AP Chemistry Summary
Acids, Bases and Buffers

Definitions:

Arrhenius:

Acid - Produces H^+ ions in solution $HCl \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$

Base - Produces OH^- ions in solution $NaOH \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$

Dissociation = Is related to the ability of a substance to "break apart" in solution.

Brønsted-Lowry:

Proton transfer direction

Acid - Proton donor $\underset{\text{Proton donor}}{HCl} + \underset{\text{Proton acceptor}}{H_2O} \rightarrow \underset{\text{Hydronium}}{H_3O^+_{(aq)}} + Cl^-_{(aq)}$

Usually H^+ and H_3O^+ (hydronium) refer to the same thing. The hydronium form shows the hydrogen ion's association with the water molecule in the aqueous solution. (In reality the hydronium ion is probably associated with several water molecules.)

Proton transfer direction

Base - Proton acceptor $\underset{\substack{\text{(ammonia)}\\ \text{Proton acceptor}}}{NH_3} + \underset{\text{Proton donor}}{H_2O} \rightarrow NH_4{}^+_{(aq)} + \underset{\text{Hydroxide}}{OH^-_{(aq)}}$

(In reality, ammonium hydroxide is unlikely to exist in solution but this form of the compound is consistent with the Arrhenius/Bronsted-Lowry definition.)

Lewis:

Acid - Electron pair acceptor (electrophile) Base - Electron pair donor (nucleophile)

Ex. $BF_3 + NH_3 \rightarrow F_3BNH_3$

In this example, the lone electron pair is donated by the nitrogen in the ammonia to the boron. BF_3 is the electron pair acceptor (acid) and the NH_3 is the electron pair donor (base).

The Lewis definition is the most inclusive for identifying substances as acids or bases.

The Lewis definition is beneficial in many reactions including those that do not take place in aqueous solutions and in other phases. They are particularly useful in organic chemistry and in the formation of complex ions.

Strengths of Acids and Bases

The strength of an acid or base is dependent upon the extent to which it performs in one of the ways as defined above (often ionizing). You should be able to differentiate between

Strong vs. weak (based on the ability of the substance to dissociate) and

Concentrated vs. dilute (based on the concentration (e.g. molarity) of the solute in solution.

A strong acid (such as HCl) dissociates completely, as in shown in the right facing arrow.
$HCl \longrightarrow H^+ + Cl^-$

A weak acid (such as acetic acid, CH_3COOH) only dissociates to a very small degree
$CH_3COOH \rightleftarrows CH_3COO^- + H^+$
The two arrows show that the bulk of the molecules remain undissociated CH_3COOH

Strong Acids and Bases

Make sure you are familiar with the 6 common strong acids

HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$

and the 8 common strong bases

LiOH, NaOH, KOH, RbOH, CsOH (hydroxides of the alkali metals) and
$Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ (hydroxides of some of the alkaline earth metals. Note: Although these are considered strong bases, their solubility is actually limited)

You should also know the weak base, ammonia (NH_3) and the weak acid, acetic acid (CH_3COOH).
These are a little tricky because NH_3 doesn't have OH^- in it. It produces OH^- by the way that it reacts with water

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

In addition CH_3COOH doesn't look like an acid because it is commonly written without a "leading hydrogen" in the formula which most acids have and it also looks like it has an OH at the end. In reality, only the H is removed from the molecule

$CH_3COOH \rightarrow CH_3COO^- + H^+$

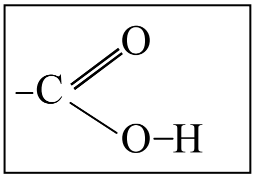
Nomenclature:

Acids:

Binary Acids (contain hydrogen and a non-oxygen containing anion)
hydro prefix -ic suffix Examples: H_2S (hydrosulfuric acid), HCl (hydrochloric acid)

Oxoacids (oxyacids) (contain hydrogen and oxygen containing polyatomic anion)(excludes organic carboxylic acids COOH)
Polyatomic ions with -ate endings are changed to -ic
Polyatomic ions with -ite endings are changed to -ous
add the word “acid” to the ending of either type
Examples: H_2SO_4 (sulfuric acid, sulfate ion), HClO (hypochlorous acid, hypochlorite ion)

Organic acids (those containing the carboxylic acid group COOH)
Add suffix -oic to the hydrocarbon chain name, then the word “acid”
Many of these acids also have common names
Examples: Ethanoic acid CH_3COOH (acetic acid, vinegar when diluted),
Methanoic acid HCOOH (formic acid)



Bases:

Those containing OH^-
Give the name of the metal cation then add “hydroxide” ending
Examples: NaOH (sodium hydroxide), $Al(OH)_3$ (aluminum hydroxide)

Those containing nitrogen (related to ammonia) are called amines and are organic bases
They are named by the hydrocarbon prefix followed by the "amine" ending
Examples: methylamine CH_3NH_2, ethylamine $CH_3CH_2NH_2$

Properties of acids and bases:

Acids:

- Turn litmus paper from blue to red
- React with active metals (e.g. $2HCl + Mg \rightarrow MgCl_2 + H_2$)
- Taste Sour
- React with bases to form water and salt

IMPORTANT NOTE: In the laboratory, always add concentrated acid to water, not water to concentrated acid!

Bases:

- Turn litmus paper from red to blue
- Feel slippery or soapy on the skin
- Taste bitter
- React with acids to form water and salts.

Acid-Base Anhydrides (without water)

When anhydrides are added to water, common acids and bases form.

Acid anhydrides are often oxides of nonmetals

Ex.: SO_2, SO_3, CO_2

Basic anhydrides are often oxides of metals

Ex: Li_2O, CaO, MgO, Al_2O_3 (CaO = lime, $Ca(OH)_2$ = slaked lime)

Trends in the strengths of acids and bases:

Binary Acids:

Two factors are related to the acid strengths of nonmetal hydrides. These are the polarity of the NM-H bond (NM stands for a nonmetal atom) and the strength of the bond between the nonmetal atom and the hydrogen atom. Acid strength increases to the right and down on the periodic table.

1. Acid strength increases as the electronegativity of the nonmetal atom increases.
2. Acid strength increases as the atomic radius of the nonmetal increases.

Oxoacids:

1. For oxoacids with the same structure, but with different attached atoms from the same group, acid strength increases with increasing electronegativity of the attached atom.
   $HOI < HOBr < HOCl$
2. For oxoacids that have the same central atom but differ in the number of attached oxygen atoms, acid strength increases with increasing oxidation number of the central atom. HNO_3 is stronger than HNO_2 for example.

To summarize, *anything that withdraws electrons from the bond where the* H^+ *is to be released makes the acid stronger.*

The proximity of the "electron withdrawing" atoms may need to be taken into account as well. For instance a slightly more electronegative atom placed further down a molecular chain from the dissociating hydrogen may have less of an effect than a less electronegative atom located much closer to the H^+.

Bases

Similarly, *any atom or group that withdraws electrons from the atom to which H^+ bonds makes a base weaker*. Amines, which are organic bases, are much weaker when attached to aromatic (benzene) rings (with delocalized electrons) than as part of an aliphatic (straight chain) structure.

Conjugate acid-base pairs (From Brønsted-Lowry)

In an acid/base reaction, the acid identified on the reactant side becomes the conjugate base on the product side (because it would be the proton acceptor in the reverse direction). The converse is true for bases.

Ex: $HF + NH_3 \leftrightarrow F^- + NH_4^+$
acid base conj base conj acid

Ex: $H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^-$
acid base conj acid conj base

Notes: 1. The stronger the acid or base, the weaker its conjugate is.
2. Conjugates generally differ by one proton (hydrogen ion).
3. Equilibrium lies in the forward reaction direction of the stronger counterpart.

Amphiprotic means able to act as an acid of a base [i.e. can gain or lose a proton]) and *amphoteric* means able to react with an acid or a base.
Ex:

$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$ (here HPO_4^{2-} acts as an acid)
$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$ (here HPO_4^{2-} acts as a base)

Water is amphoteric and amphiprotic

Autoionization of water

In pure water, a very small number of molecules at any given time dissociate into hydronium and hydroxide ions. The concentration of the hydronium or hydroxide is $1.0\text{x}10^{-7}$M
This is represented by $[H_3O^+] = 1\text{x}10^{-7}$ and $[OH^-] = 1\text{x}10^{-7}$ (measured at 25°C)
The brackets indicate "molarity".

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{or} \quad 2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$K_w = [H^+][OH^-] = 1.0\text{x}10^{-14}$ or $pK_w = 14.00$ where pK_w is defined as $-\log(K_w)$
K_w is the autopyrolysis constant (or ion product of water)

The pH (or pOH) scale is defined by the following:

pH stands for the "power of hydrogen"
$pH = -\log [H_3O^+]$
$pOH = -\log [OH^-]$
$pK_w = -\log K_w$

For pure water, since the concentrations of both hydronium and hydroxide are both $1.0\text{x}10^{-7}$, the pH and pOH for pure water are both 7. In addition pK_w is 14. For this the following equation can be derived:

$pK_w = pH + pOH = 14.00$

On a pH scale, 7 is neutral; numbers smaller than 7 are acidic; numbers greater than 7 are basic (alkaline)
On a pOH scale, 7 is neutral; numbers smaller than 7 are basic; numbers greater than 7 are acidic.

K_w is a very important constant because the product of $[H^+]$ and $[OH^-]$ must always equal K_w. This means that as you add acid to water (which increases the hydronium ion concentration) the hydroxide concentration from the autoionization of water must be suppressed so that the product is still K_w. The opposite effect occurs for adding bases which produce hydroxide.

Acid-Base Ionization Constants

Given: $HB + H_2O \leftrightarrow H_3O^+ + B^-$ where HB is a weak acid (note pure water is not included)
K_a = acid ionization constant

$$K_a = \frac{[H_3O^+]\,[B^-]}{[HB]}$$

Example: $[H^+][F^-]/[HF]$

Similarly,
$B^- + H_2O \leftrightarrow HB + OH^-$ where B^- represents a weak base

$$K_b = \frac{[HB]\,[OH^-]}{[B-]}$$

In water acids produce H_3O^+. Acids stronger than hydronium completely dissociate to hydronium ions in aqueous solutions. Since ionization is complete there is no ionization constant possible, therefore it is impossible to determine the relative strengths of these acids. This is called the *leveling effect.*
Ex:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$HI + H_2O \rightarrow H_3O^+ + I^-$$

To determine relative strengths for these stronger acids a solvent that is a weaker base than water (e.g. diethyl ether or acetone) must be used so that dissociation is not 100%.

From solving these equilibrium expressions for hydronium or hydroxide, the pH of a weak acid or base solution can be determined.

For a conjugate acid/base pairs: $K_aK_b = K_w$
This is a useful equation to know for determining one value from another.

Polyprotic acids (diprotic, triprotic)

General form:
$H_3A + H_2O \leftrightarrow H_3O^+ + H_2A^-$ K_{a1}
$H_2A^- + H_2O \leftrightarrow H_3O^+ + HA^{2-}$ K_{a2}
$HA^{2-} + H_2O \leftrightarrow H_3O^+ + A^{3-}$ K_{a3}

$K_{a1} > K_{a2} > K_{a3}$

Notes:

-Because K_{a2}, K_{a3},... are so small, few of the anions produced in the first ionization step ionize further.
-In all but extremely dilute solutions, essentially all the H_3O^+ ions come from the first ionization step alone.

Observations:

(NM = nominal molarity, which is the molarity of the acid *prior* to dissociation)

For the **first ionization** step:
$[H_3O^+][H_2A^-] / [H_3A] = K_{a1} = [X][X]/[NM - X] \cong [X][X]/[NM]$ (usually) Check the 5% rule.

This means for the **second ionization** step
$[H_3O^+][HA^{2-}] / [H_2A^-] = K_{a2}$ since $[H_3O^+] \cong [H_2A^-]$ they cancel out and you end up with
$[HA^{2-}] = K_{a2}$
in most cases

For the **third ionization** step
$[H_3O^+][A^{3-}] / [HA^{2-}] = K_{a3}$
this turns into
[hydronium molarity from first ionization]$[A^{3-}]/K_{a2} = K_{a3}$
and you can solve for $[A^{3-}]$
(Note that the K_{a2} in the denominator comes from the fact that $[HA^{2-}] = K_{a2}$ in the second step.)

(See the special notes concerning sulfuric acid on page 662)

Acid-Base Neutralization Reactions

The general form of an acid base neutralization reaction is:

Acid + Base → Salt + water (Sometimes CO_2 gas is also evolved)

Example

$HNO_{3(aq)} + KOH_{(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)}$

Here, the salt that is formed is potassium nitrate. It is important to note that the cation of the salt comes from the base and the anion comes from the acid.

For strong acid/base reactions the net ionic equation is always

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O$

Titrations:

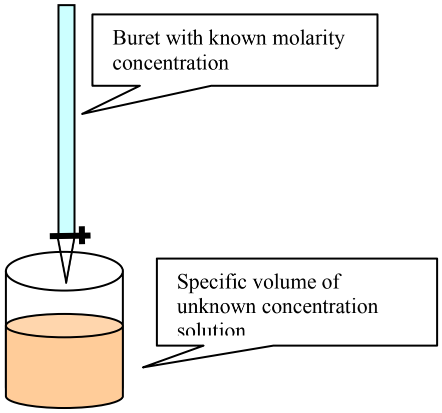
The purpose of an acid/base titration is to determine the molarity of a solution of unknown concentration by reacting (**titrating**) a sample of it with a solution of known concentration (**the standardized solution** or **titrant**) until the solution is neutralized.

By using mole ratios from the balanced equation, the concentration of the unknown can be determined.

At the **equivalence point** in a titration the acid and base have been brought together in exact stoichiometric proportions.

Example problems (to be solved in class):
A 25.0mL sample of a solution of hydrochloric acid is titrated with a .10M standardized $Ba(OH)_2$ solution.

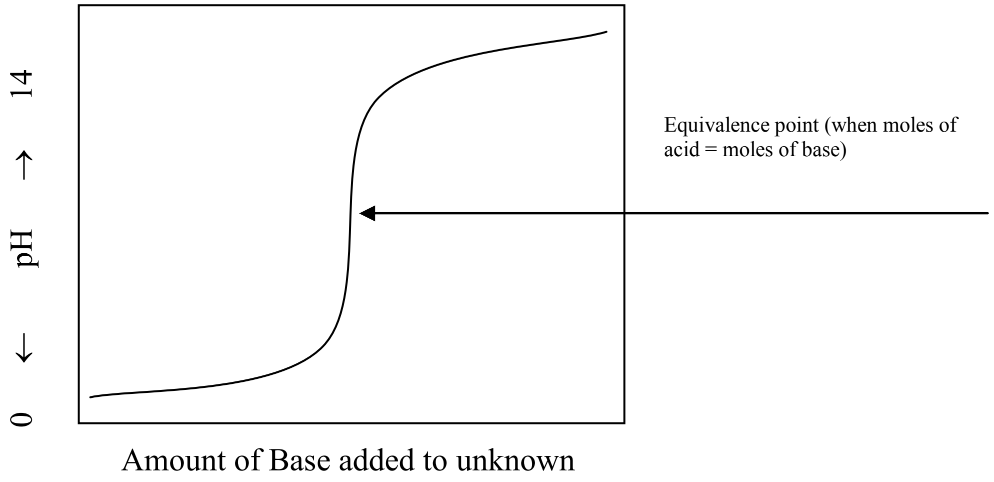
a. If 15.0mL of the $Ba(OH)_2$ is required to reach the equivalence point, what is the molarity of the original HCl solution?
b. Using the chart on page 677, would phenolphthalein be OK to use as an indicator to use for this titration? Why or why not?
c. What was the pH when exactly half of the acid had been neutralized?



Example:
$HCl + NaOH \rightarrow NaCl + H_2O$

What is the molarity of an unknown NaOH solution if 50mL of a .1M HCl solution is required to neutralize 500mL of the unknown?
1. moles HCl = (.1M)(.050L)=.005mol HCl
2. Since the coefficients are 1:1 you titrated .005mol of NaOH
3. Concentration = (.005mol)/(.500L) = **.01M NaOH**

Titration curve for titration of a strong acid with a strong base:



The equivalence point is when equal numbers of moles of acid and base have reacted with one another. The endpoint is the pH at which an indicator changes color. In order to determine the exact equivalence point, a proper pH indicator (litmus, etc.) or pH meter must be used.

The equivalence point pH will only be 7 if the titration is between a strong acid/strong base or if the K_a and K_b values are similar.

The Common Ion Effect

When a solution of an acid or a base also contains a salt with an ion that is the conjugate of that acid or base, Le Chatalier's Principle tells us that the dissociation of the acid will be suppressed. In this case, the pH of the system will also be affected.
To illustrate this, recall

$$K_a = \frac{[H^+]\,[\text{anion}]}{[\text{Undissociated acid}]}$$

If the salt contains the anion listed in the numerator of this equation, the molarity for that ion will be greater than zero before the acid begins to dissociate. When the system comes to equilibrium, i.e. = K_a, the H^+ concentration will be less than normal.

Example problem (to be solved in class):
Determine the pH of a solution that has a nominal molarity of .1M acetic acid and .05M sodium acetate.

Hydrolysis:

Recall the neutralization reaction Acid + Base → Salt + Water (and sometimes carbon dioxide)
The salt is made up of the cation of the original base and the anion of the acid.

Since the ions of the salt are related to the conjugates of the original acid and base, if the original acid and/or base is/are weak enough the conjugates can react with the water (hydrolize) and create a solution with a pH greater or less than 7.

In general:
1. Salts of strong acids and strong bases form neutral solutions (pH=7) because their conjugates are very weak. (e.g. NaCl form sodium hydroxide and hydrochloric acid)

2. Salts of weak acids and strong bases form basic solutions (pH>7) because the conjugate base of the weak acid reacts with the water. (e.g. $NaCH_3COO$ form sodium hydroxide and acetic acid)

3. Salts of strong acids and weak bases form acidic solutions (pH<7) because the conjugate acid of the weak base reacts with the water. (e.g. NH_4NO_3 from ammonia and nitric acid)

4. Salts of weak acids and weak bases form solutions that may be acidic, neutral or basic depending on the relative K values of their conjugates. (e.g. NH_4CH_3COO from ammonia and acetic acid)

Example problem (to be solved in class):
Calculate the final pH of a solution formed from combining 250.mL of .1M acetic acid with 250.mL of .1M sodium hydroxide. K_a for acetic acid is $1.8\text{x}10^{-5}$

Titration of a Weak Acid with a Strong Base

The titration curve under these conditions will be somewhat different due to the hydrolysis of the conjugate base of the weak acid being titrated. Some things to keep in mind:

a. The initial pH will be higher than that predicted by the nominal molarity because the acid only partially ionizes.
b. Ionization of the weak acid is further suppressed by its conjugate base that forms as the acid is neutralized.
c. When the pH = pKa ±1, the system acts like a buffer
d. At the half neutralization point pH = pK_a (remember Henderson-Hasselbalch equation)
e. At the equivalence point, the pH will be higher than 7 due to the hydrolysis of the conjugate base.
f. Beyond the equivalence point the system is overwhelmed by the strong base in aqueous solution.
g. The slope of the curve thru the equivalence point is much less steep than for a strong acid/strong base neutralization. Therefore the end-point of the indicator must be chosen much more carefully.

(See Figure 15.16 on page 684 for a visual diagram of these effects)
See example 15.22 and Exercise 15.22 on pages 686-687

When titrating a weak base with a strong acid the situation is reversed.

The titration of weak polyprotic acids will have more than 1 equivalence point. This will be distinctly seen only if the ionization constants differ by a factor of 10^3 or more. Otherwise the neutralizations overlap and are not distinct.

pH Indicators:

Is a weak acid which has one color as an acid and another color as its conjugate base

It is usually written in the form

$HIn + H_2O \leftrightarrow H_3O^+ + In^-$ where In stands for "indicator"
Color 1 Color 2

In an acidic solution, the dissociation of the HIn is suppressed and equilibrium lies to the left. In basic solution the situation is reversed.

It is important to choose an indicator with an **end-point** (color changing point) corresponding to the desired pH to be measured.

Different pH indicators are used in titrations depending on the nature of the acid and base, but three common indicators are:

Phenolphthalein	Endpoint 9	For Weak acid/Strong base titrations
Bromothymol Blue	Endpoint 7	For Strong acid/Strong base titrations
Methyl Red	Endpoint 5	For Strong acid/Weak base titrations

Buffer Solutions

The common ion effect can be used to create what is known as a buffer system. A buffer system resists changes in the pH of a system from the addition of an acid or a base.

In general, a buffer must contain
- a weak acid and its salt (conjugate base) OR
- a weak base and its salt (conjugate acid)

The buffer works by the following principle:
Suppose you have a system that contains acetic acid and sodium acetate at a particular pH. If a strong acid, such as HCl is added to the system, the acetate ion would react with the hydrogen ions to produce undissociated acetic acid molecules via
$H^+ + CH_3COO^- \rightarrow CH_3COOH$, thus helping to prevent the H^+ from lowering the pH
If instead a strong base, such as sodium hydroxide was added, the acetic acid would react to produce the acetate ion by
$CH_3COOH + OH^- \rightarrow H_2O + CH_3COO^-$
Note that there is a limitation to how much a system can buffer a solution before the system is "exhausted".
Rearranging the equilibrium expression and using the laws of logarithms the Henderson-Hasselbalch equation can be derived:

Henderson-Hasselbalch Equation:
$pH = pK_a + \log([\text{conjugate base}]/[\text{acid}])$ or
$pOH = pK_b + \log([\text{conjugate acid}]/[\text{base}])$

Note that if the conjugate base/acid ratio is 1, the log is zero and $pH = pK_a$ which is why you want to choose an acid with a pK_a close to the desired pH to be buffered. This will give you the best range in buffering the solution before the system "breaks down".

Buffer solutions should meet the following criteria:
- The ratio, [conjugate base]/[weak acid] has a value between 0.10 and 10.
- Both [conjugate base] and [weak acid] exceed K_a by a factor of 100 or more.

Buffer Capacity:
The buffer capacity is the number of moles of strong acid or base needed to change the pH of 1L of buffer solution by 1 pH unit.
The approximate buffer capacity = Total molarity x 0.4
Where the total molarity is the sum of the acid and conjugate base molarities.

Preparation of a buffer:
1. Determine the desired pH
2. Choose an acid with a pKa within ±1pH of the desired pH
3. Determine the moles of acid or base that need to be buffered
4. Make sure that the sum of the moles of the acid/conjugate base pair are at least 20x the amount of strong acid or base that needs to be buffered
5. Use the volume of buffer solution desired to calculate the molarity of the solution

Example problems (to be solved in class):
1. What is the pH of a buffer solution formed from the combination of 500.mL of .020M acetic acid and 500.mL of .025M sodium acetate?

2. What is the final pH if 50.0mL of 0.03M HCl is added to 0.500L of a buffer solution that is 0.24M NH_3 and 0.20M NH_4Cl?

Important equations for this chapter:

Autoionization constant for water:

$K_w = 1.0\text{x}10^{-14} = [H_3O^+][OH^-]$ Remember brackets mean molarity

The product of $[H_3O^+][OH^-]$ ALWAYS equals $1.0\text{x}10^{-14}$

$pH = -\log[H_3O^+]$ $[H_3O^+] = 10^{-pH}$ $K_w = K_{acid}K_{conj.base}$ or $pK_w = pK_a + pK_b$
$pOH = -\log[OH^-]$ $[OH^-] = 10^{-pOH}$
$pH + pOH = 14$ Molarity = mol/L or mmol/ml (millimole/milliliter)

$$K_a = \frac{[H^+]\,[\text{anion}]}{[\text{Undissociated acid}]}$$

$$K_b = \frac{[\text{dissociated cation}]\,[OH^-]}{[\text{Undissociated Base}]}$$

Henderson-Hasselbalch Equation:
$pH = pK_a + \log([\text{conjugate base}]/[\text{acid}])$ or
$pOH = pK_b + \log([\text{conjugate acid}]/[\text{base}])$

To use approximations in equilibrium:
X must be less than 5% of the nominal molarity or
The (nominal molarity)/$K_{(\text{of the acid or base})}$ must be greater than 100

For an acid-base reaction, an equivalent weight (equivalent) is a quantity of substance that will produce *or* react with one mole of H^+
Normality (N) = number of equiv. solute/number liters solution.