_2O]}$$

Again, since the water concentration doesn't change, we'll rearrange and manipulate:

$$K*[H_2O] = K_b = \frac{[NH_4^{\ +}]*[OH^-]}{[NH_3]}$$

Where K_b is the base dissociation constant.

Would you suspect, then, that there is some sort of relationship between K_a, K_b and K_w? Let's see.
Remember that:

$$K_w = [H_3O^+]*[OH^-]$$

and that:

$$K_a = \frac{[H_3O^+]*[OH^-]}{[HA]}$$

and that:

$$K_b = \frac{[HA]*[OH^-]}{[A^-]}$$

Let's multiply K_a by K_b and see what happens:

$$K_a * K_b = \frac{[H_3O^+]*[HA]*[A^-]*[OH^-]}{[HA]*[A^-]}$$

Note that all we're left with after canceling is:

$$[H_3O^+]*[OH^-] = K_a K_b = K_w$$

So that we now know that the product of the acid and base dissociation constants for the same compound is equal to the K_w.
Since $K_aK_b = 1*10^{-14}$, if the K_a or the K_b is in a reference table in a textbook or online, the other can easily be calculated.

Additionally, we can also use this same method with conjugate acid-base pairs, e.g. HF and F^- and NH_4^+ and NH_3:

$$K_w \overset{?}{=} K_a\{HF\} * K_b\{F^-\}$$

$$K_w \overset{?}{=} \frac{[H_3O^+]*[HF]*[F^-]*[OH^-]}{[HF]*[F^-]}$$

$$K_w \overset{yes}{=} [H_3O^+]*[OH^-]$$

and:

$$K_w \overset{?}{=} K_a\{NH_4^+\} * K_b\{NH_3\}$$

$$K_w \overset{?}{=} \frac{[H_3O^+]*[NH_3]*[NH_4^+]*[OH^-]}{[NH_3]*[NH_4^+]}$$

$$K_w \overset{yes}{=} [H_3O^+]*[OH^-]$$

Why is all of this important? How would you know if a salt solution or any solution from an acid and/or a base will be acidic, alkaline or neutral with both H^+ and A^- present?

Method 1:
Eyeball the pH of Solutions of Acids and Bases

A **strong acid** and a **strong base** mixed together yields a neutral solution, e.g., hydrochloric acid with sodium hydroxide.

A **strong acid** and a **weak base** yields an acidic solution, e.g., hydrochloric acid and ammonia.

A **weak acid** plus a **strong base** yields a basic solution, e.g., acetic acid and sodium hydroxide.

A **weak acid** and a **weak base** mixed together can be complex. **BUT**! If they are equal in strength they will yield a neutral solution, e.g., acetic acid and ammonia.

Method 2:

Arithmetically Determine the pH of Solutions of Acids and Bases

Example #1: Sodium hydrogen sulfite is an ampholyte. Will a solution of this salt be acidic or alkaline?

Solution: First go to the CRC Handbook of Chemistry and Physics and look up the K_a and K_b for the hydrogen sulfite ion -- $6.2*10^{-8}$ and $6*10^{-13}$, respectively.

Second set up the K_a and K_b equilibrium expressions for the ions:

$$HSO_3^- + H_2O \rightarrow H_3O^+ + SO_3^{2-}$$

$$K_a = \frac{[H_3O^+]*[SO_3^{2-}]}{[HSO_3^-]} = 6.2*10^{-8}$$

$$HSO_3^- + H_2O \rightarrow H_2SO_3 + OH^-$$

$$K_b = \frac{[H_2SO_3]*[OH^-]}{[HSO_3^-]} \Leftrightarrow \frac{K_w}{K_a} = 6*10^{-13}$$

Note that the K_a expression has the H_3O^+ in it and the K_b has the OH^- in it.

$K_b < K_a$.

This means that the first reaction (acidic) goes more than the second one (alkaline), therefore, the solution will be acidic.

Example #2: Ammonium oxalate is the salt of a weak acid and a weak base.
Will a solution of this be acidic or alkaline?
First:

$$(NH_4)_2C_2O_4 \rightarrow 2NH_4^{+} + C_2O_4^{2-}$$

$$Salt \rightarrow Acid\ cation + Basic\ anion$$

Second look up the K_a for the ammonium ion and the K_b for the oxalate ion -- $5.7*10^{-10}$ and $1.9*10^{-10}$, respectively.

Third set up the K_a and K_b equilibrium expressions for the ions:

$$NH_4^{+} + H_2O \rightarrow NH_3 + H_3O^{+}$$

$$and$$

$$K_a = \frac{[NH_3][H_3O^{+}]}{NH_4^{+}} = 5.7*10^{-10}$$

$$and$$

$$C_2O_4^{2-} + H_2O \rightarrow HC_2O_4^{-} + OH^{-}$$

$$and$$

$$K_b = \frac{[HC_2O_4^{-}][OH^{-}]}{C_2O_4^{2-}} = 1.9*10^{-10}$$

K_a is barely greater than K_b, therefore, the solution will be ever so slightly acidic.

Example #3: Ammonium formate is a salt of a weak acid and a weak base.
Will a solution of this be acidic or alkaline?
Do as you have throughout the previous 2 examples:

$$NH_4CHO_2 \rightarrow NH_4^+ + CHO_2^-$$

$$Salt \rightarrow Acid\ cation + Basicanion$$

K_a for the ammonium ion and K_b for the formate ion is $5.7*10^{-10}$ and $5.56*10^{-11}$, respectively.

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

$$K_a = \frac{[NH_3]*[H_3O^{\cdot}]}{[NH_4^{\cdot}]} = 5.7*10^{-10}$$

$$CHO_2^- + H_2O \rightarrow HCHO_2 + OH^-$$

$$K_b = \frac{[HCHO_2]*[OH^-]}{[CHO_2^-]} = 5.56*10^{-11}$$

In this case, K_a is greater than K_b, therefore, the solution is slightly acidic.

Are there any other reasons to know this information?

Yes: to determine concentrations of ions in solution, to determine the strength of an acid or base and to determine the pH of a solution.

Determining the pH of A Solution

If a solution of 0.3M HOAc dissociates in water by the following reaction:

$HOAc + H_2O \rightarrow H_3O^+ + OAc^-$,

What is the pH of the solution? K_a for HOAc is $1.8*10^{-5}$

Solution: Always write out the equation, first, in these types of questions as laid out below:

	HOAc	**+**	**H_2O**	**$\rightarrow$**	**H_3O^+**	**+**	**OAc^-**
[Before reaction]	**0.3M**				**0M**		**0M**
[After reaction]	**- x**				**+ x**		**+ x**
Total concentration of species	**0.3 - x**				**x**		**x**

Note that the concentrations change in proportion to the amount (number of mols) of reactants and products, i.e., 1 mol of HOAc begets 1 mol of hydronium ion and 1 mol of acetate ion.

Write the equilibrium expression, substitute and rearrange and solve:

$$K_a = \frac{[H_3O^+]*[OAc^-]}{[HOAc]} = \frac{X*X}{0.3-X} = \frac{X^2}{0.3-X} \approx \frac{X^2}{0.3}$$

$$(K_a)*(0.3) = X^2$$

$$\sqrt{(1.8*10^{-5})*(0.3)} = X = 0.0023\,M$$

$$X = 0.0023\,M = [H_3O^+]$$

$$pH = -\log 0.0023 = 2.64$$

What is the pOH for this aqueous solution?

Since pH + pOH = 14, it follows that 14 - 2.64 = 11.36 is the pOH.

Example #1: What is the pH of a solution that is 0.8M in ammonia? K_b for $NH_3 = 1.8*10^{-5}$.
Solution: Set up as before:

	NH_3	+	H_2O	→	NH_4^+	+	OH^-
[Before reaction]	0.8M				0M		0M
[After reaction]	- x				+ x		+ x
Total concentration of species	0.8 - x				x		x

$$K_b = \frac{[NH_4^+]*[OH^-]}{[NH_3]} = \frac{X*X}{0.8-x} \approx \frac{X^2}{0.8}$$

$$\sqrt{(1.8*10^{-5})*(0.8)} = X = 0.0038\,M$$

$$pOH = -\log 0.0038 = 2.42$$

$$pH = 14 - 2.42 = 11.58$$

Determining the Strength of An Acid or Base

Relative strengths of acids may be eyeballed, as we saw earlier.
A more appropriate manner in which to determine the strength of acids or bases is to utilize equilibria information.
Starting with acids, this information is determined from the standard acid dissociation equation

$HA + H_2O \rightarrow H_3O^+ + A^-$

in a quantitative manner by utilizing the Ka expression:

$$K_a = \frac{[\mathrm{Pr}\,oducts]}{[\mathrm{Re}\,ac\,\tan\,ts]} = \frac{[H_3O^+]*[A^-]}{[HA]}$$

Note that there is no water mentioned -- remember that water concentration does not change appreciably, hence, it's built into the K_a.

Example#1: Determine which is the strongest acid: HF or NH_4^+.

$$HF + H_2O \rightarrow H_3O^+ + F^-$$

$$K_a = \frac{[H_3O^+]*[F^-]}{[HF]} = 6.7*10^{-4}$$

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

$$K_a = \frac{[H_3O^+]*[NH_3]}{[NH_4^+]} = 5.7*10^{-10}$$

By K_a values, HF is a stronger acid than is NH_4^+.
H_3O^+ is always the standard of comparison with acids, i.e., $H^+ > HF > NH4^+$.

Bases may be studied in the same manner, utilizing the following generic equation:

$A^- + H_2O \rightarrow OH^- + HA$

And the K_b may be expressed as follows:

$$K_b = \frac{[\Pr oducts]}{[\operatorname{Re} ac \tan ts]} = \frac{[OH^-]*[HA]}{[A^-]}$$

Water is not shown as it wasn't with the acids, either -- same logic.

Example#2: Which is a stronger base: F^- or NH_3?

$$F^- + H_2O \rightarrow OH^- + HF$$

$$K_b = \frac{[OH^-]*[HF]}{[F^-]} = 1.5*10^{-11}$$

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

$$K_b = \frac{[OH^-]*[NH_4^+]}{[NH_3]} = 1.8*10^{-5}$$

Based upon this data/calculations, NH_3 is a stronger base than is F^-. OH^- is always the standard of comparison with bases, i.e., $OH^- > NH_3 > F^-$.

Henderson-Hasselbach (Hasselbalch) Equation for Calculating the pH of a Weak Acid

- The derivation of this equation is a rather lengthy one and is summarized, below.
- Note that it starts from the very simple mono-protic acid dissociation that we've pretty much beaten to death.
- The salt concentration is equivalent to the anion concentration.
- This equation is very useful in biomedical research when making buffers.

$$HA \Leftrightarrow H^{+} + A^{-}$$

$$K_a = \frac{[H^{+}]*[A^{-}]}{[HA]}$$

Rearranging, sequentially:

$$\frac{[HA]}{[A^{-}]}*K_a = [H^{+}]$$

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

$$-\log\left(\frac{[HA]}{[A^{-}]}\right) - \log K_a = pH$$

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

$$\log\left(\frac{[A^{-}]}{[HA]}\right) + pK_a = pH \Leftrightarrow pKa + \log\left(\frac{[salt]}{[acid]}\right)$$

Example #1: Find the pH of a solution that is 0.05M in carbonic acid and 0.025M in bicarbonate ion.

The K_{a1} for carbonic acid is $4.4*10^{-7}$.

Solution: First get the pK_a

$$pK_a = -\log(4.4*10^{-7}) = 6.357$$

Secondly, set up, manipulate and plug into the equation:

$$pH = pK_a + \log\left(\frac{[salt]}{[acid]}\right) \Leftrightarrow pK_a + \log\left(\frac{HCO_3^-}{H_2CO_3}\right)$$

$$pH = 6.357 + \log\left(\frac{0.025}{0.05}\right) = 6.357 + \log 0.5$$

$$pH = 6.357 - 0.301 = 6.056$$

Example #2: If a solution of carbonic acid was at a pH of 7.35 and was 0.03M in carbonic acid, what molar concentration of bicarbonate ion is present?

Use the same K_{a1} as in Example 1, above.

Solution: Manipulate the equation right off the bat and substitute right into it:

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$pH - pKa = \log\left(\frac{[HCO_3^-]}{H_2CO_3}\right)$$

$$pH - pK_a = \log[HCO_3^-] - \log[H_2CO_3]$$

$$pH - pK_a + \log[H_2CO_3] = \log[HCO_3^-]$$

$$anti\log(pH - pK_a + \log[H_2CO_3]) = [HCO_3^-]$$

$$anti\log(7.35 - 6.357 + (\log 0.03)) = [HCO_3^-]$$

$$anti\log(-0.530) = [HCO_3^-] = 0.295M$$

The Extent of Ionization

The extent of ionization may be determined by the following formula:

$$K = \frac{\alpha^2 C}{1 - \alpha}$$

Where K = K_a OR K_b, C = the molar concentration of the dissociating species and α = the extent of ionization (NOT per cent!)
When less than 10% ionization occurs, i.e., $\alpha = < 0.1$, the equation falls to:

$$K = \alpha^2 C$$

And α is solvable as follows:

$$\alpha = (K/C)^{½}$$

From this, the PER CENT ionization may be determined:

$$\% \text{ ionization} = \alpha\ (100)$$

Example 1

Determine the % ionization of 0.03M propanoic acid. $K_a = 1.3*10^{-5}$

First: write the balanced chemical reaction:

$HC_3H_5O_2 \Leftrightarrow H^+ + C_3H_5O_2^-$

Secondly: write the equilibrium and ionization extent expressions arithmetically:

$$K_a = 1.3*10^{-5} = \frac{[H^+][C_3H_5O_2^-]}{HC_3H_5O_2}$$

and

$$K_a = \frac{\alpha^2 C}{1 - \alpha} \longrightarrow \alpha^2 C = \alpha^2 (0.03)$$

Therefore, the extent of ionization (α) equals:

$$\alpha = \sqrt{\frac{1.3 * 10^{-5}}{0.03}} = 2.1 * 10^{-2}$$

And the percent ionization = $(2.1*10^{-2})(100)$ = 2.1%

Example 2:

Determine the per cent ionization of 1 M HOAc. $K_a = 1.8*10^{-5}$
First: write the balanced chemical reaction:
$HOAc \Leftrightarrow H^+ + OAc^-$
Secondly: write the ionization extent expression arithmetically:

$$K_a = 1.8*10^{-5} = \frac{\alpha^2 C}{1 - \alpha} \xrightarrow{?} \alpha^2 (1)$$

Solve for α :

$$\alpha = \sqrt{(1.8*10^{-5})(1)} = 0.00424$$

And the per cent ionization is 100 times the extent, i.e., (100)(0.00424) or 0.424% and our assumption (indicated by the question mark over the arrow, above) was correct, i.e., less than 10% ionization occurred so we were able to reduce the equation to a simpler form.

Example 3:
Determine the per cent of ionization of 2 M $H_2C_2O_4$ to $HC_2O_4^-$. $K_a = 5.4*10^{-2}$.
First: write the balanced chemical reaction:

$$H_2C_2O_4 \Leftrightarrow HC_2O_4^- + H^+$$

Secondly, write the ionization extent expression, arithmetically:

$$5.4*10^{-2} = K_a = \frac{\alpha^2 C}{1-\alpha} \xrightarrow{?} \alpha^2 C = \alpha^2 (2)$$

Solve for alpha:

$$\alpha = \sqrt{\frac{5.4 - 10^{-2}}{2}} = 0.164$$

And the per cent ionization, then, equals 16.4% -- thus our assumption of < 10% ionization is incorrect and the reduction of the equation to "remove" the denominator was incorrect and, hence, we must expand the equation and solve using the quadratic formula:

Set up in quadratic formula style:

$$K = \frac{\alpha^2 C}{1-\alpha}$$

$$EXPAND:$$

$$K(1-\alpha) = \alpha^2 C$$

$$K - K\alpha = \alpha^2 C$$

$$\text{Set equal to zero}:$$

$$C\alpha^2 + K\alpha - K = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\text{from before}:$$

$$x = \alpha = \frac{-K_a \pm \sqrt{K_a{}^2 + 4CK_a}}{2C}$$

$$x = \alpha = \frac{-(5.4*10^{-2}) \pm \sqrt{(5.4*10^{-2})^2 + 4(2)(5.4*10^{-2})}}{2(2)}$$

Hence,

$$\alpha = \frac{-(5.4 * 10^{-2}) \pm 0.6595}{4}$$

$$\alpha = 0.1514 \ or \ \alpha = -0.1784$$

Since the latter doesn't make sense, the former must be the extent of ionization, hence the extent of ionization is 15.14%.

Determining the Concentrations of Ions in Solution

Our focus, here, will be on the monoprotic acids.
Remember that the monoprotic acid, HA, dissociates as follows:

$HA + H_2O \rightarrow H_3O^+ + A^-$.

If we assume that this is in an acidic solution, i.e., at very low $[OH^-]$, the $[H^+] = [A^-]$.
If this is the case (and it is), then the K_a is as follows:

$$K_a = \frac{[H^+]*[A^-]}{[HA]} \Leftrightarrow \frac{[H^+]^2}{[HA]}$$

Let's let "C" equal the number of moles of HA dissolved in 1 liter of solution.
It follows, then, that

$$C_T = [HA] + [A^-],$$

where C_T is the total concentration, since there is no loss of $[A^-]$. It follows, then, that:

$$[HA] = C_T - [A^-]$$

Since $[A^-]$ equals $[H^+]$, we may re-write the equation as:

$$[HA] = C_T - [H^+]$$

Therefore,

$$K_a = \frac{[H^+]^2}{C_T - [H^+]}$$

After expansion of this we obtain:

$$K_a(C_T) - K_a[H^+] = [H^+]^2$$

Rearrange and set equal to zero:

$$[H^+]^2 + K_a[H^+] - K_a(C_T) = 0$$

IF, IF, IF the percent of ionization is less than 10% of the starting concentration, K_a "falls" to:

$$K_a = \frac{[H^+]^2}{C_T} \quad OR \; [H^+] = \sqrt{K_a C_T}$$

IF, IF, IF the per cent ionization is more than 10% of the starting concentration, the K_a is more difficult to solve:

$$[H^+]^2 + K_a[H^+] - K_a(C_T) = 0$$

$$\mathit{Isof\ the\ form}$$

$$ax^2 + bx + c = 0$$

Where a = 1; x = H^+; b = K_a; c = K_aC_T.

This may be solved with the quadratic formula:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In the "complicated" -- expanded -- equation,
we'll substitute into the quadratic formula as follows:

$$X = [H^+] = \frac{-K_a \pm \sqrt{Ka^2 - 4*(1)*K_a(C_T)}}{2*(1)}$$

The concentrations of bases are solvable in the same manner,
substituting K_b for K_a and $[OH^-]$ for $[H^+]$.

Many Acids are Formed from/with Non-Metals

Hydrogen

- Occurrence: Free hydrogen is present in very small amounts in the atmosphere, in gases of active volcanoes, in natural gas, in the gases present in some coal-mines and trapped in meteorites.
- Combined hydrogen makes up 11% of the weight of water; it is combined with C and O in tissues, a part of petroleum, in starch and cellulose, fats, oils, alcohols and acids and bases.
- The physical properties of hydrogen are that it is a colorless, odorless and tasteless gas.
- It is the lightest known substance, freezes to a transparent solid at -259.14° C and it diffuses faster than any other gas.

Graham’s Law

- Graham's Law says that the rates of diffusion of gases are inversely proportional to the square roots of their densities or their masses:

$$\frac{Rate\ of\ diffusion\ of\ gas\ A}{Rate\ of\ diffusion\ of\ gas\ B} = \frac{\sqrt{\rho_B}}{\sqrt{\rho_A}} = \frac{\sqrt{MW_B}}{\sqrt{MW_A}}$$

Examples

- E.g., Atomic Hydrogen vs Helium

$$\frac{\sqrt{He\ MW}}{\sqrt{H\ \ MW}} = \frac{\sqrt{2}}{\sqrt{1}} = 1.4X\ \ faster\ than\ He$$

E.g.

- E.g., Molecular Hydrogen vs Molecular Chlorine

$$\frac{\sqrt{Cl_2\ MW}}{\sqrt{H_2\ MW}} = \frac{\sqrt{71}}{\sqrt{2}} = 5.96X\ faster\ than\ Chlorine$$

Carbon: CO_2

- CO_2 is fairly soluble in water (more soluble in cold water like in cold soda; less soluble in warm water like in "flat" soda).
- A saturated solution at 1 atm and 25° C is approximately 0.033M. At equilibrium only 0.17% of dissolved CO_2 is in the form of carbonic acid (H_2CO_3).
- An aqueous solution of CO_2 is typically acidic:

$$CO_2(g) + H_2O(l) \rightarrow H^+ + HCO_3^-$$

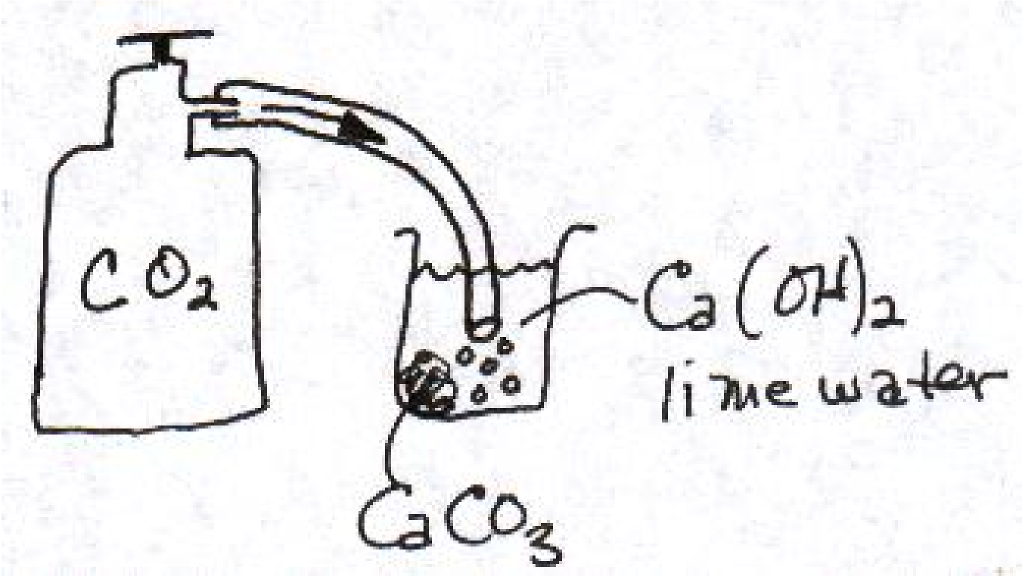
- (Remember the trick with phenolphthalein and blowing into it during titrations in CHEM 121?)

- CO_2 plays a major role in maintaining the pH of blood and sea water:

$$H_2O + CO_2 \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

CO2: for Bases, too

- CO_2 reacts with limewater ($Ca(OH)_2$) to form chalk ($CaCO_3$)



Carbon and Nitrogen: Cyanide

- HCN = hydrogen cyanide or prussic acid. It is a colorless gas or liquid.
- It has the odor of bitter almonds. The average lethal dose is 50-60 mg and is produced as follows:
- $NaCN(aq) + H+ \rightarrow HCN(g) + Na^+$
- The industrial production of HCN occurs by one of two methods and follows:
- $2CH_4(g) + 2NH_3(g) +3O_2(g) + 1100° C + 2\ atm + catalyst \rightarrow 2HCN(g) + 6H_2O(g)$
- OR
- $CH_4(g) + NH_3(g) + 1250° C + catalyst \rightarrow HCN(g) + 3H_2(g)$
- 60% of the US production of HCN is used to synthesize methyl methacrylate which is a monomer of Lucite and Plexiglass.
- 15% of HCN production is for NaCN synthesis.
- Cyanide is also used to extract gold and silver from their ores:
- $8NaCN(aq) + 4Au(s) + 2H_2O(l) +O_2(g) \rightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$
- The $Na[Au(CN)_2]$, above, is a complex salt of gold.
- HCN is used to kill rats and mice in grain bins and ship holds.
- HCN is used in gas chambers in states with the death penalty by gas inhalation.

Nitrogen: Nitric and Nitrous Acids

- The manufacture of nitric acid is a multi-stepped series of reactions:

1. $4NH_3(g) + 5O_2(g) + Pt + 920° C + 7 atm \rightarrow 4NO(g) + 6H_2O(g)$
2. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
3. $3 NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

- The acidic anhydride of nitric acid is N_2O_5:
- N_2O_5 +(s) + H_2O(l) → 2HNO_3(aq)
- The N in both reactant and product is in the +5 state, i.e., no oxidation state change!

- In the lab, nitric acid is produced as follows:
-
- $NaNO_3$(s) + H_2SO_4(l) + distillation + reduced pressure + 0° C → HNO_3(l) + $NaHSO_4$(s)
-
- Pure nitric acid is colorless. Once light reacts with it, it turns yellow due to increased NO_2 formation in solution.
- Nitric acid's number one use is for fertilizers.
- Second highest use is for explosives.
- Other uses include use in the steel industry, in dye manufacture, in plastics and in synthetic fibers.
- Nitric acid reacts with metals that do NOT react with non-oxidizing acids like HCl and phosphoric acid.
- Hot concentrated nitric acid dissolves nearly ALL metals except Au, Pt, Ir and Rh.

- Listed below are representative reactions involving nitric acid:
- **$Cu(s) + 4HNO_3$ (16M) $\rightarrow Cu(NO_3)_2(l) + 2NO_2 + 2H_2O(l)$**

- **$3Cu(s) + 8HNO_3$ (6M) $\rightarrow 3Cu(NO_3)_2(l) + 2NO + 4H_2O(l)$**

- **$C(s) + 4HNO_3$ (16M) $\rightarrow CO_2 + 4NO_2 + 2H_2O(l)$**

- **$3Zn(s) + 8HNO_3$ (6M) $\rightarrow 3Zn(NO_3)_2(aq) + 2NO + 4\ H_2O(l)$**

- **$4Zn(s) + 10\ HNO_3$ (3M) $\rightarrow 4Zn(NO_3)_2(aq) + N_2O + 5H_2O(l)$**

- **$5Zn(s) + 12\ HNO_3$ (1M) $\rightarrow 5Zn(NO_3)_2(aq) + N_2 + 6H_2O(l)$**

- **$4Zn(s) + 10HNO_3$ (0.1M) $\rightarrow 4Zn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$**

("N's" in blue, above, are in the +5 state; in red in the +4 state; in green in the +2 state; in violet in the +1 state; in orange in the -3 state and in brown in the zero (elemental) state.)

In general, the greater the concentration of the acid, the less the oxidation state change. This is easily explained, below:

Concentrated acid has LOTS of nitrate to be reduced, therefore each nitrate is only able to obtain a very few electrons.	Dilute acid has very few nitrates to be reduced, therefore each nitrate is able to obtain a LOT of electrons.

Nitric acid oxidizes compounds as well as elements:

$$3CuS(s) + 8HNO_3\ (3M) + heat \rightarrow 3Cu(NO_3)_2(aq) + 3S(s) + 2NO\uparrow + 4H_2O(l)$$

The xanthoproteic reaction occurs between nitric acid and proteins (look at your skin when you spill nitric acid on it) and turns yellow.

Nitrous Acid

- HNO_2 is a weak acid. It can not be isolated as it's a multi-stepped reaction or when it's warm.
- $3HNO_2$ (aq) → HNO_3(aq) + 2NO + H_2O(l)
- Nitrous acid is prepared as and when needed:
- HCl(aq) + $NaNO_2$(aq) + 0° C → HNO_2(aq) + NaCl(aq)
- It must be used immediately.

Nitrogen: Ammonia is a Base

- Ammonia is the hydride of nitrogen. It is easily synthesized in the lab as follows:
- $NH_4Cl(s) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$
- NH_3 is colorless, has a characteristic odor and is extremely soluble in water -- approximately 90 g of NH_3 dissolves per 100 mL of water at room temperature and 1 atm.
- Ammonium carbonate is smelling salts.
- Ammonium nitrate is used as a fertilizer.
- Under decomposition, though, ammonium nitrate reacts as follows:
- $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2$
- The products occur during the explosive decomposition. 1 mol of solid ammonium nitrate will produce 3.5 mol of gas.
- This is characteristic of explosive reactions, i.e., a small amount of solid produces a large amount of gas.

Phosphorus

- P is more metallic than nitrogen.
- The electronegativity (EN) of P is 2.1; that of N is 3.0.
- Phosphorus is active at low temperatures.
- White phosphorus is unstable; red P is stable.
- PH_3 (hydride of phosphorus called phosphine) is a stronger reducing agent than ammonia.
- Bones, teeth, muscle, nerves contain phosphorus.
- The primary commercial source of phosphorus is phosphate rock, which contains lots of calcium phosphate with other phosphates, as well.

- The most important inorganic compound of P is phosphoric acid (H_3PO_4). It is synthesized as follows in the 2 reactions below:
-
- $P_4(l) + 5O_2(g) + \text{heat} \rightarrow P_4O_{10}(s)$
-
- $P_4O_{10}(s) + 6H_2O(g) \rightarrow 4H_3PO_4$
-
- P_4O_{10} is called phosphorous pentoxide after its EMPIRICAL formula: P_2O_5; it is the P_2O_5 which is the acid anhydride of phosphoric acid.
- 0.05% phosphoric acid is added to Coca Cola (Coke) to make it taste tart at a pH of about 2.3.

- Phosphoric acid auto-ionizes:
-
- $2H_3PO_4(l) \Leftrightarrow H_4PO_4^+ + H_2PO_4^-$
-
- This, then, is an electrolyte.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{=} + H^+$$

$$HPO_4^{=} \rightleftharpoons PO_4^{\equiv} + H^+$$

$$K_1 = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} \qquad K_2 = \frac{[HPO_4^{=}][H^+]}{[H_2PO_4^-]}$$

$$K_3 = \frac{[PO_4^{\equiv}][H^+]}{[HPO_4^{=}]}$$

$$K_{overall} = K_1 \cdot K_2 \cdot K_3$$

$$K_{overall} = \frac{\cancel{[H_2PO_4^-]}[H^+]\cancel{[HPO_4^{=}]}[H^+][PO_4^{\equiv}][H^+]}{[H_3PO_4]\cancel{[H_2PO_4^-]}\cancel{[HPO_4^{=}]}}$$

$$= \frac{[H^+]^3[PO_4^{\equiv}]}{[H_3PO_4]} = K_{overall}$$

Salt Formation

First dissociation
H_3PO_4 (XS; aq) + Na_2CO_3(aq) $\rightarrow$ $2NaH_2PO_4$(aq) + $CO_2\uparrow$ + H_2O(l)

NaH_2PO_4 is water soluble. It is used to adjust the pH of water for boilers and in laxative tablets that fizz (with $NaHCO_3$):

NaH_2PO_4 (aq) + $NaHCO_3$(aq) $\rightarrow$ $CO_2\uparrow$ + Na_2HPO_4(aq) + H_2O(l)

Salt Formation

Second dissociation
$H_3PO_4(aq) + Na_2CO_3(XS; aq) \rightarrow Na_2HPO_4(aq) + CO_2\uparrow + H_2O(l)$

Na_2HPO_4 is used in pudding mixes and quick-cooking cereals. It is basic.

Salt Formation

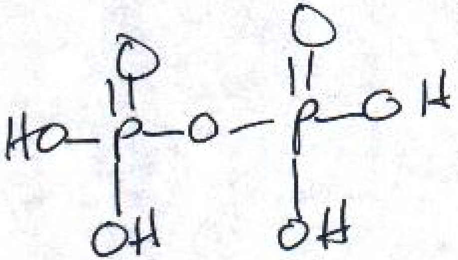
Third dissociation
H_3PO_4(aq) + 3NaOH(XS; aq) → Na_3PO_4(aq) + $3H_2O$(l)
NaOH is used here as Na_2CO_3 is not strong enough to strip off the 3d proton

Na_3PO_4 is very basic. Used in scouring powders and paint removers.

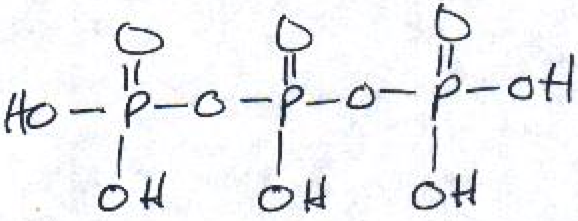
Useful Calcium salts		
$Ca(H_2PO_4)_2 \bullet H_2O$ -- used in baking powders	$CaHPO_4 \bullet 2H_2O$ – in toothpaste	$Ca_2P_2O_7$ (calcium diphosphate) is insoluble, inert, abrasive -- used in toothpaste with SnF_2 (Stannous fluoride)

- Disodium hydrogen phosphate reacts with sodium dihydrogen phosphate as follows to form sodium triphosphate, aka sodium tripolyphosphate:
-
- $2Na_2HPO_4(s) + NaH_2PO_4(s) + 450° C \rightarrow Na_5P_3O_{10}(s) + 2H_2O(g)$
-
- Sodium tripolyphosphate used to be used as the "builder" for synthetic detergents.
- Hard water, remember, contains calcium and magnesium divalent cations.
- These cations form complexes with triphosphate.
- High levels of these complexes, when dumped into bodies of water, cause eutrophication. This is brought about due to the high levels of phosphorous. These high levels increase algal growth.
- As the algae multiply and grow, they begin to decay and take up large amounts of oxygen from the water. This loss of oxygen kills the fish in the water.
- Laws were enacted prohibiting the use of tripolyphosphate as detergent builders, so industry used sodium carbonate as the builder.
- Calcium and magnesium carbonates are formed which softens the water and cleans the clothes.

There are two other acids of phosphorus: Diphosphoric (or pyrophosphoric) acid and triphosphoric acid.



Diphosphoric Acid



Triphosphoric Acid

Sulfur

Acids Contain Sulfur, Too

Sulfuric Acid

- $4FeS_2(s) + 11\ O_2(g) + \text{roasting} \rightarrow 8SO_2 + 2Fe_2O_3$
-
- The gaseous SO_2 produced is used for the production of sulfuric acid. This is a three step process:
-
- $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
-
- $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l) \leftarrow$ Disulfuric acid
-
- $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$

- Sulfuric acid is the cheapest strong acid manufactured.
- Sulfuric acid is a diprotic acid.
- The dissociation of the first proton is 100% complete in dilute solution and is, probably, between a pK_a of 0 and 1.
- The dissociation of the second proton has a K_a of $1.2*10^{-2}$, i.e., a pKa of about 1.92.
- This is very acidic.
- On a biological note, the chemistry just ain't there to support making sulfuric acid in any part of the human body as the pH in the body just doesn't get low enough to defeat the first K_a.
- Sulfuric acid will react with metals like elemental copper to form copper (II) sulfate, water and sulfur dioxide gas when heated.

Three sulfates are in the "Top 50" chemicals sold in the US and are tabulated, below:

$Al_2O_3 \bullet 2H_2O(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 5H_2O(l)$	$2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl\uparrow$	$H_2SO_4(aq) + 2NH_3(g) \rightarrow (NH_4)_2SO_4(aq)$
The first reactant on the left is bauxite; the first product is used as a water clarifier and to fill pores in paper.	The first product is used in the manufacture of brown paper bags and brown wrapping paper.	The product of this reaction is used as fertilizer.

- An important oxo-acid of sulfur is thiosulfuric acid, $H_2S_2O_3$. It is important in the production of a salt, $Na_2S_2O_3$, sodium thiosulfate. The significance of this salt is as illustrated in the reaction, below:

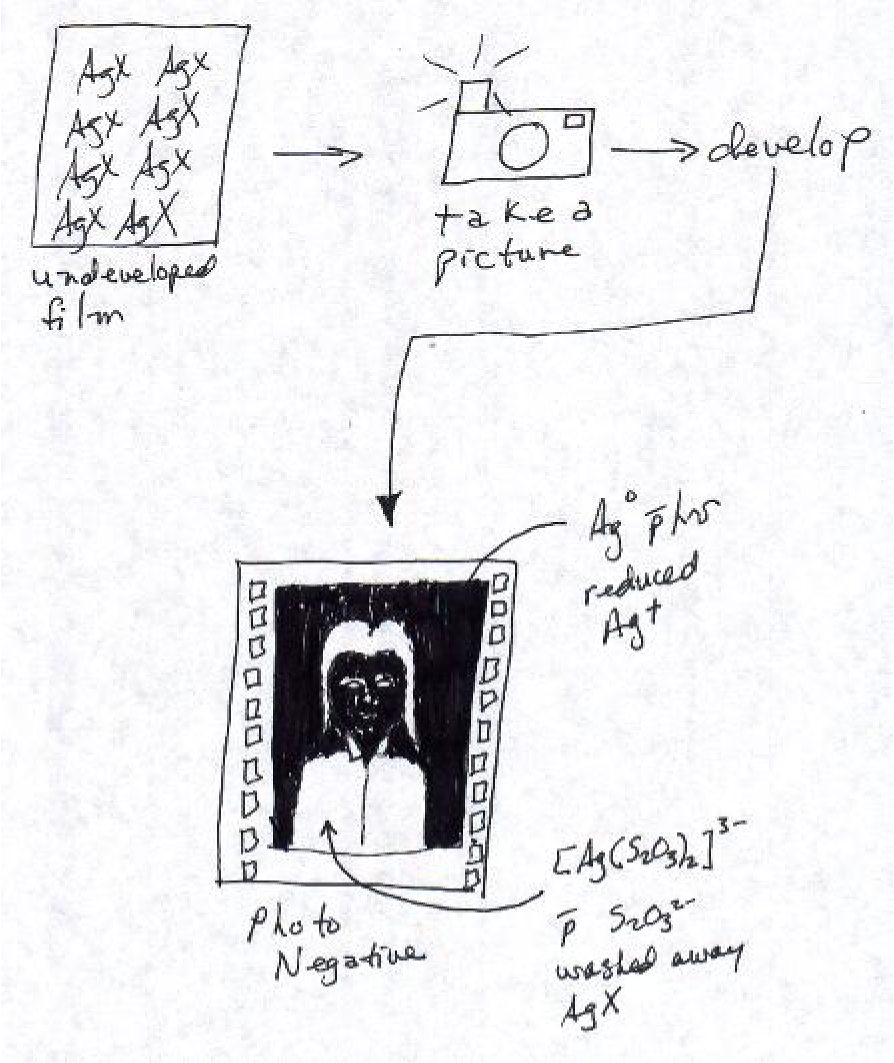
- $AgX(s) + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + X^-$, where "X" = a halogen

- This is important in photography. Undeveloped film is impregnated with AgX.
- Take the picture and send it in for developing and that's it, right? Nope! AgX dissociates to Ag^+ and X^-.
- When regions of the film that have ionized Ag on it are "hit" by light, the Ag^+ is reduced to Ag0. The regions of the film with Ag0 on it are the dark parts of the negative; conversely, the Ag^+ that is not reduced reacts with the $S_2O_3^{2-}$ to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- When the complex ion is washed away, it makes the clear area of the negative. The other name for the $S_2O_3^{2-}$ is "hypo".

Sulfur: Last Acid

- In qualitative analysis, H_2S is generated from a compound called thioacetamide (TA), the thioamide of acetic acid (C_2H_5NS).
- When TA is hydrolyzed with the addition of water and heated, the only stable "hydride" of sulfur is formed: H_2S.
- This smells like rotten eggs and is about 200 times as poisonous as cyanide.
- It is so much more poisonous because it anesthetizes the sense of smell (cranial nerve I), so people keep breathing it in and they die -- no, enough H_2S is not generated in lab, here, to cause death.
- Lots more on this compound later in the course.

Photographic Use of Sulfur



Many Acids are Formed from Halides

Occurrences of the Halogens

- Fluorine (F) is present in fluorite or fluospar (CaF_2), fluorapatite ($Ca_{10}F_2(PO_4)_6$), cryolite (Na_3AlF_6), sea water, teeth, bones and blood.
- Chlorine (Cl) is present in sea water (2.8% NaCl), the Great Salt Lake (23% NaCl, Salt beds (NaCl, $MgCl_2$, $CaCl_2$) and gastric juice (0.2-0.4% HCl).
- Bromine (Br) is found in sea water (NaBr, KBr, $MgBr_2$ and $CaBr_2$), in underground brines and salt deposits.
- Iodine (I) is found in sea water (very small amounts) and in Chilean nitrate deposits as $NaIO_3$. It is also found in oil well brines in California and in the thyroid gland in the human body.

Properties of the Halogens

Halogen →	**F**	**Cl**	**Br**	**I**	**At (?)**
Atomic number	9	17	35	53	85
Atomic mass	19	35.5	79.9	126.9	(210)
Ionic radius (Å)	1.36	1.81	1.95	2.16	?
Physical state	gas	gas	liquid	solid	solid
Color	Pale yellow	Greenish yellow	Reddish brown	Black/steel blue (s); violet to fuschia (g)	?
Electronegativity	4.1	2.8	2.7	2.2	2.1
Density	lowest	low	middle	highest	????

- Remember that all halogens prefer to "run around" as pairs, i.e., F_2, Cl_2, Br_2 and I_2.

- In terms of relative bond strengths, the strongest inter-halogen bond is the Cl-Cl bond. The weakest inter-halogen bonds are the I-I and F-F bonds. The Br-Br bond fits in between the lowest and the highest.

- When compared to the X-X bond, the H-F bond is 3.6 times stronger than the corresponding F-F bond. The rest of the hydrohalic acid bonds are each double that of the strength of the molecular halogen-halogen bonds, i.e., H-I, H-Br, H-Cl.

- When compared to the X-X bond, the C-X bonds are stronger. Only the C-F bond remains 3.6 times stronger than the F-F bond. The remaining C-X bonds, C-I, C-Br and C-Cl bonds, are each only 1.4 times stronger than the corresponding X-X bonds.

- An analogy to help remember this is the idea that a strong acid gives a weak conjugate base, i.e., the molecular halogens act are the "weak base" and the hydrohalic acids and carbon halides are the "strong conjugate base", so to speak.

Uses of Halogens

- 70% of Cl_2 is used in making PVC (polyvinyl chloride), 20% to bleach paper and textiles and to disinfect water.
- Most of the bromine is used for pesticides and flame retardants.
- Iodine compounds include radio-opaque media and antiseptics (betadine) and disinfectants.
- 70% to 80% of fluorine is used to make UF_6 to enrich uranium for nuclear power plants.

Hydrogen Halides

- $CaF_2(s) + H_2SO_4(l)$ + 200-250° $\rightarrow CaSO_4\downarrow + 2HF$
- About $8*10^8$ pounds of HF are used each year to make freons:
- $CCl_4(g) + HF(g) + SbCl_5(l)$ + 65-95° C $\rightarrow CCl_3F(g) + HCl(g)$
- $CCl_4(g) + 2HF(g) + SbCl_5(l)$ + 65-95° C $\rightarrow CCl_2F_2(g) + 2HCl(g)$
- Freons are used in air conditioners and refrigerators, but they are destructive to the ozone layer (15-30 km layer above the earth).

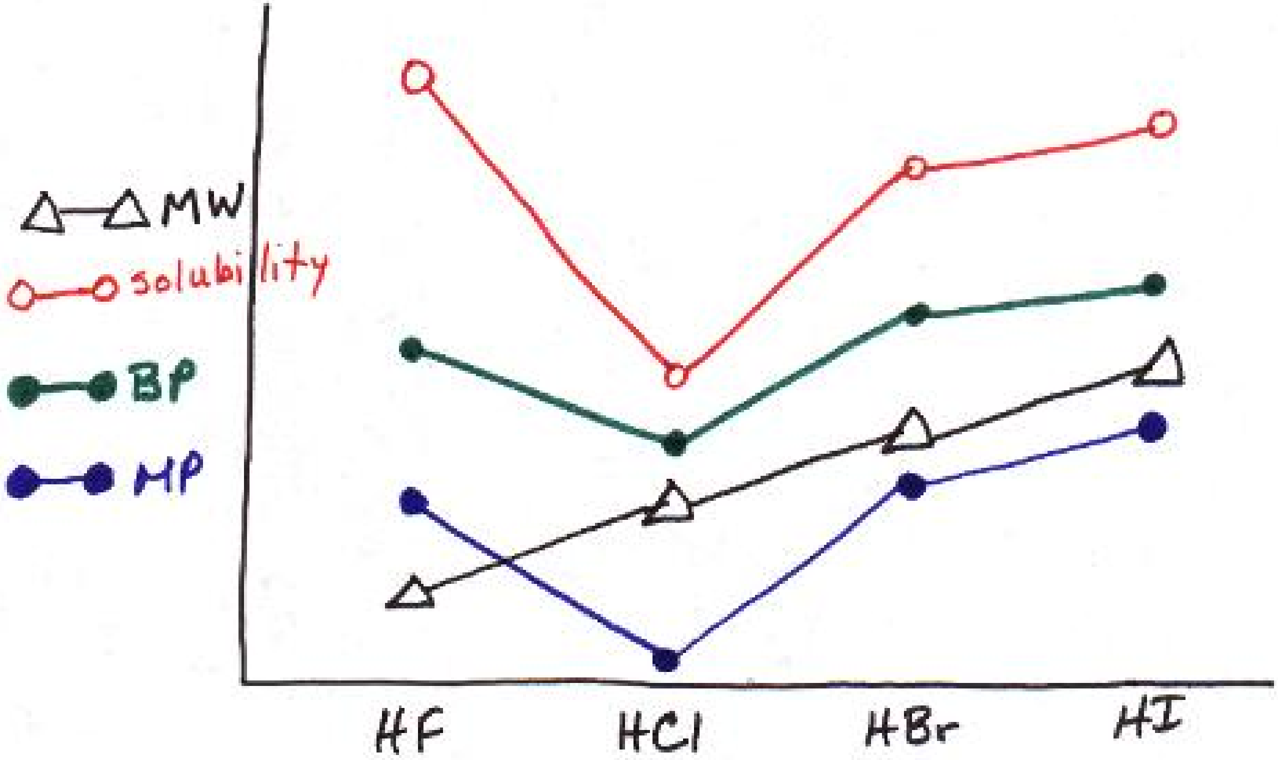
- Another $8*10^8$ pounds of HF are used per year to produce aluminum:
- $6HF(g) + Al(OH)_3(s) + 3NaOH(aq) \rightarrow Na_3AlF_6$ (synthetic cryolite) $+ 6H_2O(l)$
- Bauxite, the ore that contains aluminum (Al_2O_3) is the subjected to electrolysis in the cryolite solvent to form elemental aluminum.
- HF is used for glass etching and frosting bulbs. The reaction for this is:
- $SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 2H_2O(l)$
- and
- $CaSiO_3(s) + 8HF(aq) \rightarrow H_2SiF_6(aq) + CaF_2(s) + 3H_2O(l)$

- HCl is produced in one of three ways and follows:
- $CH_4(g) + Cl_2(g)$ + 440 ° C → $CH_3Cl + HCl$
- $H_2(g) + Cl_2(g) + h\nu \rightarrow 2HCl(g) \leftarrow$ EXPLOSIVE REACTION!
- $2NaCl(s) + H_2SO_4(l)$ + heat → $2HCl + Na_2SO_4\downarrow$
- The primary use of HCl is to remove oxide scale from rusted steel or metals.
- Bromides and iodides are formed in the same manners, the ONLY difference is that the reactions with these 2 halogens require H_3PO_4 instead of H_2SO_4.

Properties of Hydrogen Halides

Hydrogen halide→	**HF**	**HCl**	**HBr**	**HI**
MW	**20**	**36.5**	**80.9**	**127.9**
Solubility in g/100 mL water	**∞ @ 0 ° C**	**82.3 @ 0 ° C**	**221 @ 0 ° C**	**234 @ 10 ° C**
BP (° C)	**120**	**110**	**126**	**127**
MP (° C)	**-83.1**	**-114.2**	**-86.8**	**-50.8**

Properties of Hydrogen Halides



The Halogens Form Oxo-Acids

Hypohalous acids	**HOCl**	**HOF**	**HOBr**	**HOI**
halous acids	**$HClO_2$**	**------**	**$HBrO_2$**	**HIO_2**
halic acids	**$HClO_3$**	**------**	**$HBrO_3$**	**HIO_3**
perhalic acids	**$HClO_4$**	**------**	**$HBrO_4$**	**HIO_4**

$HClO_4$ is explosive by shock alone in the pure state.

- In terms of acid strengths, the acids with the halogen in the lowest oxidation state are the weakest while those that have the halogen in the highest oxidation state are the strongest oxo-acids:

Weakest			Strongest
$HClO$	$HClO_2$	$HClO_3$	$HClO_4$
Hypochlorous acid	**Chlorous**	**Chloric**	**Perchloric**
+1 Oxidation state	**+3 Oxidation state**	**+5 Oxidation state**	**+7 Oxidation state**

Semi-Metals: Metalloids

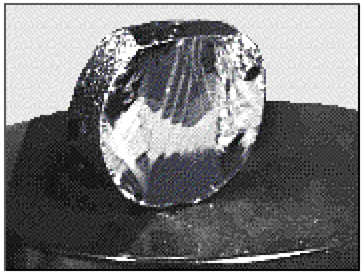
Some Form Acids, Too

- The number of metalloids depends on the author:
  - some say there are 5 elements (Si, Ge, B, Te and Sb) and
  - some say there are 7 (the 5 plus Se and As).
- They are all primarily non-reactive and their electronegativities are slightly less than that of hydrogen.

Silicones

- Used daily as sealants around the house
- Silicones mixed with rubbers form a more durable rubber-compound

Silicon -- Si



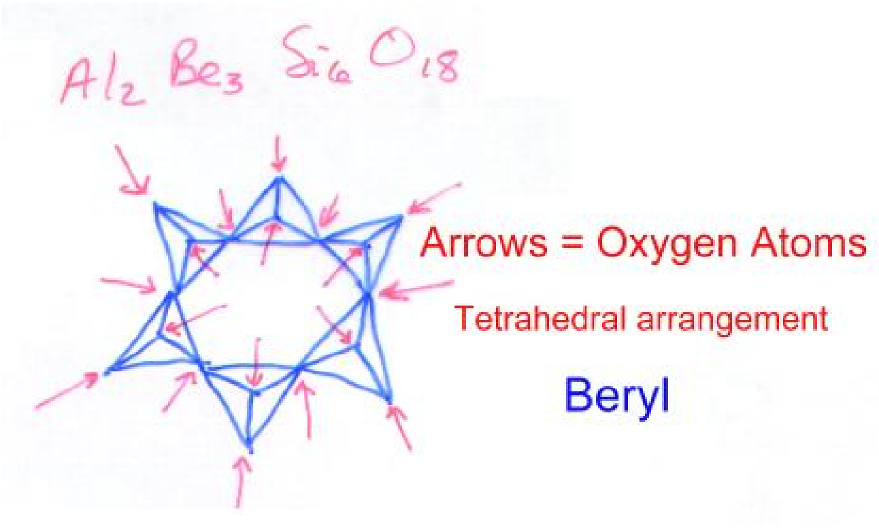
- Silicon is a shiny, blue-grey, high melting, brittle metalloid.
- Pure silicon crystallizes like diamond, but Si is less closely packed.
- Si is the 2d most abundant element on the earth.
- Oxygen combinations with Si make up three-quarters of the earth's crust.
- Si is not found naturally in the elemental form.
- It is found in various combinations with oxygen to provide silicas like sand, quartz, minerals and glasses. Si--O bonds are the key features of silicon chemistry.
- Si--O bonds are stronger than Si--Si bonds.
- SiO_2 is NOT water-soluble.
- The use of silicon forms found in nature for tools, glasses, weapons and gems was known before man kept records of history.

All 4 halides of Si exist:

SiF_4	SiI_4	$SiCl_4$	$SiBr_4$
Gas	Solid	Volatile liquids	Volatile liquids

Silica

- The most appropriate form/representation of silica is $(SiO_2)_n$ as silica is a polymer of SiO_4 (SiO_2 is found in nature as common minerals: quartz and flint).
- The other two oxygens are shared, e.g., beryl ($Al_2Be_3Si_6O_{18}$).
- Note that the SiO_4 portions are tetrahedral through the shared oxygen atoms.
- This chemical is ubiquitous and is of geological, commercial and chemical importance.
- Silica is used in huge amounts in ceramics, concretes, glasses and building materials.
- In addition, when in the amorphic form, silica is used as a reinforcing agent, detergent builder, supportive catalytic component, desiccant and absorbent.
- Fumed silicas (generated by burning silanes -- silanes are molecules with the SiH_4 formula and their derivatives) are utilized as agents of reinforcement in numerous elastomeric and rubber silicone products.



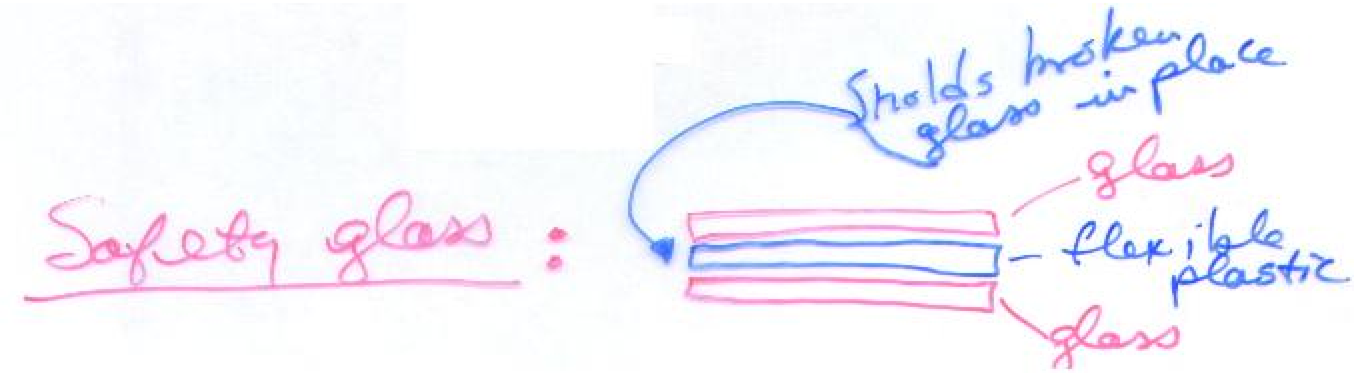
Natural Silicates

- Clays are silicates and aluminosilicates the result from the weathering of granite and other rocks.
- These are used in cement, ceramics, bricks and flower pots.
- When clays are mixed with feldspar $(KAlSi_3O_8)_n$, earthenware, porcelain and china are obtained.

Glass

- Na_2SiO_3 and $CaSiO_3$ are used in drinking glasses, bottles and window panes.
- In general, if 70-74% pure SiO_2 (sand), 13-16% Na_2CO_3 (soda) and 10-13% CaO (lime) are mixed together and heated, glass is formed.
- Pyrex and Kimax are speciality glasses where some of the Na and Ca are replaced by boron.
  - When this glass is formed, it is the glass that is used to make pots, casseroles and saucepans that may go "from the freezer to the oven".
  - These are made, generally, by mixing 13-28% B_2O_3 with 72-87% silica and heating the mixture.
- Flint glass contains potassium and lead glass contains lead.
  - Both are used as decorative glassware and for prisms and lenses.

- Tempered glass is prepared by heating glass to just below its softening point and suddenly cooling it with jets of cold gas. Tempered glass has no jagged/sharp edges when broken.
- Safety glass is prepared by sandwiching a piece of flexible plastic between two layers of glass. The plastic holds the broken glass in place.

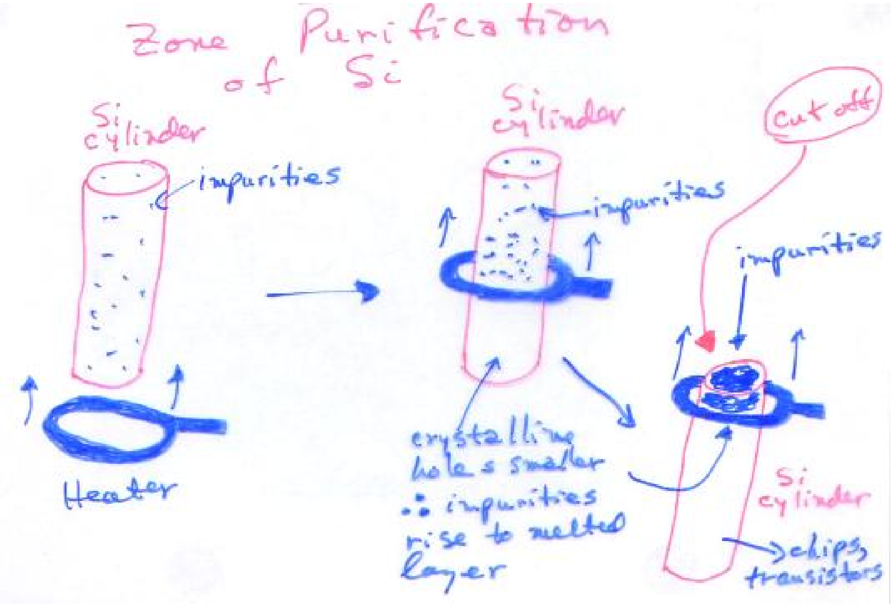


Substances That are Used to Color Glass

Substance	Color Imparted
CaF	Milky white
Cu_2O	Red/green/blue
CoO	Blue
U compounds	Yellow, green -- not in use much, any more
MnO_2	Violet
Colloidal Se	Red

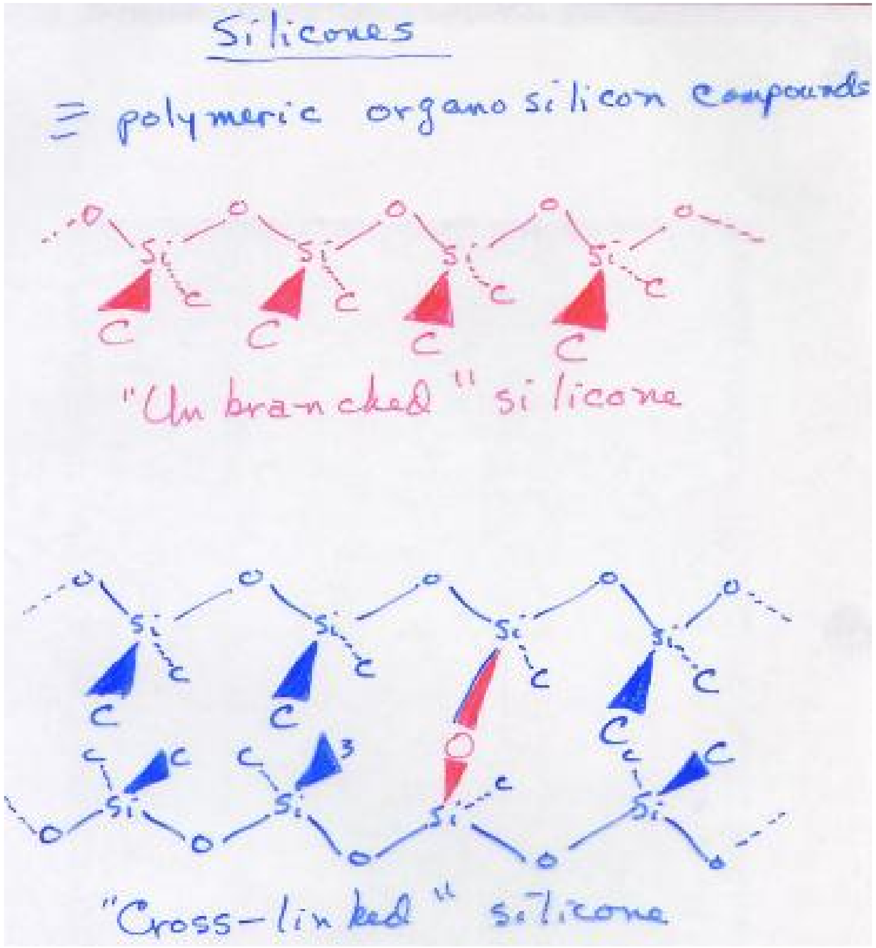
Purification

- Silicon is purified by using a Zone Purification method.
- This method is just like sucking the color out of a popsicle, only using heat.
- A ringed heater is lifted up the sides of an Si cylinder.
- As the Si heats up, the crystalline holes get smaller, forcing the impurities up into the cooler layer above the warm layer.
- When the impurities have reached the top of the cylinder, they are cut off and the pure Si sent wherever it's needed.
- The pure Si cylinder will be used to make chips and transistors, for example.
- NOTE: current purification methods involve more chemistry and reactions than the method described, here – this method is more exciting and visual, though ☺

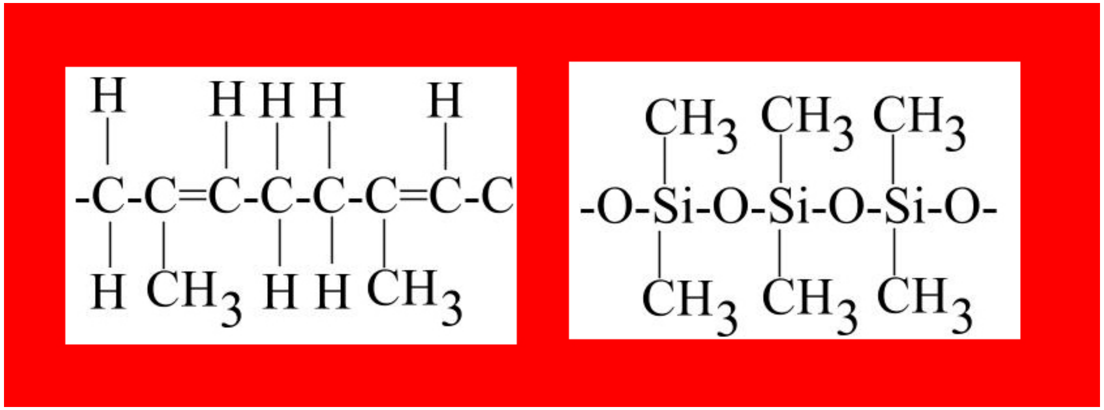


Silicones

- Silicones are polymeric organosilicon compounds. The top cartoon illustrates "unbranched silicone".
- Note that instead of 4 oxygen atoms to make the tetrahedron, there are two atoms of oxygen and two methyl (CH_3) groups. Each silicone has a repeating Si-O backbone.
- The bottom cartoon illustrates "cross-linked silicone".
- Note that there is a periodic replacement of two methyl groups (one on each of two Si atoms) with oxygen that is single bonded between two chains of "unbranched silicone" molecules.
- The repeating ($SiO(CH_3)_2$) unit is the monomer of the most common silicone isomer, poly-dimethylsiloxane (PDMS).



- There are six classes of silicone products: fluids, lubricants, elastomers (rubbers), resins, emulsions, compounds and fluids.
- Each of these classes depends upon the number of the monomeric units and the degree to which the chains are crosslinked.
- Figure,below, illustrates the similarities between natural rubber and PDMS (poly-dimethylsiloxane).



- Silicone rubber is extremely resistant to oxidation and ozone degradation (ozonolysis), unlike natural rubber.
- Natural rubber contains unsaturated double bonds which makes this material more susceptible to oxidation and ozonolysis.

- Silicones are used in rubber, lubricants, "Silly Putty", "superballs", caulking materials, waterproof films and refrigerator gaskets.
- Silicone elastomers are also used in hydrocephalic shunts, pacemaker lead coverings, catheters, pump diaphragms and replacement finger joints.
- Medical problems have been implicated with breast implants made of silicone.
- While the jury has spoken, literally, the science seems to, perhaps, be lacking.
- A more objective, prospective set of studies may be needed to really understand what goes on once silicone implants are put inside a human being.

Boron

- Boron is very rare. It is localized in dry lake beds in the southwest US as borax ($Na_2B_4O_5(OH)_4 \cdot 8H_2O$) and kernite ($Na_2B_4O_5(OH)_4 \cdot 2H_2O$). Borax is a cleansing agent, it is a mild alkali and a flux for soldering and welding. Borax reacts with 2 moles of sulfuric acid to form sodium sulfate, 5 moles of water and 4 moles of Boric acid (H_3BO_3; an old antiseptic).
- Forms of boron are very hard. They are used as semi-conductors (i.e., no electricity conducted at low temperatures, but a tiny increased temperature leads to conduction). B is found in a dark-brown, amorphous, form and purified from there:
- $B_2O_3(s) + 3Mg(s) + \text{heat} \rightarrow 3MgO(s) + 2B(s)$

- Boron hydrides are called boranes.
- There are two series of boranes and each has special nomenclature:

Stable Boranes		**Unstable Boranes**	
B_nH_{n+4}		B_nH_{n+6}	
B_2H_6	**Diborane**	B_4H_{10}	**Tetraborane (10)**
B_4H_8	**Tetraborane (8)**	B_5H_{11}	**Pentaborane (11)**
B_5H_9	**Pentaborane (9)**	B_6H_{12}	**Hexaborane (12)**
B_8H_{12}	**Octaborane (12)**	$B_{10}H_{16}$	**Decaborane (16)**
Note that the name, e.g., Tetraborane, indicates the number of B atoms (4); the number at the end, e.g., (8) tells you how many hydrogens there are per molecule (8 in this case).			

- Diborane is formed as follows:

- $4BCl_3(g) + 3LiAlH_4(s)$ in diethyl ether $\rightarrow$ $2B_2H_6 + 3LiCl(s) + 3AlCl_3(s)$

- Boron derivatives, e.g., $NaBH_4$ (sodium borohydride) are used as powerful reducing agents.

Arsenic

- Most arsenic is in the form of yellow As_2S_3. While a 100-mg dose of As is fatal, MINUTE traces of As actually increase red blood cell production.
- Yellow As_4 is tetrahedral and reminiscent of P_4.
- The hydride of significance is arsine (AsH_3 -- similar to NH_3 and PH_3) -- it is less stable than PH_3.

The tri- and pentahalides of As exist:

Trihalides	Pentahalides
$AsCl_3$	$AsCl_5$
AsF_3	AsF_5
$AsBr_3$	$AsBr_5$
AsI_3	AsI_5

- Arsenic oxyacids exist, as well.
- They are weaker than the corresponding phosphorous containing acids.
- The acid anhydride of arsenic acid (H_3AsO_4) is As_2O_5.
- The acid anhydride of arsenous acid (H_3AsO_3) is As_4O_6.

Selenium

- Se is a red-grey to black solid.
- It exists in a metallic form as Se_8.
- This form is photosensitive and is, therefore, used in photocopiers and solar cells.
- H_2Se smells worse than H_2S and is more poisonous.
- The dichloride, di-bromide, tetra-fluoride, tetra-chloride, tetra-bromide and hexa-fluoride forms exist.
- Selenous acid (H_2SeO_3) comes from its acid anhydride, SeO_2, reacting with water.
- The acid anhydride of selenic acid (H_2SeO_4) is SeO_2 when it reacts with 30% hydrogen peroxide.
- Selenic acid is about as strong as sulfuric acid.

Tellurium

- Te is a brass-colored solid with metallic luster.
- When mixed with Pb, it's used as a semiconductor.
- The mix has high resistance and improves wear of the material due to reduced heat problems.
- Te colors glass red, blue or brown.
- H_2Te smells worse than H_2S and is more poisonous.
- H_2Te is a stronger acid than H_2Se.

Unlike with Se, multiple forms of the Te halides exist:

TeI	Te_2Br	Te_3Cl_2
$TeCl_2$	Te_2F_{10}	
$TeCl_4$		
$TeBr_2$		
$TeBr_4$		
TeF_4		
TeF_6		
TeI_4		

The acid anhydride of tellurous acid is TeO_2;
that of telluric acid is TeO_2 reacting with 30% hydrogen peroxide.

Antimony

- Sb is found primarily in stibnite (Sb_2S_3) in South and Latin America.
- It is white-silvery, brittle and tarnishes slightly in dry air.
- Sb is readily attacked by halogens, P and S.
- Pb + 10-20% Sb is used to make bearings, shrapnel and bullets.
- Due to its resistance to corrosion by acids, it is used to make storage battery plates.
- The tri and pentahalides exist.

Germanium

- Ge is a gray-white metal.
- It is non-reactive with HCl or NaOH, but dissolves in concentrated HNO_3.
- The tetrachloride is known to exist.
- The properties of Ge are very similar to those of Si.

Acid-Base Titrations

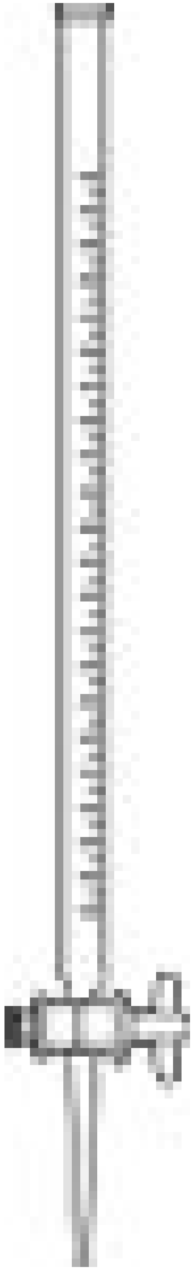
- Knowing now what we know about acids, how may we apply this information to the lab?
- By studying acid/base titrations.
- Acids and hydroxide bases react to form water and a salt.
- This sort of reaction is called a neutralization reaction.
- Bases that contain bicarbonate or carbonate in them also produce carbon dioxide in addition to the water and the salt.
- Examples of these sorts of [neutralization] reactions are summarized, below, in the table:

$HCl + NaOH \rightarrow NaCl + H_2O$
$H_2SO_4 + 2\ KOH \rightarrow K_2SO_4 + 2H_2O$
$2HNO_3 + Ba(OH)_2 \rightarrow Ba(NO_3)_2 + 2H_2O$
$H_3PO_4 + Al(OH)_3 \rightarrow AlPO_4 + 3H_2O$
$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2\uparrow + H_2O$
$6HNO_3 + Al_2(CO_3)_3 \rightarrow 2Al(NO_3)_3 + 3CO_2\uparrow + 3\ H_2O$
$H_2SO_4 + MgCO_3 \rightarrow MgSO_4 + CO_2\uparrow + H_2O$

Titration ≡ An analytical/ quantitative technique where one solution of known concentration (aka standard solution) is slowly added to a known volume but unknown concentration of another solution.

Generally, this involves the addition of an unknown amount of base to a known amount of acid.

The volume of the base is measured in a buret:



Indicator ≡ An organic dye which changes color depending on the pH of the solution, e.g.:

Phenolphthalein: colorless @ pH 8.2   red @ pH 10
Bromothymol blue: yellow @ pH 6.0   blue @ pH 7.6
Methyl red: red @ pH 4.2   yellow @ pH 6.2
Bromocresol purple: yellow @ pH 5.2   purple @ pH 6.8
Congo red: blue @ pH 3.0   red @ pH 5.2

The pH at which the color of the indicator changes ≡ the titration endpoint.

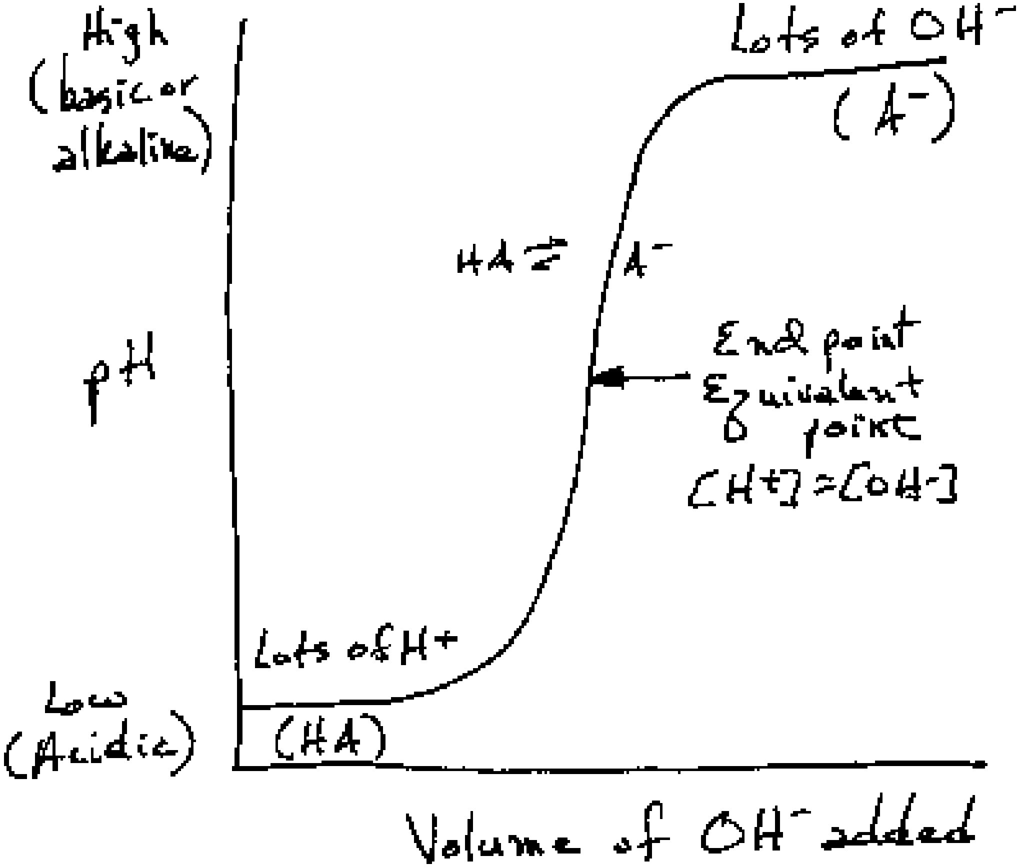
Indicators are chosen to change color within ± 1 pH unit as close as possible to the equivalence point (the significance of this will be brought out a bit later).

We will discuss at a later time the effects of reacting strong acids/bases, weak acids/bases and other combinations of acids/bases on pH.

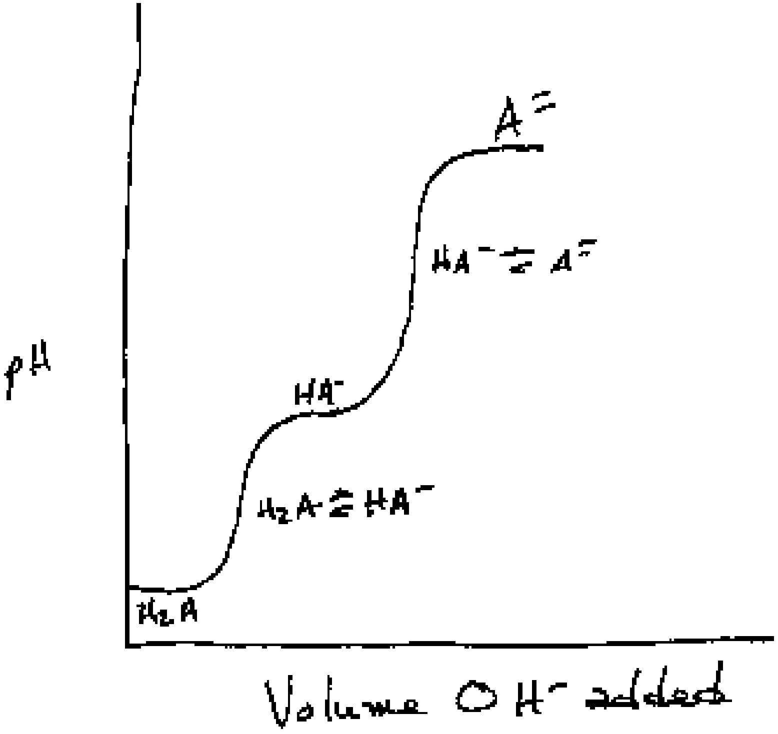
If conditions are such that an indicator won't work, e.g., doesn't change close enough to the equivalent point, the analyte is highly colored and interferes with indicator color change, a pH meter can be used to follow the titration.

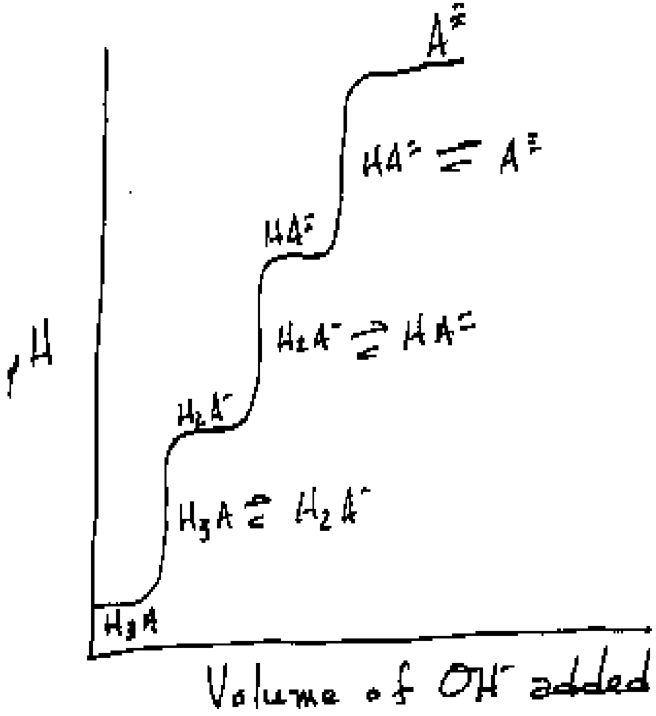
In General:

Titrations of acids and bases follow a general sigmoid-shaped curve for a mono-protic acid:

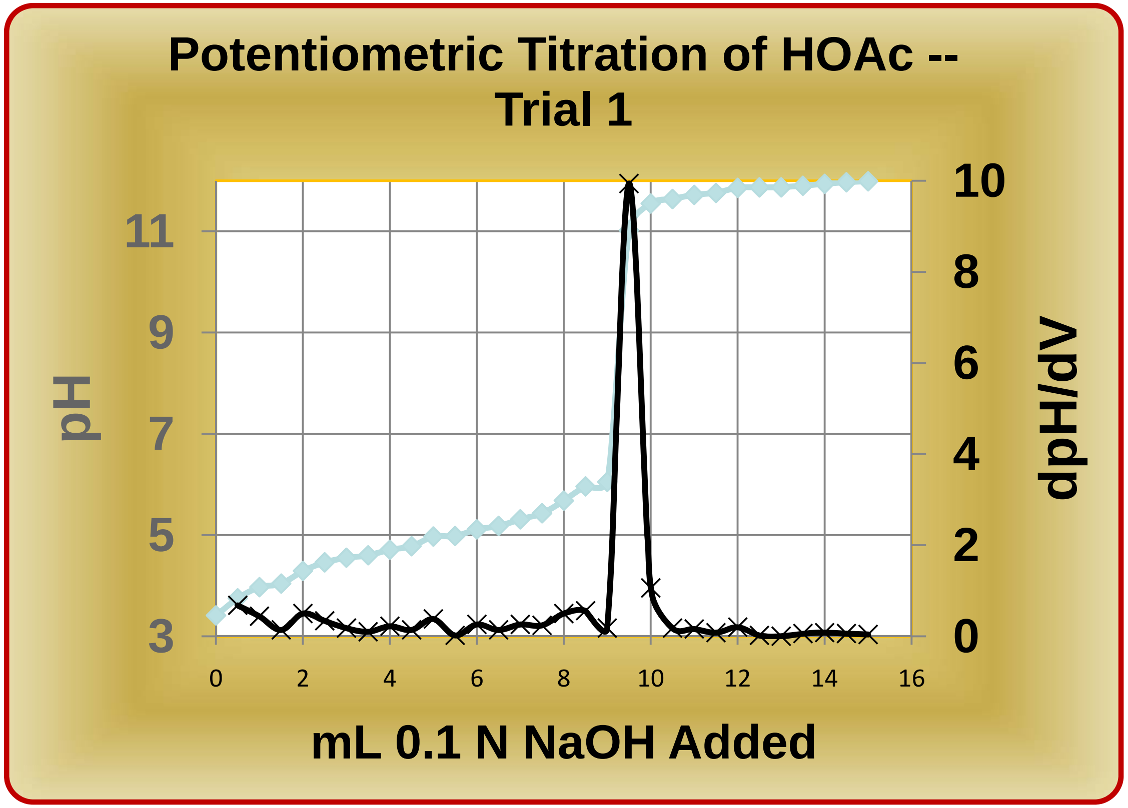


For di- and tri-protic acids, the curves are a bit more complex and allow for specific H^+ titrations to be observed:



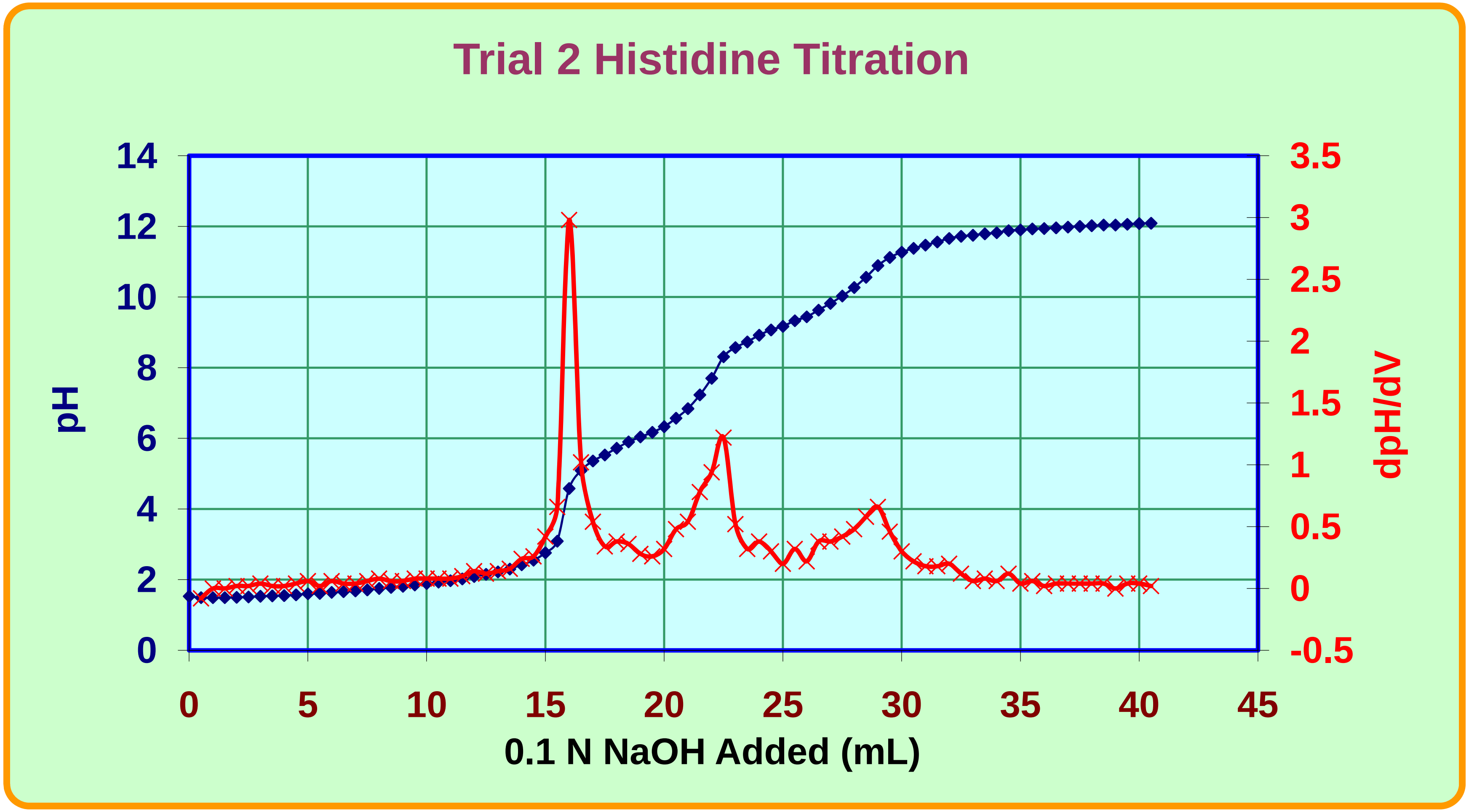


When using a pH meter to keep track of the titration, the equivalent point/end point are not obvious. Typically a technique called "taking the first derivative" of the pH curve (the sigmoid shaped curve) is used to determine these points. Without going into detail, this involves manipulating the sigmoid curve data to take on a sort of "backwards, inside out parabolic shape".



The value of the equivalence point is that it is the pH at which the $[H^+] = [OH^-]$. At that point, divide the volume at the endpoint in half, read from that volume up onto the sigmoid-shaped curve, then over to the pH curve and you will be at the numerical value for the negative log of the acid dissociation constant (pK_a)

Amino Acid Titration: 3 Endpoints



Titration Technique

- Clean the buret with soap and water; rinse well.
- Rinse buret with 5-10 mL of the standard solution (base) and partially drain through the valve tip. Do NOT allow the buret to empty and put air bubbles in the tip.
- Safely fill the buret with your standard solution (base) and place in buret clamp on the ring stand.
- Drain excess standard out and pour it in the waste container.
- Record the volume on the buret in ink (remember "0" is on the top and "50" is on the bottom of the buret).
- Obtain your unknown acid sample[s]: for a solid, mass it on the balance, then pour into an Erlenmeyer flask and add water as necessary per instructions. For a liquid, pipet the solution into your Erlenmeyer flask.
- Add indicator (phenolphthalein in most CHEM 121/122 titrations) -- 2-4 drops. NOTE: this step is the easiest to forget and the easiest to diagnose.

- Using your WEAK hand, straddle the buret with your index and society fingers on and under the back of the stop-cock and your thumb on the front of the stop-cock.
- Using your STRONG hand, grasp the outside of the Erlenmeyer flask by the neck, insert the buret tip into the neck and begin swirling the solution vigorously without spilling.
- Begin adding standard solution (base) to the analyte flask with swirling.
- In the beginning you may add base fairly rapidly -- as you get closer to the endpoint, add base slower, i.e., drop-by-drop.
- With phenolphthalein, add enough base with swirling to get the whole solution to turn pink/fuschia for 30 seconds, then back to colorless. This is the ideal end point. Record your final volume on the buret in ink in your lab book.
- NOTE: A crude way in which to see if you've gone WAY over the end point is to swirl the pink solution, take a deep breath and hold it in for approximately 15 seconds, then exhale rapidly into the sample. Do this 3 times. If the solution goes colorless, you're barely over -- if not, you're WAY over. Either way, stop, record your data in ink and go on to the next sample. What's the reaction, here?
- Dispose of your sample appropriately.

Sample Data Sheet		
Final Std Volume:	**36.34 mL**	**(why 50 on bottom)**
Initial Std Volume:	**1.25 mL**	**(why 0 on top)**
Volume Std used:	**35.09 mL**	**(how much used)**

REMEMBER: read your buret numbers DOWN! See below. The application of this type of technique and data is discussed later in lecture and lab. Example of reading a meniscus in a buret. This buret reading is 1.70 mL: