CHAPTER 2. IONIC EQUILIBRIA

An entirely different subject - that of equilibria, and in particular ionic equilibria - will be considered. This is done for two reasons, it is a very important topic in its own right, important not only to chemists but to any science that uses chemistry, *e.g.* biology, geology, biochemistry, *etc*. Titrations will also be examined, but from the standpoint of what actually happens during a titration. To do this ionic equilibria must first be discussed in some detail.

2.1 BEHAVIOUR OF IONIC SOLUTIONS

2.1.1 LAW OF MASS ACTION

If a chemical reaction is at equilibrium, there is no net change in any of the concentrations of the materials involved in that reaction over time. In this case the concentrations of these reactants are related to each other by the law of mass action (the equilibrium constant expression). For the "general" reaction,

$$aA + bB \rightarrow cC + dD,$$

the way of writing the law of mass action presented in most introductory texts is:

$$K_e = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (2\text{-}1)$$

This would be entirely correct if the solution containing the reactants were ideal. In an ideal solution the "reactivity" of a reagent would be directly proportional to its concentration. Thus the equilibrium constant expression would involve concentrations (as written above) since the equilibrium constant provides a direct measure of the driving force of the reaction.

What is an ideal solution? It is one in which the solutes do not interact with each other to an extent different from their interaction with the solvent. In simpler words, an ideal solution is one in which the solute-solute interactions are the same as the solute-solvent interactions. A solution of toluene in benzene (see Figure 2-1) should be close to ideal since the two chemicals will interact similarly. What about a solution of NaCl in H_2O? To answer this question one must realize that a solution of NaCl is really composed of Na^+ and Cl^- ions. Will a Na^+ ion interact with another Na^+ ion or a Cl^- ion in the same way it will interact with a water molecule? *NO!*

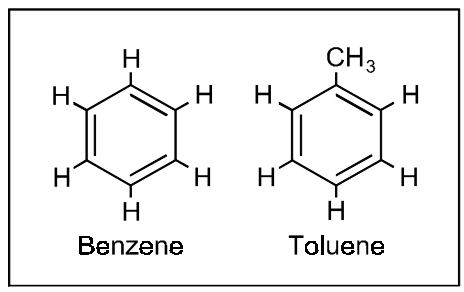

Figure 2-1

In a dilute solution the ions are far apart and do not "see" each other, they just "see" water molecules. However, as the ionic concentration increases, the ions come closer to each other and begin to notice each other. Their environment begins to change from one of just water molecules to one of water molecules and other ions. This change in environment causes the reactivity of ions to increase less rapidly than their concentration increases. This means that, strictly speaking, concentrations should not be used in the law of mass action.

What happens now? If the law of mass action is derived from first principles (using thermodynamics), the concept of *activity* is introduced. The reactivity of a species is directly proportional to activity in a real solution and it is activity that should be used in the law of mass action. We will use the symbol "A" to represent activity. Thus the law of mass action should be

$$K_e = \frac{(A_C)^c (A_D)^d}{(A_A)^a (A_B)^b} \tag{2-2}$$

Now the problem of knowing or measuring activities arises. (Measuring concentrations is a relatively simple matter.) At first one might guess that activities are closely related to concentrations, and they are. This is usually shown as follows:

$$A_C = [C]\gamma_C \tag{2-3}$$

where γ_C is a term called the activity coefficient. It essentially converts concentration into activity. In very dilute solutions $\gamma_C = 1$ (activities and concentrations are the same), but as ionic concentration increases, γ_C decreases and activity increases less rapidly than concentration (up to a point). Activity coefficients can be written for all the species in the chemical reaction.

$$A_A = [A]\gamma_A,\ A_B = [B]\gamma_B,\ A_D = [D]\gamma_D \tag{2-3a}$$

The law of mass action now becomes:

$$K_e = \left\{\frac{[C]^c[D]^d}{[A]^a[B]^b}\right\}\left\{\frac{\gamma_C{}^c\gamma_D{}^d}{\gamma_A{}^a\gamma_B{}^b}\right\} \tag{2-4}$$

2.1.2 DEBYE-HÜCKEL THEORY

Has this really made things any simpler? At first glance, no. However, Debye and Hückel have provided a theory, named in their honour, that can be employed to approximately calculate activity coefficients in ionic solutions up to about 0.1 M in concentration. This allows one to use the law of mass action in its correct form. The extended Debye-Hückel equation for activity coefficients is as follows:

$$\log(\gamma_A) = \frac{-0.51 Z_A{}^2\sqrt{\mu}}{1 + \alpha_A\sqrt{\mu}/305} \tag{2-5}$$

where Z_A is the charge on the ion (-2 for sulfate ion, for example), μ is the ionic strength of the solution, and α_A is the ion size parameter (the effective diameter of the *hydrated* ion) in pm (1 pm = 10^{-12} m = 10^{-9} mm). The constants 0.51 and 305 only apply to aqueous solutions at 25°C. Older texts use an equation slightly different from Eqn. (2-5) where the ion size parameter is in angstrom units (Å) (1 Å = 10^{-7} mm). Angstrom units are becoming less popular today with increasing use of SI units.

The ionic strength, μ, is a total ionic concentration that takes account of both the molar concentration and the charge of all ions, I, since both the concentrations and charges affect the environment of other ions.

$$\mu = (1/2)([I_1]Z_1{}^2 + [I_2]Z_2{}^2 + \cdots + [I_n]Z_n{}^2) \tag{2-6a}$$

or

$$\mu = (1/2)\sum_{i=1}^{i=n} C_i Z_i{}^2 \tag{2-6b}$$

where C_i represents the molar concentration of ion I.

This theory predicts that, since $\log(\gamma)$ is always negative, $\gamma < 1$, but that as $\mu \to 0$, $\gamma \to 1$, and $A_A \to [A]$. It also indicates that γ is very sensitive to the charge of the ion. In other words a solution with doubly charged ions will be considerably less ideal than one with only singly charged ions at the same concentration. This is because the non-ideality is caused by the charges on the ions.

The factors that affect non-ideality can be shown graphically. In Figure 2-2, which diagrams the manner in which the activity coefficient (as calculated using Eqn. (2-5)) depends on ionic concentration, the curves descend in order from Plot 1 to Plot 5. Note that the *X* axis is logarithmic and represents values of $[I^{z+}]$ from 0.001 M to 0.1 M.

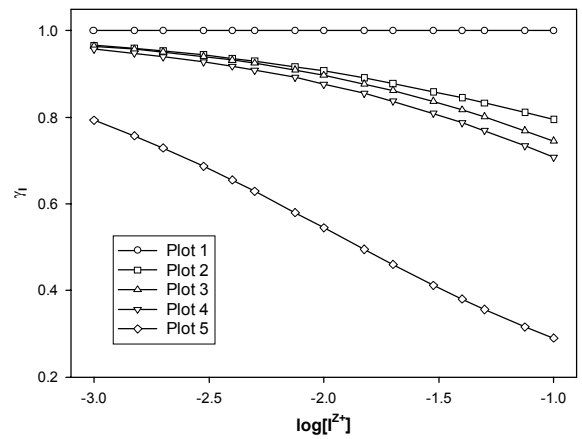

Figure 2-2

Plot 1 - ideal behaviour, $\gamma = 1.000$.

Plot 2 - real behaviour for Li^+ ($\alpha = 600$ pm) in LiCl.

Plot 3 - real behaviour for Rb^+ ($\alpha = 250$ pm) in RbCl.

Plot 4 - real behaviour for Rb^+ in Rb_2SO_4.

Plot 5 - real behaviour for Ca^{2+} ($\alpha = 600$ pm) in $CaCl_2$.

Note that the behaviour becomes more ideal as μ decreases in all cases. The difference between Plots 2 and 3 is due to the differing size of the ions (Li^+ and Rb^+), the larger ion behaving more ideally. Remember that the ion size parameter is the diameter of the *hydrated* ion, not the *bare* ion. The difference between Plots 3 and 4 is due to the difference in the anions involved (Cl^- and SO_4^{2-}). The ionic strength in the sulfate solution is somewhat higher than that in the chloride solution. The much larger difference between Plot 5 and the other plots is due to two effects, the charge on the ion (+2 *vs* +1) and the difference in ionic strength of such ions at the same concentration.

A few examples may help in understanding these concepts.

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1) What is the ionic strength of a 0.100 F solution of NaCl?

$[Na^+] = [Cl^-] = 0.100$ M

$\mu = (½)\{(0.100M)(+1)^2 + (0.100M)(-1)^2\} = (½)(0.200M) = 0.100$ M

2) What is the ionic strength of a 0.100 F solution of $CaCl_2$?

$[Ca^{2+}] = 0.100$ M, $[Cl^-] = 0.200$ M

$\mu = (½)\{(0.100M)(+2)^2 + (0.200M)(-1)^2\} = (½)(0.600M) = 0.300$ M

3) What is the activity of Na^+ in a solution of ionic strength 0.00100 M if its molarity is 0.00100 M (this has to be a solution containing only a salt like NaCl with F = 0.00100)? The ion size parameter for Na^+ is 450 pm.

$\log(\gamma_{Na}) = \{-0.51(+1)^2(0.00100)^{½}\}/\{1 + (450)(0.00100)^{½}/305\}$

$\log(\gamma_{Na}) = -0.0154$ or $\gamma_{Na} = 0.97$. Thus

$A_{Na} = [Na^+]\gamma_{Na} = (0.00100)(0.97) = 0.00097$

4) What is the activity of Na^+ in a solution if the molarity of Na^+ is 0.00100 and the ionic strength is 0.100 M? This could be a solution containing 0.00100 mol/L of NaCl and 0.100 mol/L of KCl.

$\log(\gamma_{Na}) = \{-0.51(+1)^2(0.100)^{½}\}/\{1 + (450)(0.100)^{½}/305\}$

$\log(\gamma_{Na}) = -0.110$ or $\gamma_{Na} = 0.78$. Thus

$A_{Na} = (0.00100)(0.78) = 0.00078$

5) What is the solubility of AgCl in pure water, what is its solubility in 0.100 F $NaNO_3$? If the solutions were ideal (the simple approach) the sodium nitrate would not affect the solubility and the answer would be "the same in both solutions."

The solubility product of silver chloride is very small, 1.8×10^{-10}, and the solubility will be very low. This can be used to advantage in some cases. The exact treatment of the problem requires the use of activities.

$K_{sp} = 1.8\times10^{-10} = (A_{Ag})(A_{Cl}) = [Ag^+][Cl^-]\gamma_{Ag}\gamma_{Cl}$

In using the above equation a problem arises - one must know the solubility in order to calculate the ionic strength to solve for the activity coefficients. However, the solubility is unknown and therefore one cannot calculate the γs. In this case the problem can be circumvented by assuming that the solubility will be so low that $\gamma_{Ag} = \gamma_{Cl} = 1$. Let S equal the solubility of silver chloride in mol/L.

$S = [Ag^+] = [Cl^-]$

$1.8\times10^{-10} = [Ag^+][Cl^-](1)(1) = (S)(S) = S^2$

$S = (1.8\times10^{-10})^{1/2} = 1.3\times10^{-5}$ mol/L

The above answer can be used to calculate the ionic strength, which in turn can be used to calculate the activity coefficients. When this is done, it is found that $\log(\gamma) \approx 0$ and $\gamma \approx 1$, indicating that the above answer is correct (the assumption was valid).

In 0.100 F $NaNO_3$, the γs will no longer be unity. However, one can now assume that since the solubility of AgCl will still be small, it will have no effect on the ionic strength. Thus μ can be calculated considering only the $NaNO_3$.

$\mu = (1/2)([Na^+](1^2) + [NO_3^-](-1^2)) = (0.100 + 0.100)/2 = 0.100$ M

The ion size parameter for Ag^+ is 250 pm and that for Cl^- is 300 pm. Thus

$\log(\gamma_{Ag}) = \{-0.51(1^2)(0.100)^{1/2}\}/\{1 + 250(0.100)^{1/2}/305\} = -0.128$

$\gamma_{Ag} = 0.745$

$\log(\gamma_{Cl}) = \{-0.51(-1^2)(0.100)^{1/2}\}/\{1 + 300(0.100)^{1/2}/305\} = -0.123$

$\gamma_{Cl} = 0.753$

$1.8\times10^{-10} = [Ag^+][Cl^-]\gamma_{Ag}\gamma_{Cl} = S^2(0.745)(0.753)$

$S = \{1.8\times10^{-10}/(0.745)(0.753)\}^{1/2} = 1.8\times10^{-5}$ mol/L

It is obvious that such small concentrations will not affect the ionic strength and the assumption made is valid. The results indicate that AgCl is more soluble in a solution of $NaNO_3$ than in pure water, which is what is observed experimentally.

These examples give some idea of the effect of ionic strength on the ideality of solutions. These effects may not seem tremendous, but they can be significant, especially for ions of more than a single charge.

The simple approximation that $A_A = [A]$ will normally be used throughout this text because the principles to be demonstrated do not need activity. *However*, remember in so doing that errors are made, and these errors increase as the ionic strength increases. Even though these errors will be ignored, you should realize that these errors exist.

The Debye-Hückel equation applies only to ions. What can be said about molecular species? Molecules tend to form much more ideal solutions than ions, since molecules do not interact over such long distances as ions. Thus their activity coefficients are much closer to unity, even at concentrations of 0.1 M. For molecular solutes which originate from liquids or solids, it will be assumed that $\gamma = 1$ (or activity equals concentration) at all concentrations. This assumption is much better for molecules than for ions. For molecular solutes that originate from a gas, it will be assumed that $A_{Gas} = P_{Gas}$, were P_{Gas} is the partial pressure of the gas (in atm) above the solution. This is also a good approximation as long as $P_{Gas} \leq 1$ atm (the ideal gas law applies). By convention, the activities of pure liquids and solids are both unity. Since the activity of the solvent in dilute solutions will be very close to unity, it will be assumed also to be one.

2.1.3 OTHER MASS ACTION CONSIDERATIONS

Two other characteristics of the law of mass action should now be reviewed. If one writes a chemical reaction in reverse, the equilibrium constant for the reversed reaction is the inverse of that for the reaction written normally (in the "forward" direction).

$$A + B \rightarrow AB \qquad K = [AB]/[A][B]$$

$$AB \rightarrow A + B \qquad K' = [A][B]/[AB]$$

$$K' = 1/K$$

When two reactions are added to form a third reaction, the equilibrium constant for the third reaction is the product of the other two equilibrium constants.

$$H_2A \rightarrow HA^- + H^+ \qquad K_1 = [H^+][HA^-]/[H_2A]$$

$$HA^- \rightarrow A^{2-} + H^+ \qquad K_2 = [H^+][A^{2-}]/[HA^-]$$

$$H_2A \rightarrow A^{2-} + 2H^+ \qquad K_3 = [H^+]^2[A^{2-}]/[H_2A]$$

It is obvious from the above that $K_3 = K_1K_2$

2.2 ACID-BASE REACTIONS

As mentioned above, chemical equilibrium will be examined because it is important in its own right and because it will be needed to understand the theory of titrations. Acid-base equilibria will be stressed because acid-base reactions are very important, because these illustrate the general principles as well as any type of reaction, and because titrations of all types are similar and thus understanding acid-base titrations leads to a good understanding of titrations in general.

Only Brønsted acid-base reactions will be discussed. In the Brønsted formalism:

> An acid is a proton donor and
> a base is a proton acceptor.

A general Brønsted acid-base equation can be written as follows:

$$HA + B \rightarrow HB + A$$

Here HA is the proton donor and B is the proton acceptor, thus HA is the acid and B is the base. Note that the molecule HB could be a proton donor and that A could be a proton acceptor (if the reaction were written in reverse). The portion of the molecule HA which remains after donating a proton can act like a base and the molecule formed when B accepts a proton can act like an acid. (Ionic charges have been neglected in the above discussion.) Thus it is concluded that one is really dealing with acid-base pairs, that with every acid there is associated a base and *vice versa*. These pairs are called acid-base conjugate pairs.

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{B} \rightarrow \underset{\text{acid 2}}{HB} + \underset{\text{base 1}}{A}$$

HA and A are one conjugate acid-base pair and HB and B are the other. For the reaction to proceed as written above, HA must be a stronger acid (proton donor) than HB and B must be a stronger base (proton acceptor) than A. In general, the stronger the acid, HA, the weaker its conjugate base, A. A very strong acid has a conjugate base so weak that it may not appear to be a base at all.

This is relatively straight forward. However, there is one significant problem that must be examined. Almost all solvents contain protons and many solvents are acids or bases (or both) themselves. Water is a good example. When acids or bases are dissolved in such solvents, acid-base reactions can occur which often complicate the situation.

Since water has two unshared electron pairs it can act as a base by accepting a proton, which associates with one of those pairs. The species thus formed, H_3O^+, is called the hydronium ion. The protons on water are not as tightly held as most protons bonded to carbon (for example) and thus water can also act as an acid by donating a proton and forming hydroxide ion (see Figure 2-3).

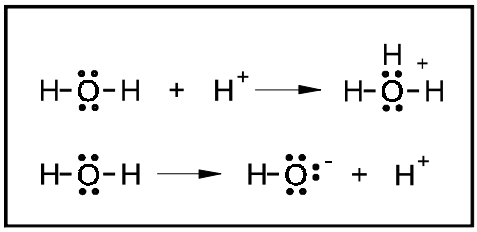

Figure 2-3

This behaviour leads to the conclusion that the strongest acid that can exist in water is H_3O^+ and the strongest base is OH^-, the hydroxide ion. Why? If a stronger acid than H_3O^+ is placed in solution, it will immediately react with H_2O (acting as a base) to form H_3O^+. For example, HI is a stronger acid than H_3O^+ and will react with H_2O (acting as a base) to form iodide ion and hydronium ion. Likewise O^{2-} is a stronger base than OH^- and it will immediately react with H_2O (acting as an acid) to form OH^-. This is illustrated in Figure 2-4.

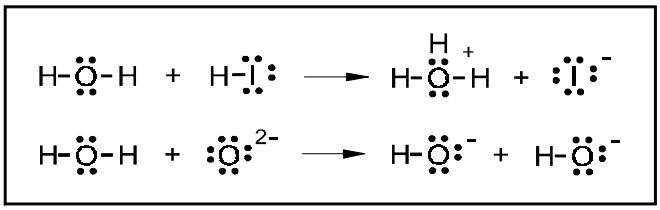

Figure 2-4

This ability to convert all strong acids to H_3O^+ and all strong bases to OH^- is called the levelling effect, since all such acids are levelled in strength to the strength of H_3O^+ and all such bases are levelled to the strength of OH^-.

Solvents that can act as both an acid and a base, like water, are called *amphiprotic* solvents. Examples of such solvents, besides water, are alcohols (CH_3OH, *etc.*), carboxylic acids (CH_3COOH, *etc.*), and ammonia and amines (NH_3, CH_3NH_2, *etc.*). In general if the amphiprotic solvent is represented as HX (for H_2O, X is OH)

1) the strongest acid in that solvent will be H_2X^+
2) the strongest base in that solvent will be X^-.

If a stronger acid is placed in that solvent it will be converted to H_2X^+, a stronger base to X^-. Thus all amphiprotic solvents exhibit the levelling effect.

It has already been stated that when a strong acid is dissolved in water, it is converted to H_3O^+. However, take a specific example. HCl is a much stronger acid than H_2O. Thus when it is dissolved in water the following occurs.

$$\underset{\text{acid 1}}{HCl} + \underset{\text{base 2}}{H_2O} \rightarrow \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{Cl^-}$$

It is usually assumed that this reaction goes to completion. HCl is referred to as a strong acid and said to completely dissociate. In fact it does not dissociate, it undergoes an acid-base reaction with the solvent. Chloride ion is a base, but it is such a weak base in water that it does not appear to be a base. However, It can show basic properties in some other amphiprotic solvents.

The other common strong acids are HBr, HI, H_2SO_4 (first proton), HNO_3, and $HClO_4$. These acids do not all have the same strength, $HClO_4$ is the strongest, but they all are levelled to the same strength once they are placed in water.

The equilibrium constant for the above reaction is

$$K_e = [H_3O^+][Cl^-]/[HCl][H_2O]$$

One is tempted to say that $[H_2O] = 55$ mol/L. However, remember that one should really use activities in equilibrium expressions, not concentrations. By convention, the activity of a pure *solvent* (a pure liquid) is unity. In most dilute solutions the activity of the solvent is so close to unity that it can be considered unity with little error. Thus "$[H_2O]$" when acting as the solvent will always be considered equal to unity in this text and will not appear in any equilibrium expression. Thus

$$K_e = [H_3O^+][Cl^-]/[HCl]$$

But if the above reaction is considered to go to completion, $[HCl] \approx 0$. Thus K_e is very large, or better it is considered undefined. This causes no problem, as will be seen. Thus for strong acids, the reaction with water is assumed to be complete and one does not write equilibrium constant expressions. Solutions 0.1 F in all strong monoprotic acids, *e.g.* HCl or HNO_3 or $HClO_4$, all have 0.1 M H_3O^+ and thus all have the same acidity in water.

In the case of a weaker acid (*e.g.* acetic acid) the same reaction occurs, but it does not go to completion.

$$\underset{\text{acid 1}}{CH_3COOH} + \underset{\text{base 2}}{H_2O} \rightarrow \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{CH_3COO^-}$$

$$K_e = [H_3O^+][CH_3COO^-]/[H_2O][CH_3COOH] = [H^+][CH_3COO^-]/[CH_3COOH]$$

When H^+ is written, H_3O^+ is intended and understood. There is no such thing as the free proton in aqueous solutions. H^+ will sometimes be used as a shorthand for H_3O^+. The equilibrium constant is often called the dissociation constant (although the reaction is *not* strictly a dissociation) and labelled K_a. In general for a weak acid:

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2\text{-}7)$$

The larger the value of K_a, the stronger the acid, and the weaker its conjugate base. Also the greater the amount of H_3O^+ formed in the reaction with water when the acid is dissolved.

Since an amphiprotic solvent has acid-base properties, one might ask if anything happens in the absence of added acids or bases? Does anything happen in the pure solvent alone? The answer is yes, all *amphiprotic* solvents undergo a self acid-base reaction called *autoprotolysis*. In general this takes the form:

$$\underset{\text{acid 1}}{HX} + \underset{\text{base 2}}{HX} \rightarrow \underset{\text{acid 2}}{H_2X^+} + \underset{\text{base 1}}{X^-}$$

In water this becomes

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

The equilibrium constant for this reaction is called the autoprotolysis constant, K_{auto}. For the solvent water:

$$K_{auto} = K_W = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ C \qquad (2\text{-}8)$$

Autoprotolysis constants are usually very small since autoprotolysis reactions proceed very little to the right.

It has been concluded that the stronger the acid, the higher the $[H^+]$ in a solution. Thus one could use $[H^+]$ as an indication of the acidity of a solution. However, this parameter can vary over a very wide range, about sixteen orders of magnitude in water, and therefore it is usual to use the logarithm of $[H^+]$ as a measure of acidity. This leads to the idea of the pH scale as a measure of solution acidity. By definition, pX means -log[X], where X can be any species present in solution. Thus pH, the standard measure of solution acidity, will be defined as:

$$pH = -\log[H^+] = -\log[H_3O^+] \qquad (2\text{-}9)$$

As will be pointed out in Chapter 5, this is not strictly correct. However, for the present this definition will be used.

2.3 GENERAL METHOD FOR THE SOLUTION OF EQUILIBRIUM PROBLEMS

It is now time to become more quantitative, to determine the actual value for the pH of a solution given the concentrations of the reagents and the equilibrium constants. Before doing this a general procedure for solving such problems will be discussed. It should be emphasized that this method will apply to all types of equilibrium problems, not just acid-base problems.

In a solution at equilibrium, all equilibrium expressions (all laws of mass action) must be obeyed. This provides a set of mathematical equations which describe the system and which can be used to determine the molarities of all the species present. In pure water there is only one equilibrium,

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

and the applicable law of mass action is Eqn. (2-8)

$$K_w = 1.00\text{x}10^{-14} = [H_3O^+][OH^-]$$

Usually, if not always, there are more unknowns than there are such equations, and, at this point, any solution would be impossible. In the above example there are two unknowns, $[H_3O^+]$ and $[OH^-]$,

and only one equation. However, there are always other expressions that can be written which will make the problem solvable. These "extra" equations can take different forms, several of which are described below.

2.3.1 MASS BALANCE EQUATIONS (MBE):

In this type of equation the left hand side is the concentration of a compound (in mols/L) which is placed in a solution (usually a formality) and the right hand side consists of all the forms (molarities) that the compound can take in solution. When writing a MBE, both the completeness of all reactions that the compound undergoes and the reaction stoichiometries must be taken into account so that the two sides of the equation are numerically equal.

For example: the MBE for a solution of NaCl would be

$F_{NaCl} = [Na^+] = [Cl^-]$ (since 1 mol of NaCl produces 1 mol of Na^+ and 1 mol of Cl^-.)

The MBE for a solution of $CaCl_2$ would be

$F = [Ca^{2+}] = [Cl^-]/2$

The MBE equation for a solution of acetic acid would be

$F = [HC_2H_3O_2] + [C_2H_3O_2^-]$

Usually a mass balance equation can be written for each material that is dissolved in a solution.

2.3.2 CHARGE BALANCE EQUATIONS (CBE):

In this type of equation *all* the positive charge in solution (in mols/L) is placed on one side of the equation, and all the negative charge in solution (in mols/L) is placed on the other. This is really a statement of electroneutrality. To get the charge (in mols/L) contributed by any ion simply multiply its molar concentration by the absolute value of its charge. To get the total positive charge, sum the charges due to all the cations in solution; to get the negative charge do the same for the anions.

For example: The CBE for a solution of NaCl would be

$[Na^+] + [H^+] = [Cl^-] + [OH^-]$ (including the autoprotolysis of water)

That for a solution of $MgSO_4$ would be

$2[Mg^{2+}] + [H^+] = 2[SO_4^{2-}] + [OH^-]$

Remember that *all* ions in a solution must be included in a charge balance equation, and that there is only one such equation per solution.

2.3.3 PROTON BALANCE EQUATIONS (PBE):

In this type of equation all the species that have lost protons are placed on one side of the equation, all the species that have gained protons are placed on the other. Each species is multiplied by the

number of protons it has lost or gained (considering the form in which it started). *Starting materials never appear in PBEs!*

For example, for pure water the chemistry is

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

and thus the PBE will be

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

since the starting material is H_2O, H_3O^+ has gained a proton and OH^- has lost a proton.

For a solution of sulfuric acid in water one must consider not only the autoprotolysis of water (see above) but also the following two reactions:

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

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$$

and thus the PBE will be

$$[H_3O^+] = [HSO_4^-] + 2[SO_4^{2-}] + [OH^-]$$

since HSO_4^- has lost one proton and SO_4^{2-} has lost two protons, starting from H_2SO_4.

There is only one PBE per solution.

2.3.4 BRUTE FORCE METHOD FOR SOLVING EQUILIBRIUM PROBLEMS

The following steps are guaranteed to lead to a solution to an equilibrium problem, provided that each step is done correctly. However, this method will not necessarily provide the quickest or easiest possible solution.

STEP 1. Write down all the chemical reactions which influence the chemical species of interest. If an unimportant reaction is included, the solution will be more difficult, but it will not be wrong. If an important reaction is not included, the solution will be wrong. Unimportant reactions are those that, while they occur to some extent, do not have a major influence on the equilibrium under consideration.

STEP 2. Write the equilibrium expressions for each of the reactions in STEP 1.

STEP 3. Determine the number of unknowns (molar concentrations) and the number of equations available. At this point equations will be fewer than unknowns.

STEP 4. Write enough other equations (MBEs, PBE or CBE) so that unknowns equal equations.

STEP 5. Solve the resulting set of simultaneous equations for the unknown of interest. This step is not necessarily trivial.

2.4 EQUILIBRIA INVOLVING ACIDS OR BASES

2.4.1 PURE SOLVENT (WATER).

The first example of the method (the BFM or brute force method) will be the calculation of the pH of water with no added solutes.

STEP 1. List the reactions that affect $[H_3O^+]$. The only reaction which does this is the autoprotolysis.

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

STEP 2. Write the law of mass action for the autoprotolysis

$$K_w = [H_3O^+][OH^-] \qquad (2\text{-}8)$$

STEP 3. List the unknowns and the number of equations. There are two unknowns, $[H_3O^+]$ and $[OH^-]$, and one equation.

STEP 4. Write one additional equation. This equation cannot be a mass balance equation since no solute has been added to the water.

$$[H_3O^+] = [OH^-] \qquad (2\text{-}10)$$

This can be viewed as either a CBE or PBE.

STEP 5. Solve Eqns. (2-8) and (2-10) for $[H_3O^+]$. Substitute (2-10) into (2-8) and solve for $[H_3O^+]$.

$$K_w = [H_3O^+]^2 \quad \text{or} \quad [H_3O^+] = K_w^{1/2} \qquad (2\text{-}11)$$

If one takes the negative logarithm of both sides of (2-11), the following results

$$-\log[H_3O^+] = pH = -(½)\log K_w = -(-14.00)/2 = 7.00 \qquad (2\text{-}12)$$

Keep in mind that the values of equilibrium constants change with temperature, and in fact K_w increases with increasing temperature. Thus the pH of pure water is 7.00 only at 25°C. Pure water must be neutral since we have added neither acid nor base to it. Water solutions can also be neutral; this occurs also when $[H_3O^+] = [OH^-]$, when the concentration of the acidic species equals that of the basic species. Since the K_w expression *must* be obeyed at equilibrium in *all* water solutions, a neutral solution must also have a pH of 7.00 at 25°C. The "pH" of any amphiprotic solvent can be calculated in exactly the same way from the autoprotolysis constant.

Remember that the definition of neutrality is that $[H_3O^+] = [OH^-]$, not that the pH = 7.00.

What is the pD of pure D_2O (heavy water) at 25°C if pK_{auto} is 14.869? The problem is solved in exactly the same manner as above except that D is substituted for H in all equations, *e.g.* H_3O^+ becomes D_3O^+. As above the result is

$$pD = -(½)\log K_{auto} = (½)pK_{auto} = 14.869/2 = 7.435$$

2.4.2 SOLUTIONS OF STRONG ACIDS.

For such solutions one could solve for the concentration of several different species, but one usually wants the pH (or $[H^+]$) of the resulting solution. Using the BFM the procedure is as follows:

STEP 1. List the reactions that affect the pH. Let HS represent the strong acid. In this case there are two reactions that affect the pH.

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

$$HS + H_2O \rightarrow S^- + H_3O^+$$

STEP 2. Write the equilibrium expressions for the above reactions. Since the reaction involving HS is considered to go to completion, there is only one equilibrium expression.

$$K_w = [H_3O^+][OH^-] \qquad (2\text{-}8)$$

STEP 3. List the unknowns and the number of equations. There are three unknowns, $[S^-]$, $[OH^-]$, and $[H_3O^+]$, and one equation.

STEP 4. Write two additional equations.

$$F_{acid} = [S^-] \qquad \text{MBE} \qquad (2\text{-}13)$$

$$[H_3O^+] = [S^-] + [OH^-] \qquad \text{CBE or PBE} \qquad (2\text{-}14)$$

STEP 5. Solve Eqns. (2-8), (2-13), and (2-14) for $[H_3O^+]$. Substitute (2-13) into (2-14) to begin.

$$[H_3O^+] = F_a + [OH^-] \qquad (2\text{-}15)$$

Substitute (2-8) into (2-15).

$$[H_3O^+] = F_a + K_w/[H_3O^+] \qquad (2\text{-}16)$$

Rearrange (2-16) as follows:

$$[H_3O^+]^2 - F_a[H_3O^+] - K_w = 0 \qquad (2\text{-}17)$$

Using the quadratic formula this leads to the final result.

$$[H_3O^+] = \frac{F_a \pm \sqrt{F_a^{\,2} + 4K_W}}{2} \qquad (2\text{-}18)$$

All quadratic equations have two mathematically correct roots (solutions), as denoted by the "±" symbol in the quadratic formula. Only one of these roots will be chemically correct, however. In Eqn. (2-18) the term $(F_a^{\,2} + 4K_W)^{1/2}$ will always be larger than F_a, and thus the root with the negative sign will always be negative. Since negative concentrations are chemically impossible, this root is "chemically" incorrect and can be neglected. Thus we can write Eqn. (2-18) as

$$[H_3O^+] = \frac{F_a + \sqrt{F_a^{\,2} + 4K_W}}{2} \qquad (2\text{-}18a)$$

If the concentration of strong acid is high enough, that is if $F_a^{\,2} >> 4K_w$, or if $F_a >> 2(K_w)^{1/2}$, or if $F_a >> 2x10^{-7}$, then

$$[H_3O^+] = \frac{F_a + F_a}{2} = F_a \qquad (2\text{-}19)$$

This is the result when the autoprotolysis of water can be neglected. When the concentration of strong acid is very low, then the autoprotolysis provides a significant amount of hydronium ion and it must be included. This is the case for a 10^{-7} F solution of HCl.

$$[H_3O^+] = \{1.00x10^{-7} + (1.00x10^{-14} + 4.00x10^{-14})^{1/2}\}/2$$

$[H_3O^+] = 1.62x10^{-7}$

In the case of a solution of a strong acid hydronium ion is involved in two equilibria, that with water and that with the strong acid. Each reaction attempts to influence the final result and usually only one succeeds. That reaction which controls the concentration of interest could be called the "important" reaction, those which do not could be termed "unimportant". In most cases one, or at most just a few, of the possible reactions are important. The difficulty is recognizing the important reactions. As stated earlier, neglecting unimportant reactions does not affect the final result and usually makes the problem easier to solve. Neglecting important reactions leads to incorrect solutions.

Two factors determine whether a reaction is important to the final solution, the magnitude of the equilibrium constant and the concentrations of the reactants. One would suspect that, since the strong acid is much stronger than the weak acid water, only the reaction involving the strong acid would be important, and this is so until the strong acid reaches a concentration of less than 10^{-6} F. Between 10^{-6} and 10^{-8} F, both reactions are important, and finally below 10^{-8} F, only the reaction with water is important (the pH will be 7.0).

When solving such problems, how does one know when to neglect a reaction because it is unimportant? Experience and chemical intuition play a large part in this. Often one has to solve the problem with *all* reactions considered important and let the results determine which reaction is actually the most important. The approach taken in this text will be to set the problem up considering all possible reactions, and then to use intuition to simplify the problem.

What is the pH of a 0.00734 F solution of tetrafluoroboric acid? HBF_4 is a strong acid in water. Since the formality of the acid is much larger than $2x10^{-7}$, Eqn. (2-19) derived above can be used.

$[H^+] = F_a = 0.00734$

pH = -log(0.00734) = 2.13

2.4.3 SOLUTIONS OF STRONG BASES.

The usual examples of strong bases are the hydroxides of the alkali and alkaline earth elements (groups 1 and 2 or Ia and IIa). In basic solution the hydroxide ion is in excess and therefore it is more convenient to solve for the concentration of this ion (rather than H^+) and convert to pH as the last step. The procedure is as above with MOH representing the strong base.

STEP 1. The two reactions that affect $[OH^-]$ are as follows:

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

$$MOH \rightarrow M^+ + OH^-$$

STEP 2. Write the equilibrium expressions

$$K_w = [H_3O^+][OH^-] \qquad (2\text{-}8)$$

STEP 3. Unknowns: $[M^+]$, $[H_3O^+]$, $[OH^-]$; equations: one

STEP 4. Write two additional equations.

$$F_{base} = [M^+] \qquad \text{MBE} \qquad (2\text{-}20)$$

$$[M^+] + [H_3O^+] = [OH^-] \qquad \text{CBE} \qquad (2\text{-}21)$$

STEP 5. Substitute (2-20) into (2-21) to begin solving for $[OH^-]$.

$$F_b + [H_3O^+] = [OH^-] \qquad (2\text{-}22)$$

Substitute (2-8) into (2-22).

$$F_b + K_w/[OH^-] = [OH^-] \qquad (2\text{-}23)$$

Rearrange (2-23) as follows:

$$[OH^-]^2 - F_b[OH^-] - K_w = 0 \qquad (2\text{-}24)$$

and use the quadratic formula to obtain

$$[OH^-] = \frac{F_b \pm \sqrt{F_b^{\,2} + 4K_W}}{2} \qquad (2\text{-}25)$$

Notice the similarity between this equation and that for a strong acid, Eqn. (2-18). This similarity will continue all the way through acid-base equilibria. As with the strong acid, the strong base completely controls the $[OH^-]$ until F_b goes below 10^{-6} F. This results in the simple expression below.

$$[OH^-] = F_b \qquad (2\text{-}26)$$

Both the base and water share control until F_b drops below 10^{-8} F, after which the pOH is 7.0 (as is the pH) and water is in complete control. The pH is easily calculated from $[OH^-]$ using either

$$[H_3O^+] = K_w/[OH^-] \qquad (2\text{-}27)$$

or

$$pH = pK_w - pOH \qquad (2\text{-}28)$$

What mass of lithium hydroxide (a strong base, GFM = 23.948 g/mol) must be used to prepare 500 mL of a solution of pH 10.50? Since the pH is much greater than 8, the value below which the strong base is no longer in total control of the pH, Eqns. (2-26) and (2-28) above can be used to solve the problem.

$K_w = [H^+][OH^-]$ or $pK_w = pH + pOH$

$pOH = pK_w - pH = 14.00 - 10.50 = 3.50$

$[OH^-] = \text{antilog}(-3.50) = 10^{-3.50} = 3.16\text{x}10^{-4}$ M $= F_b$

mol $= F_b V = (3.16\text{x}10^{-4}$ mol/L$)(0.500$ L$) = 1.58\text{x}10^{-4}$ mol

mass = (mol)(GFM) = $(1.58\text{x}10^{-4}$ mol$)(23.948$ g/mol$) = 3.79\text{x}10^{-3}$ g = 3.79 mg.

2.4.4 SOLUTIONS OF WEAK ACIDS.

The approach taken to solve for the pH of solutions of weak acids is just the same except that the problem is a bit more complicated because of the incomplete reaction of the weak acid. Here the weak acid will be represented by HA.

STEP 1. The two reactions that affect $[H_3O^+]$ are:

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

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

STEP 2. List the equilibrium expressions.

$$K_w = [H_3O^+][OH^-] \tag{2-8}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{2-7}$$

STEP 3. Unknowns: $[H_3O^+]$, $[OH^-]$, $[HA]$, $[A^-]$; equations: two.

STEP 4. Write two additional equations.

$$[H_3O^+] = [OH^-] + [A^-] \qquad \text{CBE or PBE} \tag{2-29}$$

$$F_a = [HA] + [A^-] \qquad \text{MBE} \tag{2-30}$$

STEP 5. Solve for $[H_3O^+]$. Start by solving (2-29) for $[A^-]$ and substituting into (2-7).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-])}{[HA]} \tag{2-31}$$

Solve (2-30) for [HA] and substitute it into (2-31).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-])}{F_a-[A^-]} \tag{2-32}$$

Solve (2-29) for $[A^-]$ and substitute into (2-32).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-])}{F_a-[H_3O^+]+[OH^-]} \tag{2-33}$$

Equation (2-33) will be used to good advantage along with a little chemical intuition later.

The final step is to use (2-8) to remove $[OH^-]$ from (2-33) and give an equation involving only $[H_3O^+]$.

$$K_a = \frac{[H_3O^+]([H_3O^+]-K_W/[H_3O^+])}{F_a-[H_3O^+]+K_W/[H_3O^+]} \tag{2-34}$$

A little algebra can be used to rearrange this result as follows:

$$[H^+]^3 + K_a[H^+]^2 - (K_aF_a + K_w)[H^+] - K_aK_w = 0 \tag{2-35}$$

The final result is a *cubic*, what can be done now? (No one said that a reasonably exact treatment of nature would produce simple results.) There are three choices: 1) solve the cubic by successive approximation, 2) look at the cubic or any of its antecedents to see if there are any simplifications that can be made, 3) eliminate one of the original reactions and come up with a simpler solution (and perhaps make a mistake). If all else fails, choose the first option, it will give the correct answer. In this case method (2) will be attempted; this is most easily done by going back to Eqn. (2-33) and looking for methods of simplification.

again

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-])}{F_a-[H_3O^+]+[OH^-]} \tag{2-33}$$

Two sums appear in Eqn. (2-33), one in the numerator, one in the denominator. Sums are an excellent place to look when trying to make simplifications. If one or more of the terms in a sum is

small compared to the rest, it can be neglected and the sum can be simplified. *This does not apply to products*. In the case under study, the solution contains an acid and $[H_3O^+]$ must be greater than $[OH^-]$. If $[H_3O^+]>>[OH^-]$, then $[OH^-]$ can be dropped from both the numerator and denominator of Eqn. (2-33) and the equation becomes much simpler.

$$K_a = \frac{[H_3O^+][H_3O^+]}{F_a - [H_3O^+]} \tag{2-36}$$

Two questions arise: 1) how much larger must one term be than the other to be able to drop it, 2) how does one know that the first term is indeed that much larger than the second term? The answer to the first question (for the purposes of this text) is 20 times. If $[H_3O^+] \geq 20[OH^-]$, then one can neglect $[OH^-]$. This is conservative. The answer to the second question is "one doesn't know", but one goes ahead with the assumption and uses the final answer to determine if the assumption was valid. It does no harm to try an assumption; if it does not work, then try a different (but logical) assumption or solve the problem in its more complicated form by approximation. Assuming that $[H_3O^+] >> [OH^-]$, (2-36) is rearranged as follows:

$$[H^+]^2 + K_a[H^+] - K_aF_a = 0 \tag{2-37}$$

And applying the quadratic formula gives

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^{\,2} + 4K_aF_a}}{2} \qquad \text{if } [H^+] >> [OH^-] \tag{2-38}$$

The solution with the negative sign before the square root sign is chemically incorrect and therefore is not shown.

Examining (2-36) again, it will be noticed that a sum still exists in the denominator, and thus there is the possibility of further simplification. If it can be assumed that $F_a >> [H_3O^+]$ (this will occur if the weak acid "dissociates" very little), then (2-36) becomes

$$K_a = [H_3O^+][H_3O^+]/F_a \tag{2-39}$$

or

$$[H_3O^+] = \sqrt{K_aF_a} \qquad \text{if } [H_3O^+] >> [OH^-] \text{ and } F_a >> [H_3O^+] \tag{2-40}$$

What happens if it cannot be assumed that $[H_3O^+] >> [OH^-]$? There is still an assumption that can usually be made that will simplify the exact expression. Even if $[H_3O^+] \approx [OH^-]$, it usually can be assumed that $F_a >> ([H_3O^+]-[OH^-])$, since the two terms on the right hand side of this inequality are approximately equal. If this assumption can be made, the denominator of (2-33) becomes simply F_a, leading to

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-])}{F_a} \tag{2-41}$$

Substituting (2-8) into (2-41) gives

$$K_a = \frac{[H_3O^+]([H_3O^+] - K_W/[H_3O^+])}{F_a} \tag{2-42}$$

or

$$K_aF_a = [H_3O^+]^2 - K_w \tag{2-43}$$

which gives the final result

$$[H_3O^+] = \sqrt{K_aF_a + K_W} \qquad \text{if } F_a >> ([H_3O^+]-[OH^-]) \tag{2-44}$$

Thus one of the three equations, (2-38), (2-40), and (2-44), each listed above with the assumptions that apply to it, can be used for almost any case of a solution of a simple monoprotic weak acid. Eqns. (2-38) and (2-40) would result if the reaction of water to produce H_3O^+ were considered unimportant and not included in the derivation. This is the usual approach taken in introductory chemistry. Eqn. (2-44) includes the contribution of autoprotolysis and could not be derived using the simpler approach.

When does each equation apply? First it should be noted that (2-40) is a special case of (2-38), and thus (2-38) is more general and will apply any time that (2-40) applies. Eqn. (2-40) is just simpler to use when it can be applied. Eqn. (2-38) is usually used for solutions of "strong" weak acids ($pK_a < 4$), (2-40) is used for solutions of "medium" weak acids ($4 < pK_a < 10$), and (2-44) for "weak" weak acids ($pK_a > 10$).

A very easy approach is to try the simplest equation, (2-40), first and use the answer you get to check the assumptions. If both assumptions check, you have the correct answer. If the assumption that $[H_3O^+] >> [OH^-]$ fails, then use (2-44) and if the assumption that $F_a >> [H_3O^+]$ fails, then use (2-38). Whichever equation you finally use, you *must* check the assumptions associated with that equation.

Two examples will demonstrate the use of these equations.

Calculate $[H^+]$ in a solution 0.0100 F in $NaHSO_4$. To solve this problem one must first answer the question, "What sort of material is $NaHSO_4$?" Since it is a sodium salt it will undergo complete ionization according to

$$NaHSO_4 \rightarrow Na^+ + HSO_4^-$$

Does Na^+ interact in any way to affect the pH? Since the sodium ion is the cation of a strong base, it will have no effect on the pH. Does HSO_4^- have any affect on the pH? One can imagine two possible ways:

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-} \quad \text{(acts as an acid)}$$

$$HSO_4^- + H_2O \rightarrow H_2SO_4 + OH^- \quad \text{(acts as a base)}$$

Do one or both reactions occur? The first does, the second does not. How is this known? Sulfuric acid is a strong acid in water (the first proton only). Thus HSO_4^- has no desire to gain a proton (it is not a base in water) and the second reaction does not occur. However, HSO_4^- is a weak acid, since it has a K_a value of 1.02×10^{-2}. Thus the first reaction proceeds. Therefore, the solution in question is that of a monoprotic weak acid. Try Eqn. (2-40) first.

$$[H^+] = (K_aF_a)^{1/2} = \{(0.0102)(0.0100)\}^{1/2} = 0.0101 \text{ M}$$

Now the assumptions must be checked. Is $[H^+]>>[OH^-]$? If $[H^+]$ is approximately 0.01 M, then $[OH^-] = 1 \times 10^{-14}/0.01 = 1 \times 10^{-12}$ and the assumption checks. Is $F_a>>[H^+]$ or is 0.01>>0.0101? NO! This assumption does not check. Thus you should now use the equation which has as its only assumption the one which proved correct above, namely that $[H^+]>>[OH^-]$. That is Eqn. (2-38)

$$[H^+] = \{-K_a+(K_a^2+4K_aF_a)^{1/2}\}/2 = \{-0.0102+(1.04 \times 10^{-4}+4.08 \times 10^{-4})^{1/2}\}/2$$

$$[H^+] = 6.21 \times 10^{-3}$$

The assumption checks for this answer and therefore it must be correct.

What is the pH of a 0.00100 F solution of phenol (hydroxybenzene)? The pK_a of phenol is 10.00. Do not be fooled into thinking that hydroxybenzene is a base because of the hydroxy group. Any substance with a pK_a of 10 must be a weak acid. As usual try Eqn. (2-40) first. However, the first step is to calculate the value of K_a.

$pK_a = -\log K_a = 10.00$

$\log K_a = -10.00$ or $K_a = 10^{-10.00} = 1.00\times10^{-10}$

$[H^+] = (K_aF_a)^{½} = \{(1.00\times10^{-10})(0.00100)\}^{½} = 3.16\times10^{-7}$

Check the assumptions. Is $[H^+]>>[OH^-]$? $[OH^-] = 1\times10^{-14}/3.16\times10^{-7} = 3.16\times10^{-8}$. Thus $[H^+]$ is 10 times greater than $[OH^-]$, but not 20 times greater. This is not quite good enough. Note that although hydronium and hydroxide ion are approximately equal in concentration, both are much smaller than the formality of the acid. Thus use the equation with the assumption that $F_a>>[H^+]-[OH^-]$, Eqn. (2-44).

$[H^+] = (K_aF_a+K_w)^{½} = \{(1.00\times10^{-10})(0.00100)+1.00\times10^{-14})^{½} = 3.32\times10^{-7}$.

The assumption is that $F_a>>[H^+]-[OH^-]$ or $0.00100>>3.32\times10^{-7}-3\times10^{-8}$, which checks. Thus

$pH = -\log 3.32\times10^{-7} = 6.48$

Note that the exact answer was 3.32×10^{-7} and the approximate answer was 3.16×10^{-7}, very close to the exact answer. The reason for this is that the assumption that failed just barely failed. The greater the measure of failure in the assumption, the farther the approximate answer will be from the exact answer.

2.4.5 SOLUTIONS OF WEAK BASES.

pH calculations in solutions of bases are discussed much less often than acids, but these are no less important. *There are as many weak bases as there are acids, since each acid has a conjugate base*. What types of substances are weak bases? The first type that usually comes to mind is ammonia (NH_3) and the amines (CH_3NH_2, $C_2H_5NH_2$, $(CH_3)_2NH$, *etc.*). These react as follows:

$$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^-$$

The conjugate pairs are (acid/base): H_2O/OH^- and RNH_3^+/RNH_2 and the equilibrium expression is

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \qquad (2\text{-}45)$$

Remember that all weak acids have conjugate weak bases and thus solutions containing ions such as F^-, CO_3^{2-}, PO_4^{3-}, SO_3^{2-}, CH_3COO^-, *etc*. all contain weak bases.

The method of solution is exactly the same as the case of a weak acid. Since the hydroxide ion is the predominant species in a basic solution, it is easier to solve for its concentration and convert to hydronium ion in the final step. Here the weak base will be represented as B.

STEP 1. The reactions which affect $[OH^-]$ are:

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

$$B + H_2O \rightarrow HB^+ + OH^-$$

STEP 2. Write the equilibrium expressions.

$$K_w = [H_3O^+][OH^-] \qquad (2\text{-}8)$$

$$K_b = \frac{[HB^+][OH^-]}{[B]} \qquad (2\text{-}46)$$

STEP 3. Unknowns: $[H_3O^+]$, $[OH^-]$, $[HB^+]$, $[B]$; equations: two.

STEP 4. Write two more equations.

$$[H_3O^+] + [HB^+] = [OH^-] \qquad \text{CBE or PBE} \qquad (2\text{-}47)$$

$$F_b = [B] + [HB^+] \qquad \text{MBE} \qquad (2\text{-}48)$$

STEP 5. Eliminate all unknowns except $[OH^-]$. Solve (2-47) for $[HB^+]$ and substitute it into (2-46).

$$K_b = \frac{[OH^-]([OH^-]-[H_3O^+])}{[B]} \qquad (2\text{-}49)$$

Solve (2-48) for [B] and substitute it into (2-49)

$$K_b = \frac{[OH^-]([OH^-]-[H_3O^+])}{F_b - [HB^+]} \qquad (2\text{-}50)$$

Solve (2-47) for $[HB^+]$ and substitute it into (2-50)

$$K_b = \frac{[OH^-]([OH^-]-[H_3O^+])}{F_b - [OH^-] + [H_3O^+]} \qquad (2\text{-}51)$$

Another cubic equation results if (2-8) is used to eliminate $[H_3O^+]$ from (2-51). This will not be attempted, instead (2-51) will be simplified by making the appropriate assumptions. *Note* the similarity between (2-51) above and the equivalent equation, Eqn. (2-33), for a weak acid. The details of the simplification are exactly the same as in the case of the weak acid. Since the solution has to be basic, the first assumption is that $[H_3O^+] << [OH^-]$. This and the other assumptions listed below lead to the following results.

$$[OH\text{-}] = \frac{-K_b + \sqrt{K_b^{\,2} + 4K_bF_b}}{2} \qquad \text{if } [OH^-] >> [H_3O^+] \qquad (2\text{-}52)$$

$$[OH^-] = \sqrt{K_bF_b} \qquad \text{if } [OH^-] >> [H_3O^+] \text{ and if } F_b >> [OH^-] \qquad (2\text{-}53)$$

$$[OH^-] = \sqrt{K_bF_b + K_W} \qquad \text{if } F_b >> [OH^-]\text{-}[H_3O^+] \qquad (2\text{-}54)$$

These equations are used in exactly the same way as those for a weak acid and apply to the same types of solutions: use (2-52) for "strong" weak bases ($pK_b < 4$), use (2-53) for "medium" weak bases ($4 < pK_b < 10$), use (2-54) for "weak" weak bases ($pK_b > 10$). Note that you do not have to remember two sets of equations, one for acids and one for bases. The symmetry of acid-base systems in amphiprotic solvents allows the base equations to be obtained from the acid equations by the following simple substitutions:

$$K_a \rightarrow K_b, \quad F_a \rightarrow F_b, \quad [H_3O^+] \rightarrow [OH^-], \quad [OH^-] \rightarrow [H_3O^+]$$

One problem still remains, tables of equilibrium constants usually do not contain entries for both acids and bases, the only base constants normally listed are those for ammonia and the amines. Otherwise only acid constants are listed. If you were asked to determine the pH of a solution of NaF, what would you do? First of all you would have to realize that Na^+ does not affect the pH and that F^- is a weak base (the conjugate of HF). Thus the solution must have a pH greater than 7. You now attempt to find the K_b for F^-, but all you can find is the K_a for HF. However, this is all you need to calculate K_b. One proceeds by writing the acid-base reactions for the base and its conjugate acid and adding the two:

$$B + H_2O \rightarrow HB^+ + OH^- \qquad K_b = [HB^+][OH^-]/[B] \qquad (2\text{-}46)$$

$$HB^+ + H_2O \rightarrow B + H_3O^+ \qquad K_a = [B][H_3O^+]/[HB^+] \qquad (2\text{-}7)$$

$$2H_2O \rightarrow H_3O^+ + OH^- \qquad K_w = K_aK_b \qquad (2\text{-}55)$$

Thus if you know either K_a or K_b (and also K_w) you can calculate the other constant from Eqn. (2-55). This is a general relationship that applies to all amphiprotic solvents. Thus you would use the K_a value for HF to calculate the K_b for F^- in a solution of NaF.

Calculate the pH of a 0.0647 F solution of trimethyl amine. Trimethyl amine is a weak base with a K_b of $6.25\text{x}10^{-5}$. Try the simplest equation (2-53) first,

$$[OH^-] = (K_bF_b)^{1/2} = \{(6.25\text{x}10^{-5})(0.0647)\}^{1/2} = 2.01\text{x}10^{-3}$$

Check the assumptions. If $[OH^-] \approx 0.002$, then $[H^+] = 1\text{x}10^{-14}/0.002 = 5\text{x}10^{-12}$. Is $[OH^-]>>[H^+]$ or is $0.002>>5\text{x}10^{12}$? Yes, the assumption is valid. Is $F_b>>[OH^-]$ or is 0.0647>>0.00201? Yes, by a factor of 30. This assumption also is valid. Thus

$$pOH = -\log(0.00201) = 2.70$$

$$pH = 14.00 - 2.70 = 11.30$$

What is $[H_3O^+]$ in a solution 0.00125 F in sodium formate (HCOONa)? Again one needs to ask "What sort of material is sodium formate?" Since it is a sodium salt it will completely ionize.

$$HCOONa \rightarrow HCOO^- + Na^+$$

As mentioned above, the sodium ion will not affect the pH. What about the formate ion? One might imagine that the proton remaining on the ion might be acidic and react as follows:

$$HCOO^- + H_2O \rightarrow H_3O^+ + COO^{2-}$$

However, protons bonded to carbon are almost never acidic in aqueous solutions and the loss of a second positive charge to form the COO^{2-} ion will be very difficult. This reaction does not occur. On the other hand the formate ion could accept a proton, acting like a base.

$$HCOO^- + H_2O \rightarrow HCOOH + OH^-$$

This reaction forms formic acid, a well known compound. Thus this reaction is possible and it is concluded that sodium formate is a weak base, the formate ion being the conjugate of formic acid. The first step in the solution is the determination of K_b. This constant is not listed in the tables, thus it must be calculated from the K_a of formic acid, which is listed as $1.77\text{x}10^{-4}$, using Eqn. (2-55).

$$K_b = K_w/K_a = 1.00\text{x}10^{-14}/1.77\text{x}10^{-4} = 5.65\text{x}10^{-11}$$

Try the simplest equation (2-53) first.

$$[OH^-] = (K_bF_b)^{1/2} = \{(5.65\text{x}10^{-11})(0.00125)\}^{1/2} = 2.66\text{x}10^{-7}$$

Check the assumptions. $[H^+] = 1\text{x}10^{-14}/2.66\text{x}10^{-7} = 3.76\text{x}10^{-8}$. Is $[OH^-]>>[H^+]$ or is $2.66\text{x}10^{-7}>>3.76\text{x}10^{-8}$? No, not by a factor of 20. This assumption is not valid. However, it is obvious that both $[OH^-]$ and $[H^+]$ are much smaller than F_b. Therefore use Eqn. (2-54) for which this assumption is valid.

$[OH^-] = (K_bF_b+K_w)^{1/2} = \{(5.65x10^{-11})(0.00125)+1.00x10^{-14}\}^{1/2} = 2.84x10^{-7}$

The assumption that $F_b >> [OH^-]-[H^+]$ is valid. Thus

$[H_3O^+] = K_w/[OH^-] = 1.00x10^{-14}/2.84x10^{-7} = 3.52x10^{-8}$

2.5 ACID-BASE MIXTURES

With the equations derived above you should be able to determine the pH of any solution containing a single monoprotic acid or base, regardless of its strength or concentration. Unfortunately, nature seldom allows one the luxury of such simple solutions in the real world. Actual samples such as sea water, body fluids, and industrial wastes are usually complex mixtures. The topic of mixtures must therefore be considered, but only the surface will be scratched.

2.5.1 A MIXTURE OF A WEAK ACID AND ITS CONJUGATE BASE.

Such mixtures are quite common and very useful in many branches of science. When acetic acid and sodium acetate are mixed, most individuals think of this as a mixture of an acid and a "salt". However, it should be thought of as a mixture of a weak acid and a weak base. The more acid that is present, the lower the pH will be, the more base, the higher the pH. The amount of base present can be determined by titration with a strong acid, the amount of acid by titration with a strong base.

The pH of the solution will be determined not only by the amounts of acid and base present, but by the relative strengths of the acid and the base. Remember that as the acid gets stronger, its conjugate base gets weaker ($K_w = K_aK_b$). The only unusual aspect about such a mixture is that the acid and the base do not react directly with each other. We usually think of acids and bases as reacting when mixed, but in this case there is no net reaction

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

The pH of such a mixture is determined in the usual manner. As in the chemical equation above HA will represent the weak acid and A^- its conjugate base. The A^- must come from some salt such as NaA or KA. If the weak base is a derivative of ammonia, then its conjugate acid must come from a salt such as NH_4Br or CH_3NH_3Cl.

STEP 1. There are now three reactions which affect the pH:

$2H_2O \rightarrow H_3O^+ + OH^-$	contribution of water
$HA + H_2O \rightarrow H_3O^+ + A^-$	contribution of weak acid
$A^- + H_2O \rightarrow HA + OH^-$	contribution of weak base

STEP 2. Write the equilibrium expressions for the above reactions.

$$K_w = [H_3O^+][OH^-] \qquad (2\text{-}8)$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2\text{-}7)$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} \qquad (2\text{-}46)$$

STEP 3. Unknowns: $[H_3O^+]$, $[OH^-]$, $[HA]$, $[Na^+]$, $[A^-]$ (here it is assumed that the base was introduced as the sodium salt). One might be tempted to say that there are three equations, but remember that for a mathematical solution to the problem the equations must be *independent*. The three equilibrium expressions above are not independent; from any of the two, one can obtain the third, since $K_w = K_aK_b$. Thus there are only *two* independent equations and three additional equations must be written to solve the problem.

STEP 4. List the three additional equations.

$$[H_3O^+] + [Na^+] = [OH^-] + [A^-] \qquad \text{CBE} \qquad (2\text{-}56)$$

$$F_b = [Na^+] \qquad \text{MBE} \qquad (2\text{-}57)$$

$$F_a = [HA] + [H_3O^+] - [OH^-] \qquad \text{MBE} \qquad (2\text{-}58)$$

The "derivation" of (2-58) is not necessarily intuitively obvious. If only a weak acid were present in solution, the MBE would be $F_a = [HA] + [A^-]$ and one might be tempted to try the same approach here. However, here there is an independent source of A^-, NaA, and this approach *cannot* be used. Normally very little of the acid "dissociates", especially in the presence of added amounts of its conjugate base. Thus $F_a \approx [HA]$, but $[HA]$ will not be exactly equal to F_a since some of the acid will react with water, tending to make $[HA] < F_a$, and some of the base will react with water, tending to make $[HA] > F_a$. To correct for the reaction of the acid with water one might be tempted to write that $F_a \approx [HA] + [H_3O^+]$, since one H_3O^+ forms for every HA that reacts. The right hand side of this latter expression is larger than F_a since H_3O^+ is also produced by the autoprotolysis of water and HA is produced by the reaction of A^- with water, neither of these has yet been taken into account. However, from these latter two reactions, one also obtains one OH^- each. Thus the final correction can be made by subtracting $[OH^-]$ to get (2-58).

STEP 5. Eliminate all unknowns except $[H_3O^+]$. Equations (2-7) and (2-8) will be used as the two independent equilibrium expressions. Solve (2-56) for $[A^-]$ and substitute into (2-7).

$$K_a = \frac{[H_3O^+]([H_3O^+]+[Na^+]-[OH^-])}{[HA]} \qquad (2\text{-}59)$$

Substitute (2-57) into (2-59).

$$K_a = \frac{[H_3O^+](F_b+[H_3O^+]-[OH^-])}{[HA]} \qquad (2\text{-}60)$$

Solve (2-58) for [HA] and substitute into (2-60).

$$K_a = \frac{[H_3O^+](F_b+[H_3O^+]-[OH^-])}{F_a-[H_3O^+]+[OH^-]} \qquad (2\text{-}61)$$

As in the other cases that have been discussed, one could go on to solve (2-8) for $[OH^-]$ and eliminate all unknowns except $[H_3O^+]$ from (2-61), producing a cubic equation. Again, as before, the possibility of simplifications will be examined.

If the weak acid is a much stronger acid than its conjugate base is a base, one might reasonably assume that $[H_3O^+] >> [OH^-]$, which would lead to:

$$K_a = \frac{[H_3O^+](F_b+[H_3O^+])}{F_a-[H_3O^+]} \qquad (2\text{-}62)$$

or $$K_aF_a - K_a[H_3O^+] = [H_3O^+]^2 + F_b[H_3O^+] \quad (2\text{-}63)$$

or $$[H_3O^+]^2 + (F_b + K_a)[H_3O^+] - K_aF_a = 0 \quad (2\text{-}64)$$

Applying the quadratic formula leads to the result:

$$[H_3O^+] = \frac{-(F_b + K_a) + \sqrt{(F_b + K_a)^2 + 4K_aF_a}}{2} \qquad \text{if } [H^+] >> [OH^-] \quad (2\text{-}65)$$

If, on the other hand, the base is much stronger than the acid, then (2-61) becomes:

$$K_a = \frac{[H_3O^+](F_b - [OH^-])}{F_a + [OH^-]} \quad (2\text{-}66)$$

In this case (2-8) is solved for $[OH^-]$ and used to eliminate $[OH^-]$ in (2-66).

$$K_a = \frac{[H_3O^+](F_b - K_W/[H_3O^+])}{F_a + K_W/[H_3O^+]} \quad (2\text{-}67)$$

Through standard algebraic manipulation this gives

$$F_b[H_3O^+]^2 - (K_aF_a + K_w)[H_3O^+] - K_wK_a = 0 \quad (2\text{-}68)$$

Application of the quadratic formula gives

$$[H_3O^+] = \frac{K_aF_a + K_w + \sqrt{(K_aF_a + K_W)^2 + 4K_WK_aF_b}}{2F_b} \qquad \text{if } [OH^-] >> [H^+] \quad (2\text{-}69)$$

Very often both the acid and base are "medium" weak and thus neither $[H_3O^+]$ nor $[OH^-]$ will be very large (less than 10^{-4}). If this is the case one can almost always assume that $F_a >> [OH^-]-[H^+]$ and that $F_b >> [H^+]-[OH^-]$. Eqn. (2-61) then simplifies to

$$K_a = \frac{[H_3O^+]F_b}{F_a} \quad (2\text{-}70)$$

or $$[H_3O^+] = \frac{K_aF_a}{F_b} \qquad \text{if } F_a >> [OH^-]-[H^+] \text{ and } F_b >> [H^+]-[OH^-] \quad (2\text{-}71)$$

This is the infamous Henderson-Hasselbalch equation, used, sometimes incorrectly, in calculations involving buffer solutions. More about this later. These are three of the more useful equations for a mixture of a weak acid and its conjugate base. There are other simplifications that lead to somewhat different results, depending on the circumstances.

To apply these equations one might ask, "How do you know when an acid is much stronger than its conjugate base?" Look at the value of K_a. If $pK_a < 4$, then $pK_b > 10$ and the acid will be much stronger; if $4 < pK_a < 10$, then $10 > pK_b > 4$ and the two will be "very roughly" the same strength; if $pK_a > 10$, then $pK_b < 4$ and the base will be much stronger. However, rather than memorize these three equations, two of which are rather complicated, and then guess which one to use, it is usually better to remember (2-71), the H-H equation, and the assumptions used in its derivation, and (2-61), the exact equation. Try (2-71) first and check its assumptions. If both assumptions are valid, your answer is correct. If not, the inaccurate answer obtained will still lead you to the correct assumptions to make in (2-61) to get the proper equation to solve the problem.

What is the pH of a solution made by mixing 50.0 mL of 0.0200 F pyruvic acid ($CH_3COCOOH$) and 100.0 mL of 0.0100 F sodium pyruvate? K_a of pyruvic acid is $3.24x10^{-3}$. The name indicates that pyruvic acid is an acid and the K_a indicates that it is a weak acid. What is sodium pyruvate? The conjugate base of pyruvic acid. Thus the resulting solution is a mixture of a weak acid and its conjugate base.

F_a = (0.0200 mol/L)(50 mL/150 mL) = 0.00667 F

F_b = (0.0100 mol/L)(100 mL/150 mL) = 0.00667 F

Try the simplest equation (2-71) (H-H) first.

$[H^+] = K_aF_a/F_b = 3.24x10^{-3}(0.00667)/0.00667 = 3.24x10^{-3}$ mol/L

Check the assumptions. Is $F_a >> [H^+] - [OH^-]$ (in this case $[OH^-]$ will be about $3x10^{-12}$ and is so small compared to $[H^+]$ that it can be neglected) or is 0.00667 >> 0.00324? No, this assumption is not valid. The same will be true of the assumption involving F_b. However, it is obvious that since $[H^+] >> [OH^-]$, equation (2-65) derived above will be appropriate.

$[H^+] = \{-(F_b+K_a)+[(F_b+K_a)^2 + 4K_aF_a]^{1/2}\}/2$

$[H^+] = \{-(0.00667+0.00324)+[(0.00991)^2 + 8.64x10^{-5}]^{1/2}\}/2 = 0.00184$ mol/L

In this case the assumption that $[H^+] >> [OH^-]$ is valid. Thus

pH = -log(0.00184) = 2.47

What is the pH of the solution that results when 50.0 mL of 0.100 F HNO_3 are mixed with 100.0 mL of 0.10 F NH_3? When solving such a problem the first question to ask is "What are the reactants?" Nitric acid is a strong acid, ammonia is a weak base. Will these substances react. Yes, a strong acid will always react with a base, either weak or strong. The next step is to write the chemistry.

$$NH_3 + HNO_3 \rightarrow NH_4^+ + NO_3^-$$

This is a valid way to write the reaction and it provides the correct stoichiometry, which is important, but it does not describe what really happens, since the molecule, HNO_3, does not exist in solution. A more accurate chemical description would be

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

The next step is to determine the extent of the reaction.

mol HNO_3 = (0.100 mol/L)(0.0500 L) = 0.00500 mol

mol NH_3 = (0.100 mol/L)(0.100 L) = 0.0100 mol

Since this is a 1:1 reaction, nitric acid is the limiting reagent. Thus no nitric acid remains, 0.00500 mol of NH_3 is converted to NH_4^+, and 0.00500 mol of NH_3 remains unreacted. The solution is therefore a mixture of NH_4^+ and NH_3, a mixture of a weak acid and its conjugate base. The K_b for ammonia is $1.75x10^{-5}$.

F_a = 0.00500 mol/0.150 L = 0.0333 mol/L

F_b = 0.00500 mol/0.150 L = 0.0333 mol/L

K_a (for ammonium ion) = $1.00x10^{-14}/1.76x10^{-5} = 5.68x10^{-10}$

Try the simplest equation (H-H) first.

$[H^+] = K_aF_a/F_b = 5.68x10^{-10}(0.0333)/(0.0333) = 5.68x10^{-10}$ mol/L

Check the assumptions. In this case $[OH^-] = 1.76x10^{-5}$. Since $F_a = F_b$, both assumptions are the same. Is $F_a >> [H^+] - [OH^-]$ or is $0.0333 >> 5.68x10^{-10} - 1.76x10^{-5}$? Yes, both assumptions are valid. Thus

$pH = -log(5.68x10^{-10}) = 9.25$

2.5.2 A MIXTURE OF A STRONG ACID AND A WEAK ACID.

To solve a problem involving such a mixture, it might not be unreasonable to assume that the strong acid would control the pH, or that its reaction with water (its "dissociation") would be the important reaction and that other reactions could be neglected. This is often the case, as will be shown. However, the usual procedure of not neglecting any reactions will be followed.

STEP 1. The reactions that affect the $[H_3O^+]$ are as follows:

$2H_2O \rightarrow H_3O^+ + OH^-$	contribution of water
$HS + H_2O \rightarrow H_3O^+ + S^-$	contribution of strong acid
$HA + H_2O \rightarrow H_3O^+ + A^-$	contribution of weak acid

STEP 2. List the equilibrium expressions.

$$K_w = [H_3O^+][OH^-] \tag{2-8}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{2-7}$$

STEP 3. Unknowns: $[H_3O^+]$, $[OH^-]$, $[HA]$, $[S^-]$, $[A^-]$; equations: two.

STEP 4. Write three more equations:

$$[H_3O^+] = [S^-] + [A^-] + [OH^-] \quad \text{CBE or PBE} \tag{2-72}$$

$$F_s = [S^-] \quad \text{MBE} \tag{2-73}$$

$$F_w = [HA] + [A^-] \quad \text{MBE} \tag{2-74}$$

STEP 5. Eliminate all unknowns except $[H_3O^+]$. Solve (2-72) for $[A^-]$ and substitute into (2-7).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[S^-]-[OH^-])}{[HA]} \tag{2-75}$$

Solve (2-74) for [HA] and substitute into (2-75).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-]-[S^-])}{F_w-[A^-]} \tag{2-76}$$

Solve (2-72) for $[A^-]$ and substitute into (2-76).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-]-[S^-])}{F_w-[H_3O^+]+[S^-]+[OH^-]} \tag{2-77}$$

Substitute (2-73) into (2-77).

$$K_a = \frac{[H_3O^+]([H_3O^+]-[OH^-]-F_s)}{F_w - [H_3O^+] + [OH^-] + F_s} \tag{2-78}$$

Again, rather than trying to eliminate $[OH^-]$ with (2-8), simplifications to (2-78) above will be made. With two acids present, it is extremely unlikely that $[H_3O^+]$ will not be much larger than $[OH^-]$. Thus it will be assumed that $[H_3O^+] >> [OH^-]$. This results in

$$K_a = \frac{[H_3O^+]([H_3O^+]-F_s)}{F_w - [H_3O^+] + F_s} \tag{2-79}$$

A little algebra and the application of the quadratic formula lead to:

$$[H_3O^+] = \frac{F_s - K_a \pm \sqrt{(F_s - K_a)^2 + 4K_a(F_w + F_s)}}{2} \qquad \text{if } [H^+] >> [OH^-] \tag{2-80}$$

Further simplifications can be easily made to (2-80) without having to make any guesses. Both F_s and K_a are known, and it will be obvious if one is large with respect to the other. Usually $F_s >> K_a$, in which case the following results:

$$[H_3O^+] = \frac{F_s \pm \sqrt{F_s^2 + 4K_a(F_w + F_s)}}{2} \tag{2-81}$$

Again from the knowns it will be obvious whether $F_s^2 >> 4K_a(F_w+F_s)$. When $F_s >> K_a$, usually $F_s^2 >> 4K_a(F_w+F_s)$. Then the result is very simple.

$$[H_3O^+] = \frac{F_s + \sqrt{F_s^2}}{2} = F_s \qquad \text{if } [H_3O^+] >> [OH^-] \text{ and } F_s >> K_a \tag{2-82}$$

Equation (2-79) would result if the autoprotolysis of water were considered unimportant, and (2-82) would result if both the autoprotolysis and the reaction of the weak acid were considered unimportant. This latter is the usual case, provided that the concentration of strong acid is not too low. Again it is perhaps simplest to remember (2-82) and the assumptions associated with it. Apply it first and check the assumptions. If these should fail, then use (2-78) to get to the correct equation.

Calculate the pH of a solution made by mixing 50.0 mL of 0.00400 F HCl and 50.0 mL of 0.00200 F sodium acetate. Again you must first ask the question "What are the materials involved?" HCl is a strong acid and sodium acetate is a weak base (the conjugate of acetic acid). These will react according to

$$HCl + CH_3COONa \rightarrow CH_3COOH + NaCl$$

A more accurate chemical picture is as follows:

$$H_3O^+ + CH_3COO^- \rightarrow CH_3COOH + H_2O$$

Mol HCl = 0.00400 mol/L(0.0500 L) = 0.000200 mol

Mol CH_3COONa = 0.00200 mol/L(0.0500 L) = 0.000100 mol

Thus the sodium acetate is the limiting reagent, since the reaction is 1:1. All the sodium acetate is consumed, 0.000100 mol of acetic acid is produced, and 0.000100 mol of HCl remains unreacted. The result is a

mixture of a weak acid (pK_a = 4.76) and a strong acid (plus some sodium chloride which does not affect the pH).

F_w = 0.000100 mol/0.100 L = 0.00100 mol/L

F_s = 0.000100 mol/0.100 L = 0.00100 mol/L

Try the simplest equation (2-82) first.

$[H^+] = F_s = 0.00100$ F

The assumption that $[H^+] >> [OH^-]$ is certainly valid. Is $F_s >> K_a$? K_a = antilog(-4.76) = 1.75×10^{-5}. Is 0.001 >> 1.75×10^{-5}? Yes, by about a factor of 50. Is $F_s^2 >> 4K_a(F_w + F_s)$ or is $1 \times 10^{-6} >> 1.41 \times 10^{-7}$? No, not by a factor of 20. Thus use (2-81).

$[H^+] = \{F_s + (F_s^2 + 4K_a(F_w + F_s))^{1/2}/2$

$[H^+] = \{0.00100 + (1.00 \times 10^{-6} + 1.41 \times 10^{-7})^{1/2}\}/2 = 0.00103$ mol/L

pH = -log(0.00103) = 2.99

The result from the simple equation would have been pH 3.00, the exact equation gave pH 2.99. The simple equation ignores both the contribution of water and the weak acid, the more exact equation ignores only the contribution of water. Thus the acetic acid reduced the pH from 3.00 (which would have been the pH if the solution contained no acetic acid) to 2.99. The strong acid almost completely controls the pH of this solution.

2.5.3 A MIXTURE OF A STRONG BASE AND A WEAK BASE.

The derivation is exactly the same as above. Rather than go through it, use will be made of the ability to make substitutions to go from the acid case to the base case. Any equation for an acid system can be converted to the corresponding base system (you can check this with the equations derived above) using the following substitutions: $[H^+] \rightarrow [OH^-]$, $[OH^-] \rightarrow [H^+]$, $K_a \rightarrow K_b$, and $F_a \rightarrow F_b$. The exact equation for the acid case, (2-78) above, becomes for the case of a mixture of bases:

$$K_b = \frac{[OH^-]([OH^-] - [H_3O^+] - F_s)}{F_w - [OH^-] + [H_3O^+] + F_s} \qquad (2\text{-}83)$$

This almost always simplifies to (assuming $[OH^-] >> [H_3O^+]$):

$$K_b = \frac{[OH^-]([OH^-] - F_s)}{F_w - [OH^-] + F_s} \qquad (2\text{-}84)$$

On application of algebra and the quadratic formula this leads to:

$$[OH^-] = \frac{F_s - K_b \pm \sqrt{(F_s - K_b)^2 + 4K_b(F_w + F_s)}}{2} \qquad \text{if } [OH^-] >> [H_3O^+] \qquad (2\text{-}85)$$

And (2-85) usually simplifies to:

$$[OH^-] = F_s \qquad \text{if } [OH^-] >> [H_3O^+] \text{ and } F_s >> K_b \qquad (2\text{-}86)$$

In all the above equations F_s and F_w are the formalities of the strong and weak bases respectively.

2.5.4 SUMMARY

It probably seems that the above involves a considerable amount of algebra which is almost impossible to remember. However, all the equations involving weak acids are very similar and have the same general form. Table 2-1 below lists the exact equations and the simplest equations, along with the associated assumptions, for all the systems considered above. This is all that really needs to be remembered.

Table 2-1

System	Exact Equation	Simplest Equation	Assumptions
HS	$[H^+] = \frac{F_a + \sqrt{F_a^2 + 4K_w}}{2}$	$[H^+] = F_a$	$F_a > 40(K_w)^{1/2}$
HA	$K_a = \frac{[H^+]([H^+]-[OH^-])}{F_a - [H^+] + [OH^-]}$	$[H^+] = \sqrt{K_a F_a}$	$[H^+] > 20[OH^-]$ $F_a > 20[H^+]$
HA + A^-	$K_a = \frac{[H^+](F_b + [H^+] - [OH^-])}{F_a - [H^+] + [OH^-]}$	$[H^+] = \frac{K_a F_a}{F_b}$	$F_a > 20([OH^-]-[H^+])$ $F_b > 20([H^+]-[OH^-])$
HS + HA	$K_a = \frac{[H^+]([H^+]-[OH^-]-F_s)}{F_w - [H^+] + [OH^-] + F_s}$	$[H^+] = F_s$	$[H^+] > 20[OH^-]$, $F_s > 20K_a$ $F_s^2 > 80K_a(F_s+F_w)$

To obtain the equations for solutions containing bases, simply use the equation above which would fit the base case and make the following substitutions:

$$[H^+] \rightarrow [OH^-],\ [OH^-] \rightarrow [H^+],\ K_a \rightarrow K_b,\ F_a \rightarrow F_b$$

Try the simplest equation first and check the assumptions. If all assumptions are valid, the answer is correct. If one or more assumptions are not valid, use the approximate result from the simple equation to make appropriate simplifications to the exact equation and solve, with a little algebra, for the desired quantity.

2.6 THEORY OF TITRATIONS

Some of the solution equilibrium theory that was presented above will now be used in determining what occurs during a titration. It is important to understand what happens during a titration in order to be able to set up a titration and choose an indicator properly. Studying titrations is also a good way to learn some basic chemistry, since titrations are just chemical reactions carried out in a rather specific manner.

If one considers the general titration reaction:

$$T + U \rightarrow P_1 + P_2$$

The driving force for this reaction is related to the magnitude of the equilibrium constant:

$$K_e = \frac{[P_1][P_2]}{[T][U]} \qquad (2\text{-}87)$$

In the above T is the titrant (it will be considered to be the standard), U is the titrand (considered to be the unknown), and P_1 and P_2 are products. F_t will be the formality of the titrant (*in the buret*) and F_u will be the formality of U in the titration flask *before any titrant has been added*. In an actual titration F_t must be known and F_u is unknown. In studying titrations it will be assumed that both F_t and F_u are known.

A single step titration can be considered to consist of four distinct regions for the purpose of understanding what is occurring in the titration flask:

REGION 1, before the addition of any titrant. At this point there is no T, P_1, or P_2 in the flask. $[U] = f(F_u)$, but [U] is not necessarily equal to F_u.

REGION 2, after the addition of titrant but before the equivalence point. In this region T is the limiting reagent, and therefore there will be very little T in solution. If the reaction went totally to completion, [T] would be zero. Only U, P_1, and P_2 are present in measurable amounts.

REGION 3, the equivalence point. By definition this is the point at which there would be neither T nor U present if the reaction went to completion. In reality there is very little of either present and there is a simple relationship between [U] and [T]. Only P_1 and P_2 are present in measurable amounts.

REGION 4, after the equivalence point. In this region U is the limiting reagent, and therefore there will be very little U in solution. If the reaction went totally to completion, [U] would be zero. Only T, P_1, and P_2 are present in measurable amounts.

The method for determining what is actually present during a titration depends on the region, as will be demonstrated below.

2.6.1 STRONG ACID - STRONG BASE TITRATIONS

Acid-base titrations will be used as examples of titrations in general. Although it is not correct to state that "if you've seen one titration, you've seen them all", all titrations are very similar, and studying only one type in detail will cover the material sufficiently for the purposes of this text.

All strong acids are levelled to H_3O^+ and all strong bases are levelled to OH^- in water, so the titration reaction is simply:

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

and the equilibrium constant is

$$K_e = 1/[H_3O^+][OH^-] = 1/K_w = 1.00\text{x}10^{14}$$

Any reaction with an equilibrium constant this large is driven strongly to the right.

For this case the variation in the concentrations of all substances present during the titration will be examined just to obtain a general idea of what happens during the titration. The reaction between HCl (considered the unknown or titrand) and NaOH (considered the titrant) will be used as the example. Keep in mind that any strong acid or base would give the same results, since these are levelled to H_3O^+ and OH^- in water. In this example Na^+ and Cl^- are spectator ions and do not enter into the titration reaction. Nevertheless the concentrations of these ions will be determined, as well as those of H_3O^+ and OH^-.

One problem in understanding titrations is keeping the formalities of all the materials straight in one's mind. F_t is the formality of the titrant in the buret and is a fixed value; F_u is the formality of the

unknown in the flask *before* the titration and is also a fixed value. In all the examples to be considered, F_t will be considered equal to F_u and the volume of unknown at the start will be 50.00 mL, just for convenience. Thus, since all reactions considered will be 1:1, the equivalence point will always be at 50.00 mL of titrant added. The actual formalities of the materials in the flask during the titration will be different from either F_t or F_u, but will be related to these values and the volume of titrant added. Most readers realize that the titration reaction causes the major part of this difference, but remember that the volume in the titration flask is also increasing and that dilution will also have an effect on the formalities.

In the case of the reaction of HCl and NaOH, Cl^- is neither added to the flask nor is it consumed in the reaction. Thus the number of moles of Cl^- is constant and the $[Cl^-]$ decreases slightly due to dilution. The calculation of the concentration of Cl^- does not depend on the region of the titration.

$$[Cl^-] = \text{mol}/V = F_u V_u/(V_u+V_t) = 0.05F_u/(0.05+V_t) \qquad (2\text{-}88)$$

and

$$\text{pCl} = -\log[Cl^-] \qquad (2\text{-}89)$$

Here V_u and V_t refer to the volumes of unknown and titrant respectively.

Na^+ is continuously being added to the flask, but is not reacting in any way. Thus $[Na^+]$ will continuously increase and the calculation of $[Na^+]$ will not depend on the region of the titration.

$$[Na^+] = F_t V_t/(V_u+V_t) = F_t V_t/(0.05+V_t) \qquad (2\text{-}90)$$

and

$$\text{pNa} = -\log[Na^+] \qquad (2\text{-}91)$$

The calculation of $[H_3O^+]$ and $[OH^-]$, since these are involved in the titration reaction, will depend on the titration region. This will now be examined. In the following F_a will be the formality of the strong acid *actually present* in the flask at any point and F_b will be the formality of the strong base *actually present* in the flask at any point in the titration. These are almost always different from F_t and F_u.

REGION 1. This is simply a solution of a strong acid.

$$[H^+] = F_a = F_u \qquad (2\text{-}92)$$

$$\text{pH} = -\log[H^+] \qquad (2\text{-}9)$$

and

$$\text{pOH} = 14.00 - \text{pH} \qquad (2\text{-}28)$$

REGION 2. Some of the strong acid has been consumed, but no strong base is yet present. Only the strong acid affects the pH.

Mol acid remaining = mol acid original - mol base added

$$F_a = (\text{mol acid remaining})/(\text{total volume}) = (V_u F_u - V_t F_t)/(V_u+V_t) \qquad (2\text{-}93)$$

$$[H^+] = F_a = (0.05F_u - V_t F_t)/(0.05+V_t) \qquad \text{if } F_a > 40K_w^{1/2} \qquad (2\text{-}94)$$

REGION 3. In this region there is neither strong acid nor strong base present. This is simply a solution of NaCl in this example. Since neither Na^+ nor Cl^- affect the pH, the pH is that of pure water.

$$[H^+] = (K_w)^{1/2} \quad \text{or} \quad \text{pH} = 7.00 \text{ at } 25^oC \qquad (2\text{-}12)$$

REGION 4. All the strong acid is now gone and there is excess strong base present. Thus the pH of the solution is calculated with this in mind.

Mol base present = total mol base - mol of orig. acid

$$F_b = \text{(mole base present)/(total volume)} = (V_tF_t - V_uF_u)/(V_u+V_t) \quad (2\text{-}95)$$

$$[OH^-] = F_b = (V_tF_t-0.05F_u)/(0.05+V_t) \qquad \text{if } F_b>40K_w^{1/2} \quad (2\text{-}96)$$

$$[H_3O^+] = K_w/[OH^-] \quad (2\text{-}8)$$

Examples of calculations in each of the regions are shown below. In all of these it is assumed the $F_t = F_u$ = 0.100 and that V_u = 50.0 mL.

REGION 1, before addition of any titrant. The solution contains a strong acid and the total volume is 50.0 mL

$[Na^+]$ = 0 mol/L

$[Cl^-]$ = (0.0500 L)(0.100 mol/L)/(0.0500 L) = 0.100 mol/L

$[H^+] = F_a = F_u$ = (0.0500 L)(0.100 mol/L)/(0.0500 L) = 0.100 mol/L

$[OH^-] = 1.00\text{x}10^{-14}/0.100 = 1.00\text{x}10^{-13}$ mol/L

REGION 2, after 30.0 mL of base have been added. The solution still contains a strong acid and the total volume is 80.0 mL.

$[Na^+]$ = 0.100 mol/L(0.0300 L)/(0.0800 L) = 0.0375 mol/L

$[Cl^-]$ = 0.100 mol/L(0.0500 L)/(0.0800 L) = 0.0625 mol/L

$[H^+]= F_a$ = ((0.0500 L)(0.100 mol/L)-(0.0300 L)(0.100 mol/L))/(0.0800 L) = 0.0250 mol/L

$[OH^-] = 1.00\text{x}10^{-14}/0.0250 = 4.00\text{x}10^{-13}$ mol/L

REGION 3, after 50.0 mL of base have been added. The solution contains neither a strong acid nor a strong base and the total volume is 100.0 mL.

$[Na^+] = [Cl^-]$ = 0.100 mol/L(0.0500 L)/(0.100 L) = 0.0500 mol/L

$[H^+] = [OH^-] = 1.00\text{x}10^{-7}$ mol/L

REGION 4, after 70.0 mL of base have been added. The solution contains a strong base and the total volume is 120.0 mL.

$[Na^+]$ = 0.100 mol/L(0.0700 L)/(0.120 L) = 0.0582 mol/L

$[Cl^-]$ = 0.100 mol/L(0.0500 L)/(0.120 L) = 0.0417 mol/L

$[OH^-] = F_b$ = ((0.0700 L)(0.100 mol/L)-(0.0500 L)(0.100 mol/L))/(0.120 L) = 0.0167 mol/L

$[H^+] = 1.00\text{x}10^{-14}/0.0167 = 6.00\text{x}10^{-13}$ mol/L

The result of a series of such calculations is shown in Figure 2-5. Note that the concentrations of the reactants, but not the products or the spectator ions, go through a large change exactly at the equivalence point. It is this change that allows one to pinpoint the equivalence point. This phenomenon holds for all titrations and for this reason all calculations below will involve only the reactants in the titration reactions. The equivalence point could be determined, in this case, by monitoring either [OH^-] or [H^+]. It is customary in acid-base titrations to monitor [H^+] (or pH), and this custom will be followed in all future examples.

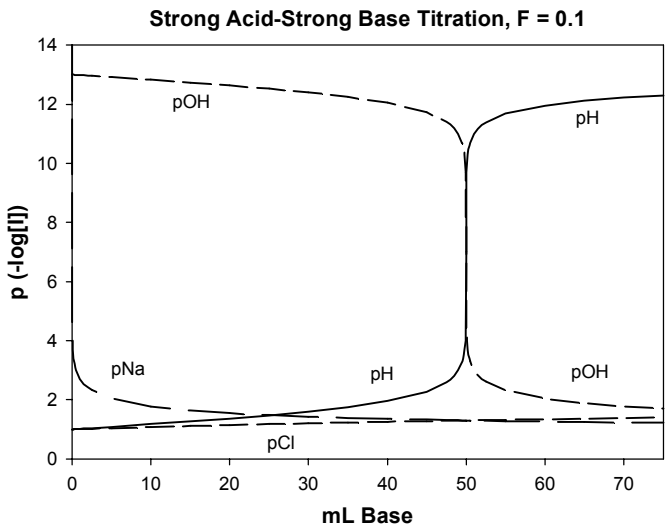

Figure 2-5

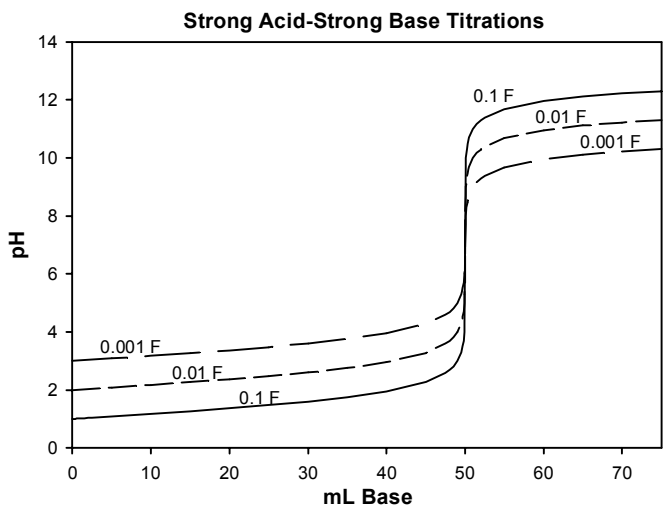

Figure 2-6

The results of changing the formality of the reactants is shown in Figure 2-6. In this case the change in concentrations at the equivalence point decreases as the formality of the reactants is lowered, making the equivalence point harder to determine. Such behaviour is not the case for all titration reactions; the exact behaviour will depend on the reaction stoichiometry.

2.6.2 WEAK ACID - STRONG BASE TITRATIONS

Here it will again be assumed that the weak acid is the unknown and that the titrant is a strong base. At first such titrations might seem to be just like strong acid-strong base titrations, but there is a significant difference that makes them more complicated. The product of the titration reaction and the spectator ions in a strong acid-strong base titration (*e.g.* H_2O, Na^+, and Cl^-) do not affect the pH of the solution and can be neglected in the calculations. Thus the only species present in Regions 1 and 2 that affects the pH is a strong acid, no pH affecting species are present in Region 3 (except water), and only a strong base exists in Region 4. When a weak acid is titrated with a strong base, one of the products is a weak base which does affect the pH in all regions except Region 1. This must be taken into account.

The titration reaction is often written as:

$$HA + NaOH \rightarrow NaA + H_2O$$

This is more accurately represented as:

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

The equilibrium constant will thus be:

$$K_e = \frac{[A^-]}{[HA][OH^-]} = \frac{1}{K_b} = \frac{K_a}{K_w} \qquad (2\text{-}97)$$

The equilibrium constant for the titration of a weak acid with a K_a of $1x10^{-5}$ (similar to acetic acid) will be $1x10^9$, not as large as for a strong acid, but still large enough for the reaction to be considered to go well to completion. As the value of K_a of the weak acid decreases, so does the value of K_e for the titration. Thus if the acid is too weak, it cannot be easily titrated, as will be seen later.

The four regions of the titration will be considered in the same manner as for a strong acid-strong base titration. Again it will be assumed that $F_u = F_t$ and that $V_u = 50.0$ mL.

REGION 1. Before any base is added, the solution contains only a weak acid, HA, and $F_a = F_u$. To calculate the $[H^+]$, use a weak acid equation and check the assumptions. For example:

$$[H_3O^+] = \sqrt{K_a F_a} \qquad (2\text{-}40)$$

REGION 2. After the addition of some titrant, the solution contains some unreacted acid, HA, and some conjugate base, A^-, due to the titration reaction.

mol acid remaining = orig. mol acid - mol strong base added

$$F_a = (\text{mol acid remaining})/\text{vol} = (V_u F_u - V_t F_t)/(V_u + V_t) \qquad (2\text{-}93)$$

mol weak base formed = mol strong base added

$$F_b = V_t F_t/(V_u + V_t) \qquad (2\text{-}98)$$

To calculate the $[H^+]$, use an equation for a mixture of a weak acid and its conjugate base and check the assumptions. For example:

$$[H_3O^+] = \frac{K_a F_a}{F_b} \qquad (2\text{-}71)$$

REGION 3. At the equivalence point, all the weak acid has been consumed and only the weak base remains. No excess strong base is present. Note that since the solution contains a weak base, *the pH will not equal 7.00, it must be greater than 7.00, and can be considerably greater than 7.00*.

mol weak base present = moles of strong base added

$$F_b = V_t F_t/(V_u + V_t) \qquad (2\text{-}98)$$

To calculate $[OH^-]$, use a weak base equation and check the assumptions. For example:

$$[OH^-] = \sqrt{K_b F_b} \qquad (2\text{-}53)$$

REGION 4. After the equivalence point both the weak base, A^-, and excess strong base, OH^-, are present.

mol weak base present = moles weak acid orig.

$$F_w = V_u F_u/(V_u + V_t) \qquad (2\text{-}99)$$

mol strong base present = mol titrant added - orig mol weak acid

$$F_s = (V_t F_t - V_u F_u)/(V_u + V_t) \quad (2\text{-}95)$$

To calculate $[OH^-]$, use an equation for a mixture of a weak base and a strong base and check the assumptions. For example:

$$[OH^-] = F_s \quad (2\text{-}86)$$

Butanoic acid (butyric acid, $pK_a = 4.98$) will be used in an example of a weak acid - strong base titration. As above it will be assumed that $F_t = F_u = 0.100$ mol/L and that $V_u = 50.0$ mL. Since $pK_a = 4.98$, $K_a = 1.05\text{x}10^{-5}$. In this example only the pH will be calculated (although $[OH^-]$ must also be calculated to check the assumptions). The concentrations of the other ions behave in much the same fashion as in a strong acid - strong base titration.

REGION 1, before addition of any strong base, $F_a = 0.100$ mol/L. Try the simplest equation for a solution of a weak acid and check the assumptions.

$[H^+] = (K_a F_a)^{1/2} = \{(1.05\text{x}10^{-5})(0.100)\}^{1/2} = 1.02\text{x}10^{-3}$ mol/L

$[OH^-] = 1.00\text{x}10^{-14}/1.02\text{x}10^{-3} = 9.77\text{x}10^{-12}$ mol/L

Both assumptions, that $[H^+] >> [OH^-]$ and $F_a >> [H^+]$, are valid. Thus

$pH = -\log(1.02\text{x}10^{-3}) = 2.99$

REGION 2, after the addition of 20.0 mL of strong base. The total volume of solution is now 70.0 mL and the solution is a mixture of a weak acid and its conjugate base.

$F_a = \{(0.100 \text{ mol/L})(0.0500 \text{ L}) - (0.100 \text{ mol/L})(0.0200 \text{ L})\}/0.0700 \text{ L} = 0.0429$ mol/L

$F_b = (0.100 \text{ mol/L})(0.0200 \text{ L})/0.0700 \text{ L} = 0.0286$ mol/L

Try the simplest equation for a mixture of a weak acid and conjugate base and check the assumptions.

$[H^+] = K_a F_a / F_b = 1.05\text{x}10^{-5}(0.0429)/(0.0286) = 1.57\text{x}10^{-5}$ mol/L

$[OH^-] = 1.00\text{x}10^{-14}/1.57\text{x}10^{-5} = 6.37\text{x}10^{-10}$ mol/L

Both assumptions, that $F_a >> [H^+]-[OH^-]$ and $F_b >> [H^+]-[OH^-]$, are valid. Thus

$pH = -\log(1.57\text{x}10^{-5}) = 4.80$

REGION 3, after the addition of 50.0 mL of strong base. The total volume of solution is now 100.0 mL and the solution contains only a weak base.

$F_b = (0.100 \text{ mol/L})(0.0500 \text{ L})/0.100 \text{ L} = 0.0500$ mol/L

$K_b = 1.00\text{x}10^{-14}/K_a = 1.00\text{x}10^{-14}/1.05\text{x}10^{-5} = 9.55\text{x}10^{-10}$.

Try the simplest equation for a weak base and check the assumptions.

$[OH^-] = (K_b F_b)^{1/2} = \{(9.55\text{x}10^{-10})(0.0500)\}^{1/2} = 6.91\text{x}10^{-6}$ mol/L

$[H^+] = 1.00\text{x}10^{-14}/6.91\text{x}10^{-6} = 1.45\text{x}10^{-9}$ mol/L

Both assumptions, that $[OH^-] >> [H^+]$ and $F_b >> [OH^-]$, are valid. Thus

$pH = -\log(1.45\times10^{-9}) = 8.84$

REGION 4, after the addition of 60.0 mL of strong base. The total volume of solution is now 110.0 mL and the solution contains both a weak base and a strong base.

$F_w = (0.100\ mol/L)(0.0500\ L)/0.110\ L = 0.0455\ mol/L$

$F_s = \{(0.100\ mol/L)(0.0600\ L) - (0.100\ mol/L)(0.0500\ L)\}/0.110\ L = 0.00909\ mol/L$

Try the simplest equation for a mixture of a strong and weak base and check the assumptions.

$[OH^-] = F_s = 0.00909\ mol/L$

$[H^+] = 1.00\times10^{-14}/0.00909 = 1.10\times10^{-12}\ mol/L$

All three assumptions, that $[OH^-] >> [H^+]$, $F_s >> K_b$, and $F_s^2 >> 4K_b(F_w+F_s)$, are valid. Thus

$pH = -\log(1.10\times10^{-12}) = 11.96$

The complete titration curve will result when a series of calculations like those above is carried out. A comparison of a strong acid-strong base titration and a weak acid (pK_a of 5)-strong base titration is shown in Figure 2-7. The large change in the pH at the equivalence point is less for the weak acid than for the strong acid and the weak acid exhibits a larger change in pH at the start of the titration than does the strong acid. This will be considered again when buffer solutions are discussed. It is true of all titrations that as the equilibrium constant decreases, so do the changes in concentrations at the equivalence point. This makes the equivalence point harder to locate.

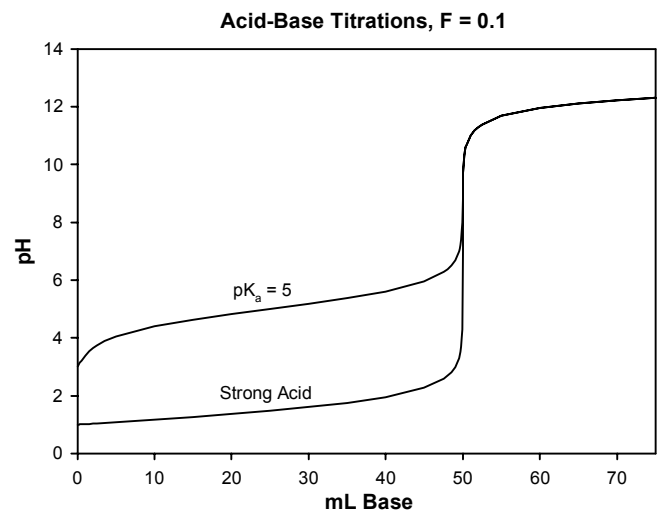

Figure 2-7

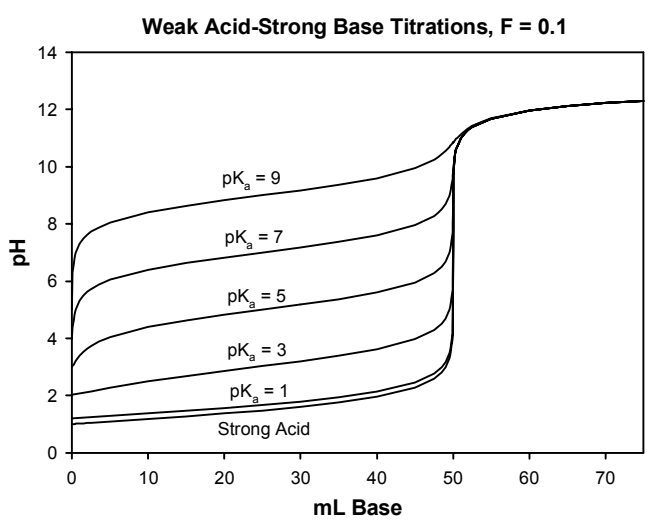

Figure 2-8

A family of curves for acids with various pK_as is shown in Figure 2-8. Here it is obvious that the change in pH at the equivalence point decreases as the K_a gets smaller, and disappears if the pK_a is greater than 9. The titration of an acid with a pK_a greater than 7 (at 0.1 F) will be difficult and it will be almost impossible if the pK_a is greater than 10. It is also obvious that any acid with a pK_a less than 1 acts like a strong acid, as far as the titration is concerned. Note that the

curves are all the same after the equivalence point. This is due to the excess in strong base, which is the same in all cases, controlling the pH in this region.

Finally the effect of varying the concentrations of titrant and titrand is shown in Figure 2-9. An effect is noted after the equivalence point (just as in the strong acid case) due to the dilution of the excess strong base. However, very little effect is observed in Region 2. In this region the pH is controlled by both the weak acid, HA, and its conjugate base, A^-, and any dilution or lowering in concentration affects both the acid and base equally and does not change the pH to any extent. This will come up again in the discussion of buffer solutions. Even so, the change in pH at the equivalence point is reduced as the concentrations are lowered, again making the titration more difficult.

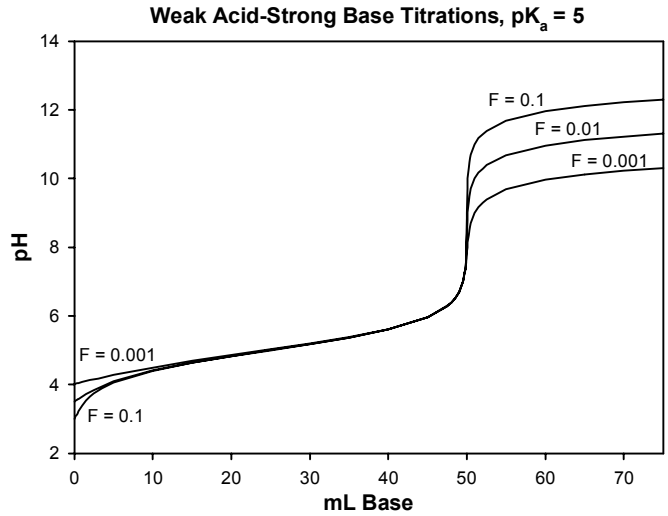

Figure 2-9

2.6.3 WEAK BASE - STRONG ACID TITRATIONS

These titrations are very similar to their weak acid-strong base counterparts. In this case the titration reaction could be written:

$$B + HCl \rightarrow HB^+ + Cl^-$$

but is more accurately represented as:

$$B + H_3O^+ \rightarrow HB^+ + H_2O$$

The equilibrium constant will thus be:

$$K_e = \frac{[HB^+]}{[B][H_3O^+]} = \frac{1}{K_a} = \frac{K_b}{K_w} \qquad (2\text{-}100)$$

The equilibrium constant for the titration of a weak base with a K_b of $1x10^{-5}$ (similar to ammonia) will be $1x10^9$. As the value of K_b decreases, so will the equilibrium constant for the titration reaction, and the base will become more difficult to titrate.

No calculations will be demonstrated for these titrations Such calculations are exactly the same as for the weak acid-strong base case. You should keep in mind which species are present in each of the regions of these titrations before doing the calculations.

REGION 1. The only material in solution is the pure weak base, B. The pH will be greater than 7.

REGION 2. Both the weak base, B, and its conjugate weak acid, HB^+, are present. The solution can be either acidic or basic, depending on the circumstances.

REGION 3. The only material in solution is the weak acid, HB^+. *The solution will be acidic, not neutral*.

REGION 4. The solution contains both the weak acid, HB^+, and strong acid, H_3O^+. The pH will be much less than 7.

The titration curves for weak base-strong acid titrations, shown in Figure 2-10, look exactly like those for weak acid-strong base titrations except that they are rotated around an axis passing through pH 7, a consequence of the symmetry of acid-base reactions. In the curves shown in Figure 2-10 F_u and F_t are both 0.100 and V_u is 50.0 mL.

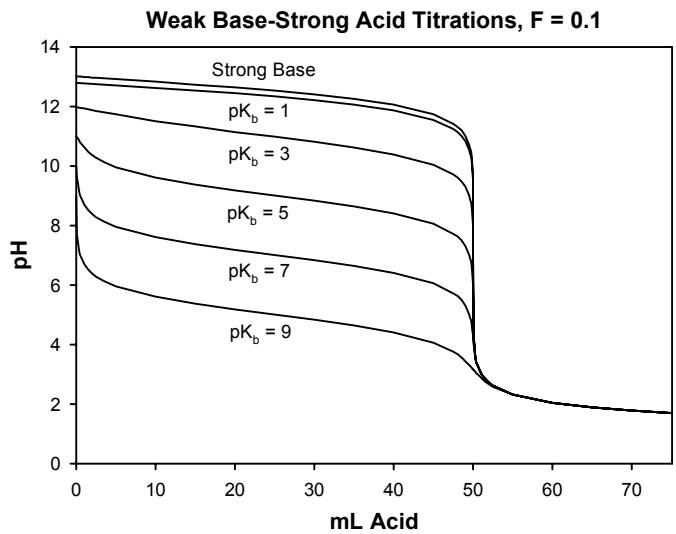

Figure 2-10

The same comments can be made here as before. The change in pH at the equivalence point decreases as the K_b decreases, making the base more difficult to titrate. The pH for all curves is the same after the equivalence point because the pH is controlled by the strong acid, which is the same in all cases. It is obvious that such titrations will be difficult if pK_b is greater than 7 and impossible if it is much greater than 9. The question might be asked, what can be done if one needs to determine the amount of base in a sample and the pK_b of the base is greater than 9. The answer is to convert it to its conjugate acid (with a pK_a of less than 5) and titrate the acid with a strong base. This is not necessarily easy, but may be the only option.

2.6.4 WEAK ACID - WEAK BASE TITRATIONS

This is a purely academic topic. In the real world one would never titrate a weak acid with a weak base when one could use a strong base and get a better equivalence point. However, one point that is not academic can be addressed by discussing such reactions. This is as follows, "When an acid and a base are mixed, will they always react?" A strong acid will always react with a weak base and *vice versa*. What about a weak acid and a weak base? The reaction is as follows:

$$HA + B \rightarrow HB^+ + A^-$$

and the equilibrium constant is:

$$K_e = \frac{[HB^+][A^-]}{[HA][B]} = \frac{(K_a)_{HA}(K_b)_B}{[H_3O^+][OH^-]} \qquad (2\text{-}101)$$

$$K_e = \frac{(K_a)_{HA}(K_b)_B}{K_w} \qquad (2\text{-}102)$$

If $K_e > 1$ for such a reaction, it will generally proceed as written. Thus if $(K_a)_{HA}(K_b)_B > K_w$ (or $pK_a + pK_b < 14$), the reaction will proceed and if $(K_a)_{HA}(K_b)_B < K_w$ (or $pK_a + pK_b > 14$), the reaction will not proceed.

Will acetic acid react with ammonia to form ammonium acetate? The pK_a for acetic acid is 4.75 and the pK_b for ammonia is the same, 4.75. Since 4.75 + 4.75 = 9.5 < 14, the reaction will proceed. Will sodium fluoride react with hydrocyanic acid (HCN) to form hydrofluoric acid and sodium cyanide? The pK_b of F^- is 10.83 and the pK_a of HCN is 9.40. Since 9.40 + 10.83 = 20.23 > 14, this reaction will not proceed.

2.7 INDICATORS IN ACID-BASE TITRATIONS

There are many ways of determining the end points in titrations. As mentioned above, any probe which can follow the concentration of one of the reactants in the titration can indicate the equivalence point. When one speaks of an indicator, one generally means some chemical substance added to the titration flask which changes colour to indicate the equivalence point. All such indicators behave in the same fashion, although there are slight differences in indicators, depending on the type of chemistry involved. Thus acid-base indicators will be used as examples of indicators in general.

Logic dictates that an indicator must react with the titrant (just as the unknown does), that it must be coloured, and that the colour must be different before and after the end point in order to be visible to the human eye. The chemical reaction involved must be something like:

$$\underset{}{T} + I \rightarrow \underset{\text{colour 1}}{P_t} + \underset{\text{colour 2}}{P_i}$$

Here T is the titrant, I is the indicator, P_t is the product which "originates" from the titrant and is also present due to the reaction with the unknown, and P_i is that due to the indicator.

After a bit more thought it can be stated that an indicator must have the following properties:

1. It must react with the titrant *at the appropriate point in the titration*.
2. I and P_i must be sufficiently different in colour to be clearly discernible by the eye.
3. Either I or P_i (or both) must be highly coloured so that very little indicator is needed. Since the indicator reacts with the titrant, it will cause the endpoint to be past the equivalence point if very much of the indicator is present.

For an acid-base reaction, the indicator must also be an acid-base system, and will be a weak acid-weak base conjugate pair, HIn/In^-. Assuming that the titration involves an acid as the unknown and a strong base as the titrant, the indicator reaction will be:

$$\underset{\text{colour 1}}{HIn} + OH^- \rightarrow H_2O + \underset{\text{colour 2}}{In^-}$$

Colours 1 and 2 depend on the indicator. For example, it will be assumed that colour 1 is blue and colour 2 is yellow. To the eye when $[HIn] \geq 10[In^-]$, the colour of the solution appears as only that of HIn, colour 1 or blue. Likewise, when $[In^-] \geq 10[HIn]$, the colour of solution appears as only that of In^-, colour 2 or yellow. Furthermore, the maximum colour change appears when $[Hin] \approx [In^-]$. This colour change occurs at a specific pH which is predicted by the K_a of the indicator, which will be denoted as K_{in}, to distinguish it from the K_a of the unknown acid. For the indicator:

$$HIn + H_2O \rightarrow In^- + H_3O^+$$

$$K_{in} = \frac{[In^-][H_3O^+]}{[HIn]} \qquad (2\text{-}103)$$

For the solution to be colour 1 (blue), $[HIn]/[In^-] \geq 10$. Using this inequality in (2-103) gives:

$$[H_3O^+] \geq 10K_{in} \qquad \text{for colour 1 (blue)} \qquad (2\text{-}104)$$

or

$$pH \leq pK_{in} - 1 \qquad (2\text{-}105)$$

Likewise for the solution to be seen as colour 2 (yellow), $[In^-]/[HIn] \geq 10$. Using this in (2-103) gives:

$$[H_3O^+] \leq K_{in}/10 \qquad \text{for colour 2 (yellow)} \qquad (2\text{-}106)$$

$$pH \geq pK_{in} + 1 \qquad (2\text{-}107)$$

Finally the maximum colour change occurs at $[HIn] \approx [In^-]$, which gives

$$[H_3O^+] \approx K_{in} \qquad \text{for maximum colour change} \qquad (2\text{-}108)$$

or

$$pH_{cc} \approx pK_{in} \qquad (2\text{-}109)$$

where pH_{cc} is the pH of the maximum colour change.

This very simple result indicates that the maximum colour change for any indicator occurs at a pH near its pK_{in}. This leads to a very simple method for the choice of a proper indicator in an acid-base titration (this applies whether the unknown is an acid or a base):

1. Calculate the pH of the equivalence point (Region 3), pH_{ep}. This is the point at which you wish the indicator to change colour.

2. Select the indicator which has pK_{in} closest to pH_{ep}.

For example, consider the titration of 0.100 F ammonia (NH_3, the unknown, $pK_b = 4.76$) with 0.100 F HCl. What would be a suitable indicator to use for this titration? The first step is to calculate the pH at the equivalence point. At this point all the weak base has been converted to its weak conjugate acid, ammonium ion, but there is no excess strong acid. Thus the solution contains only a weak acid. Its formality will be half that of the original base (since $F_u = F_t$, the volume of standard HCl added at the equivalence point will equal the original volume of unknown, the total volume will be double that of the original volume, and the concentration of weak acid will be half that of the original weak base, or 0.0500 mol/L).

$K_b = \text{antilog}(-4.76) = 1.74\text{x}10^{-5}$

$K_a = 1.00\text{x}10^{-14}/1.74\text{x}10^{-5} = 5.75\text{x}10^{-10}$

$[H^+] = (K_aF_a)^{1/2} = \{(5.75\text{x}10^{-10})(0.0500)\}^{1/2} = 5.36\text{x}10^{-6}$ mol/L

For this solution $[OH^-] = 1.86\text{x}10^{-9}$ and thus both assumptions, that $[H^+]>>[OH^-]$ and $F_a>>[H^+]$, are valid. Thus the pH of the colour change should be close to $-\log(5.36\text{x}10^{-6})$ or about 5.27. Methyl red with a pK_{in} of 4.97 has the closest pK_{in} to the pH of the equivalence point of those indicators listed in Appendix B. It would make a suitable indicator for the titration.

Two questions need to be answered before leaving this topic: (1) does selecting an indicator with $pK_{in} = pH_{ep}$ always guarantee a "good" end point, and (2) what harm will occur if the pK_{in} of the indicator is not quite equal to pH_{ep}? The answers to both questions come from noting that the complete colour change usually occurs over a pH range of about two ($pK_{in}-1 < pH < pK_{in}+1$) and observing the change in pH at the equivalence point in various titrations. Three different titrations are shown in Figure 2-11. The strong acid-strong base titration has such a large change in pH at the equivalence point that many different indicators can be used, even those with pK_{in} several units away from 7. For the titration of a weak acid with pK_a of 5, the indicator should be properly selected for a sharp colour change. The change in pH is so small at the equivalence point in the titration of the weak acid with pK_a

of 9 that even a properly selected indicator will not produce a sharp colour change. In general the stronger the acid and the higher its concentration, the more freedom one has in selecting an indicator that will produce a sharp colour change.

These effects are more quantitatively demonstrated in Table 2-2. Keep in mind that one drop of titrant is approximately 0.05 mL, and that it would be desirable to have the colour change take place in this volume for a sharp end point.

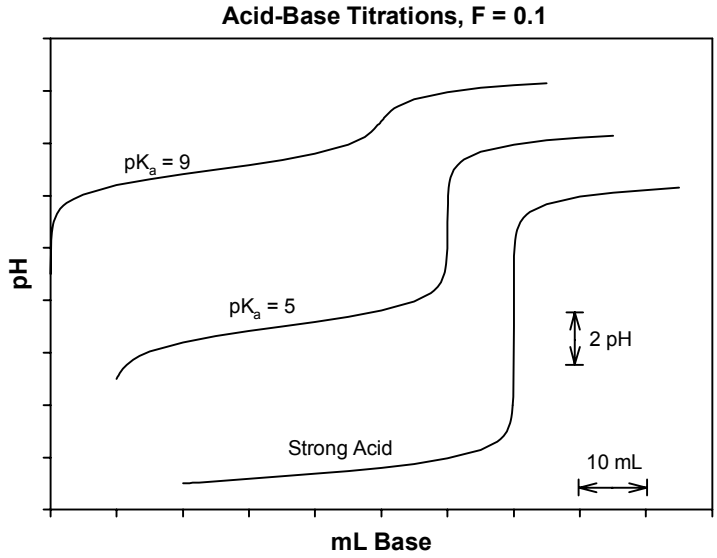

Figure 2-11

Table 2-2

Acid	Formality	pH 49.95 mL	pH 50.05 mL	ΔpH (0.1 mL)
Strong	0.1 F	4.30	9.70	5.40
Strong	0.001 F	6.30	7.70	1.40
Weak, pK = 5	0.1F	7.99	9.70	1.71
Weak, pK = 5	0.001 F	7.70	8.00	0.30
Weak, pK = 9	0.1 F	10.83	10.86	0.03

2.8 BUFFER SOLUTIONS

Many reactions in aqueous solution involve H_3O^+, including almost all reactions of biochemical interest, and therefore it is usually necessary to maintain the pH constant (or reasonably so) when such reactions are studied. This means that the pH must be nearly constant even though the reaction of interest generates or consumes H_3O^+. How can this be done? To answer this question one can turn to the titration curves that have just been discussed, as shown in Figure 2-12. There are two regions on these curves where the pH does not change much even though strong acid or base is being added to the solution. These are in the middle of Regions 2 and 4. For this

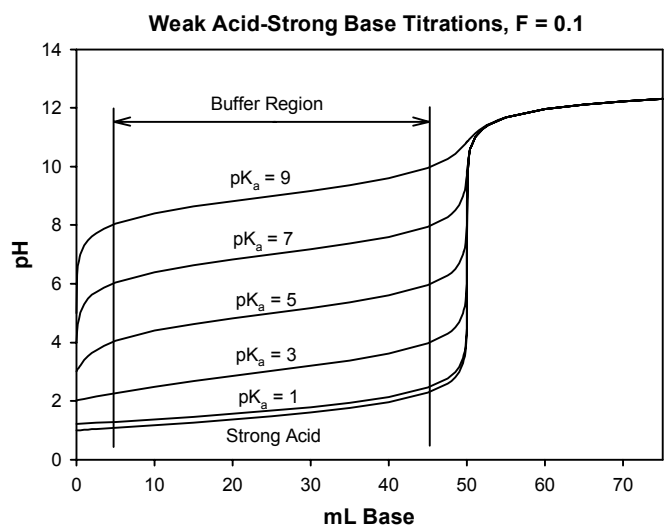

Figure 2-12

reason the middle of Region 2 is called the buffer region. For the curves displayed in Figure 2-12, adding strong base will shift toward the right (as in a titration) and the pH will increase; adding strong acid will shift toward the left and the pH will decrease. These observations lead to the methods needed to select a proper buffer for whatever application is at hand.

If the pH of the buffer is to be less than 2, one observes from Figure 2-12 that the curve which is situated near this pH is that for a strong acid. Thus one would choose a strong acid to act as the buffer. One does not usually think of a strong acid as a buffer, but it works very well as a buffer. The pH of such a solution is not easily changed, provided the concentration is high enough. Many readers might think it necessary to have the "salt" also present to make such a buffer. This is not necessary with a strong acid. The "salt" (*e.g.* NaCl) does not affect the pH and whether it is in the solution or not will make no difference in either the pH or the capacity of the buffer to withstand pH changes.

To select the proper buffer all that is needed is to calculate the formality needed to give the desired pH (remember all strong acids are the same in water). Choose

$$F_a = [H^+]_{desired} \tag{2-110}$$

For example, if you want a pH of 1.50, choose $F_a = 10^{-1.50} = 0.0316$ mol/L

If the pH of the buffer is to be greater than 12, then one would choose a strong base to act as the buffer (see Region 4 after the equivalence point in Figure 2-12). To select the proper buffer simply calculate the formality needed to give the desired pH (again remember that all strong bases act similarly in water). Choose

$$F_b = [OH^-] = K_w/[H^+]_{desired} \tag{2-111}$$

For example, if you want a pH of 12.70, select $F_b = 10^{-14}/10^{-12.70}$ or $F_b = 0.0501$ mol/L

Again looking at Figure 2-12, the titration curves that fall between pH 2 and pH 12 are those for weak acids and bases. Thus if the buffer must hold the pH constant at a value between 2 and 12, then the solution must be prepared from a weak acid *and* its conjugate base. It is obvious from the curves in Figure 2-12 that the weak acid (or likewise the weak base) alone will provide no buffering, since a large change in pH is observed at the start of many titrations and this is the region in which there is little or no weak base present. The selection of the proper buffer now becomes more difficult since not only must the concentration of both acid and conjugate base be determined, but also the proper acid/base pair must be chosen. It is also obvious from the curves in Figure 2-12 that, if the desired pH is near 7, the pK_a of the weak acid must also be close to 7. The final observation which will be made from the titration curves is that the flattest portion of the curve in Region 2 is at the midpoint (25 mL on Figure 2-12), and normally this will be the best place to have the buffer. At this point $[HA] \approx [A^-]$.

Since most buffers need fairly large quantities of both weak acid and conjugate base, the assumptions made in deriving the Henderson-Hasselbalch (H-H) equation, Eqn. (2-71), are normally valid, namely that $F_a >> [H^+]-[OH^-]$ and $F_b >> [H^+]-[OH^-]$, and thus very simply choose

$$[H^+]_{desired} = K_a F_a/F_b \tag{2-71}$$

If $F_a \approx F_b$, then $[H^+] \approx K_a$ or $pH \approx pK_a$.

To select the proper acid-base system, select a suitable one with its pK_a as close to the desired pH as possible. In no case should the pK_a be more than one unit different from the desired pH. The problem of choosing the correct concentrations still remains. There are several methods of approaching this, depending on the circumstances.

Assume that you wish to prepare a buffer of pH 5.00. The first step is to choose the acid/base pair. The pK_a must be within 1 unit of 5.00, and the closer to 5.00, the better. Acetic acid, with a pK_a of 4.76, would be a good choice. You might simply pick one of the concentrations (F_a or F_b) and calculate the other.

For example: select F_a = 0.100. Since this is a mixture of a weak acid and its conjugate base, try using H-H to calculate F_b and then check the assumptions.

$F_b = K_aF_a/[H^+] = (1.74\text{x}10^{-5})(0.100)/1.00\text{x}10^{-5} = 0.174$ mol/L

The assumptions check, since 0.100 and 0.174 are both much larger than $1\text{x}10^{-5}$. Thus the buffer could be made by adding 0.100 mol of acetic acid and 0.174 mol of sodium acetate to enough water to make 1.00 L of solution.

You may wish to have the buffer components establish a certain ionic strength. Again if H-H can be used, the calculation is quite simple. For a buffer of pH 5.00 the only ions present in high amounts are Na^+ and $C_2H_3O_2^-$ (assuming the weak base is added as sodium acetate), since acetic acid ionizes very little and hydrogen and hydroxide ion are present in very low amounts. Thus the ionic strength is established by the weak base alone, $\mu = F_b$. If the buffer were formed from ammonia or an amine and its conjugate weak acid, the ionic strength would be established by the weak acid (the ammonium salt) alone, or $\mu = F_a$.

Assume that you wish a buffer of pH 5.00 (acetic acid/sodium acetate) with an ionic strength of 0.0100. Thus F_b = 0.0100. Calculate F_a from H-H and check the assumptions.

$F_a = [H^+]F_b/K_a = (1.00\text{x}10^{-5})(0.0100)/1.74\text{x}10^{-5} = 0.00575$ mol/L

The assumptions check since 0.01 and 0.006 are both much larger than $1\text{x}10^{-5}$. Thus the buffer can be prepared by adding 0.01 mol of sodium acetate and 0.00575 mol of acetic acid to enough water to make 1.00 L of solution.

The numbers in the two examples above raise an interesting question. Obviously one can obtain the same pH with two (or more) different sets of concentrations. The reason for this is that the ratio of F_a to F_b is the same in both cases (0.575), and for any buffer where H-H holds, this is all that is needed. Are these two buffers equivalent? They provide the same pH! However, their ability to maintain that pH is quite different. The ability to hold the pH "constant" (the pH cannot be held exactly constant by such a buffer) on addition of acid or base is called the buffer capacity. The higher the values of F_a and F_b, the higher the buffer capacity. The biggest problem with buffers is choosing the buffer capacity such that the pH will remain sufficiently constant during the experiment under study. To do this one must know (1) the limit in the pH change which one can tolerate and (2) the maximum amount of acid or base that will be generated during the experiment. The following method assumes that H-H will be valid. If this is not the case, then the calculations become much more complicated.

Assume that your buffer (at pH 5.00) must not change pH by more than 0.10 unit and that a maximum of 0.005 mol of base (OH^-) can be generated in 100 mL of solution. The initial pH as established by the initial formalities of acid and base will be 5.00. Since base (OH^-) is being generated in solution and this will react with the weak acid of the buffer to form weak conjugate base, the final formality of the weak acid will be less than the initial formality and the final formality of the weak base will be larger than the initial formality. The pH must also be higher, in fact in this problem it will be 5.10, since the pH is allowed to change by 0.10. This leads to two equations:

(1) Initial $[H^+] = [H^+]_i = K_a(F_a)_i/(F_b)_i$

(2) Final $[H^+] = [H^+]_f = K_a(F_a)_f/(F_b)_f$

where the subscript "i" refers to the initial conditions and "f" to the final conditions. This gives two equations with four unknowns; however, two more equations can be written knowing the amount of base generated and the volume of solution.

(3) $(F_a)_f = (F_a)_i - (0.00500 \text{ mol})/0.100 \text{ L} = (F_a)_i - 0.0500$

(4) $(F_b)_f = (F_b)_i + (0.00500 \text{ mol})/0.100 \text{ L} = (F_b)_i + 0.0500$

There is usually no need to solve for either $(F_a)_f$ or $(F_b)_f$. Thus solve for either $(F_a)_i$ or $(F_b)_i$. Substitute (3) and (4) into (2).

(5) $[H^+]_f = K_a((F_a)_i - 0.0500)/((F_b)_i + 0.0500)$

This produces two equations, (1) and (5), with two unknowns, $(F_a)_i$ and $(F_b)_i$. Solve (1) for $(F_a)_i$ and substitute this into (5).

(6) $[H^+]_f = K_a\{((F_b)_i[H^+]_i/K_a) - 0.0500\}/((F_b)_i + 0.0500)$

Substitute the values for $[H^+]_i$ ($1x10^{-5}$), $[H^+]_f$ ($7.94x10^{-6}$), and K_a ($1.74x10^{-5}$) into (6).

$7.94x10^{-6} = (1.00x10^{-5}(F_b)_i - 8.70x10^{-7})/((F_b)_i + 0.0500)$ or

$7.94x10^{-6}(F_b)_i + 3.97x10^{-7} = 1.00x10^{-5}(F_b)_i - 8.70x10^{-7}$ or

$2.06x10^{-6}(F_b)_i = 1.27x10^{-6}$ which gives

$(F_b)_i = 0.615$ mol/L

Substitute this value into (1) and solve for $(F_a)_i$.

$(F_a)_i = 0.615(1.00x10^{-5})/1.74x10^{-5} = 0.353$ mol/L

Thus if the reaction of interest were carried out in 100 mL of solution containing 0.0615 mol of sodium acetate and 0.0353 mol of acetic acid, the pH would be guaranteed to change no more than 0.10 units if the reaction that generated the OH^- went to completion. The H-H assumptions should be checked to make sure the above approach is valid. Both assumptions check easily, since both 0.615 and 0.353 are much larger than $1x10^{-5}$.

The obvious method of preparing one litre of the above buffer is to measure 0.615 mol of sodium acetate (potassium acetate would do just as well) and 0.353 mol of acetic acid and add to enough water to make 1.00 L of solution. However, often one of the two components is not available. What happens then? Assume that you can only obtain acetic acid, no sodium acetate is available. You can make the sodium acetate by

adding strong base (NaOH) to acetic acid. This can be done during the buffer preparation step. The acetic acid must now supply both the weak acid and its conjugate base, so you measure 0.615+0.353 or 0.968 mol of acetic acid and 0.615 mol of sodium hydroxide and add these to enough water to make 1.00 L of solution. The 0.615 mol of NaOH creates 0.615 mol of sodium acetate, leaving 0.353 mol of acetic acid unreacted, which produces the desired result.

One final question might be asked, "How does a buffer work?" The last example above hints at how buffers made from weak acid/base conjugate pairs ($2 < pH < 12$) function. Such solutions contain both a weak acid and a weak base. If H_3O^+ is added to such a solution, the weak base reacts with it, forming a weak acid, and the pH changes very little. If OH^- is added, it reacts with the weak acid forming a weak base and again the pH changes very little. However, keep in mind that when the weak acid or base is used up, the pH will change dramatically (the buffer capacity is exceeded). This would be equivalent to moving too far to either the right (by adding base) or the left (by adding acid) along the curves displayed in Figure 2-12.

How does a strong acid buffer ($pH < 2$) function? If OH^- is added to such a buffer, the strong acid neutralizes it and the pH changes very little. Such buffers are already so acidic that the addition of more acid has very little effect on the pH. Strong base buffers ($pH > 12$) work in the same fashion. Added acid is neutralized and added base has little effect on a solution already so basic.

Finally, why not make a buffer of $pH < 2$ or $pH > 12$ with a weak acid and its conjugate base? Simply because most weak acids cannot produce pH values less than two and most weak bases cannot produce values greater than 12.

2.9 POLYFUNCTIONAL ACIDS AND BASES

Nature provides many useful and important materials with more than one acid or base functional group per molecule, *e.g.* H_3PO_4, $NH_2CH_2CH_2NH_2$, and NH_2CH_2COOH. All such materials react with water in steps. For example, a diprotic acid reacts as follows:

$$H_2A + H_2O \rightarrow HA^- + H_3O^+ \qquad K_1 = \frac{[HA^-][H_3O^+]}{[H_2A]}$$

$$HA^- + H_2O \rightarrow A^{2-} + H_3O^+ \qquad K_2 = \frac{[A^{2-}][H_3O^+]}{[HA^-]}$$

If $K_1 \approx K_2$, the two steps occur simultaneously and both must be considered in solving any problems involving the pH of solutions of the acid. It will be stated, *without proof*, that if $K_1 >> K_2$ (a factor of 10^4 or more), only the reaction involving the major species present need be considered. This is very convenient since one can now apply the simple monobasic equations that have been derived above in almost every situation. This is important in preparing buffer solutions because it allows one to use polyfunctional acids and do the calculations very simply. Take phosphoric acid as an example:

$$H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+ \qquad K_1 = 7.11\text{x}10^{-3} = [H^+][H_2PO_4^-]/[H_3PO_4]$$

$$H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+ \qquad K_2 = 6.32\text{x}10^{-8} = [H^+][HPO_4^{2-}]/[H_2PO_4^-]$$

$$HPO_4^{2-} + H_2O \rightarrow PO_4^{3-} + H_3O^+ \qquad K_3 = 7.1\text{x}10^{-13} = [H^+][PO_4^{3-}]/[HPO_4^{2-}]$$

Since the Ks are each at least 10^4 apart, this seemingly very complicated system can be treated very much like a series of monobasic weak acids and conjugate bases. Examples to illustrate how this is done are given below.

A solution of pure phosphoric acid. Here only Step 1 is important and only H_3PO_4 and $H_2PO_4^-$ are present to any extent. Thus use an equation for a monoprotic weak acid and set $K_a = K_1$.

A solution of phosphoric acid and sodium dihydrogen phosphate. Here there is still only H_3PO_4 and $H_2PO_4^-$ present, but the latter is added independently and acts like a weak base, thus use an equation for a mixture of a weak acid and its conjugate base with $K_a = K_1$.

A solution of sodium dihydrogen phosphate and sodium monohydrogen phosphate. Now there will only be $H_2PO_4^-$ and HPO_4^{2-}, the former acts as the acid, the latter as the conjugate base. Thus again use an equation for a mixture of a weak acid and its conjugate base, but this time set $K_a = K_2$.

A solution of sodium monohydrogen phosphate and trisodium phosphate. This solution will contain only HPO_4^{2-} and PO_4^{3-}, the former acting as the weak acid, the latter as the conjugate base. Again use an equation for a mixture of a weak acid and its conjugate base, but here set $K_a = K_3$.

A solution of pure trisodium phosphate. In this solution you have only a weak base. Thus use an equation for a weak base with $K_b = K_w/K_3$.

The only two solutions which cannot be treated in the above manner are those containing only $H_2PO_4^-$ (*e.g.* from NaH_2PO_4) or only HPO_4^{2-} (*e.g.* from Na_2HPO_4). These substances are unique in that they can act as both an acid or a base (they are called ampholytes). There is no situation corresponding to this in a monoprotic system, and thus there are no monoprotic equations that can be used to predict the pH in these solutions. Such materials will not be treated in this text.

The most important thing is to realize that buffers can be just as easily made from polyprotic acids and their conjugate bases (where the Ks are far apart) as from monoprotic systems. Again the pK must be within one unit of the desired pH. Then select the materials to make your buffer which match those in the step to which the equilibrium constant applies. (This is often confusing.) For example, you wish to make a buffer of pH 10. You note that pK_2 for carbonic acid is 10.33. Since K_2 applies to the step,

$$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+ \qquad K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$$

you would choose sodium bicarbonate and sodium carbonate to prepare the buffer. Finally you treat the system just like a monoprotic mixture with bicarbonate acting as the acid and carbonate as its conjugate base.

You wish to prepare 500 mL of a buffer of pH 7.00 in which the formality of the conjugate weak acid is 0.0100 mol/L. How would you do this? The first step is to select the acid-base system. You note that pK_2 for phosphoric acid is 7.20, which is quite close to the pH you desire. You also note that the pKs for this polyprotic system are far apart, allowing the use of the monoprotic equations. Since the second step (that for K_2) involves $H_2PO_4^-$ and HPO_4^{2-}, you select NaH_2PO_4 as the weak acid and Na_2HPO_4 as the conjugate base.

At pH = 7.00, the H-H equation will always be valid since $[H^+] = [OH^-]$, $[H^+] - [OH^-] = 0$, and F_a and $F_b >> 0$. Thus use H-H to calculate F_b, knowing F_a.

$K_a = K_2 = \text{antilog}(-7.20) = 6.32\text{x}10^{-8}$.

$F_b = K_aF_a/[H^+] = 6.32\text{x}10^{-8}(0.0100)/1.00\text{x}10^{-7} = 0.00632$ mol/L

Thus you would weigh 0.00500 mol of sodium dihydrogen phosphate and 0.00316 mol of sodium monohydrogen phosphate and dissolve these in enough water to make 500 mL of solution.

What is the pH of the solution that results from mixing 100.0 mL of 0.0750 F Na_2HPO_4 and 30.0 mL of 0.500 F HCl? To solve this problem you must first determine the chemistry involved. To do this you must ask "What type of material is HCl; what type of material is Na_2HPO_4?" Obviously HCl is a strong acid. Na_2HPO_4 can act as either an acid or a base (it is an ampholyte). However, when combined with a strong acid, it will act like a base according to:

$$HCl + Na_2HPO_4 \rightarrow NaH_2PO_4 + NaCl$$

The next step is to determine which reagent, if either, is limiting.

Mol HCl = (0.0300 L)(0.500 mol/L) = 0.0150 mol

Mol Na_2HPO_4 = (0.100 L)(0.075 mol/L) = 0.00750 mol

The sodium monohydrogen phosphate is obviously the limiting reagent. It is tempting to say that the final solution will contain 0.00750 mol of NaH_2PO_4 and 0.00750 mol of unreacted HCl. However, this ignores the fact that the phosphate system is polyprotic and that another reaction step is possible. NaH_2PO_4 can also act as a weak base (it is also an ampholyte), and it will do so with a strong acid according to:

$$HCl + NaH_2PO_4 \rightarrow H_3PO_4 + NaCl$$

Again you must determine which reagent, if either, is limiting.

Mol HCl (remaining after step 1) = 0.00750 mol

Mol NaH_2PO_4 (formed in step 1) = 0.00750 mol

Neither reagent (or both) is limiting. Thus 0.00750 mol of phosphoric acid is formed and no HCl or dihydrogen phosphate remains. The reaction stops here since no reactant remains. What is in this solution? A weak polyprotic acid. However, since the Ks are far apart, it can be treated as a monoprotic acid. Try the simplest equation first using $K_a = K_1 = 7.11\text{x}10^{-3}$ to determine the pH.

$F_a = 0.00750$ mol/0.130 L = 0.0577 mol/L

$[H^+] = (K_aF_a)^{1/2} = \{(0.00711)(0.0577)\}^{1/2} = 0.0203$ mol/L

The assumption that $[H^+]>>[OH^-]$ is certainly valid, but F_a is not 20 times greater than $[H^+]$. Thus you must use

$[H^+] = \{-K_a+(K_a^2+4K_aF_a)^{1/2}\}/2$

$[H^+] = \{-0.00711+(5.06\text{x}10^{-5}+4(0.00711)(0.0577))^{1/2}\}/2 = 0.0170$ mol/L

The only assumption involved with this equation, that $[H^+]>>[OH^-]$, is certainly valid. Thus

pH = -log(0.0170) = 1.77

2.10 PROBLEMS

Section 2.1: Activity Effects

2-1) Calculate the ionic strengths of 0.0500 F solutions of the following salts, neglecting any acid-base effects: LiCl, $CaBr_2$, $MgSO_4$, Na_2SO_4, and $La(NO_3)_3$. Ans: 0.0500, 0.150, 0.200, 0.150, and 0.300 mol/L.

2-2) Calculate the activity of the cation at 25°C in the following solutions: 0.100 F LiCl, 0.0500 F Li_2SO_4, 0.100 F $ZnCl_2$, and 0.100 F $ZnSO_4$. Ans: 0.0795, 0.0773, 0.0290, 0.0266.

2-3) Calculate the pH of a 0.100 F solution of HCl (a) if the definition of pH is $-\log[H^+]$, and (b) if the definition of pH is $-\log A_H$. Ans: 1.00, 1.08.

2-4) What is the solubility of $BaSO_4$ in pure water and in 0.100 F NaCl if the solubility product is 1.3×10^{-10}? Ans: 1.2×10^{-5} and 3.1×10^{-5} mol/L.

Challenge Problem

2-5) The solubility product of $Ba(BrO_3)_2$ is 5.5×10^{-6}. Calculate the solubility of this salt in pure water taking activity effects into account. (HINT - try approaching the answer by successive approximation starting with the assumption that all γs are unity to get a first approximation for μ.) Ans: 0.0165 mol/L.

Sections 2.2 to 2.4: Acid-Base Equilibria

2-6) Write mass balance, charge balance, and proton balance equations for solutions containing the following single compounds: Calcium bromide, sodium chromate, magnesium sulfate, barium hydroxide, sodium acetate, nitrous acid, potassium cyanide, and hydrogen fluoride. Assume that the first three substances do not exhibit acid/base properties in water. There is a problem with barium hydroxide and the PBE, what is it?

2-7) What is the "pH" of a pure non-aqueous amphiprotic solvent with an autoprotolysis constant of 1.00×10^{-6}? Ans: 3.00.

2-8) What is the pH of a neutral aqueous solution at 0ºC ($K_w = 1.14\times10^{-15}$)? Ans: 7.47.

2-9) Calculate the pH of a solution prepared by mixing 15.0 g of 37.0% by weight concentrated HCl with enough water to make 100.0 mL of solution. Ans: -0.18.

2-10) Derive the exact equation for the $[OH^-]$ to be found in a solution of $Ba(OH)_2$ as a function of the formality of the base. Assume a temperature of 25ºC and that $Ba(OH)_2$ is a strong base. What would be the pH of a 5.00×10^{-8} F solution of barium hydroxide according to your equation? Ans: 7.21.

2-11) What is the pH of a solution formed by dissolving 4.00×10^{-3} moles of benzoic acid in water to form 100.0 mL of solution? Ans: 2.80.

2-12) Calculate the pH of a 0.0100 F solution of dichloroacetic acid. Ans: 2.06.

2-13) Compute the pH of a 1.00×10^{-4} F solution of the weak acid phenol (hydroxybenzene). Ans: 6.84.

2-14) Weak acids are said to become "stronger" as their concentrations decrease because they ionize more completely. Demonstrate this effect by calculating the percent ionization of acetic acid at 1.00×10^{-2} F and at 1.00×10^{-6} F. Use the following definition:

%ionization = (moles ionized)(100)/(total moles present, all forms)

Ans: 4.17, 93.8%.

2-15) 0.0100 mol of NH_3 is dissolved to form 0.100 L of solution. Calculate the pH of this solution. Ans: 11.12.

2-16) Calculate the pH of a 0.0100 F solution of sodium acetate. Ans: 8.38.

2-17) Calculate the pH of a 0.200 F solution of ethylamine. Ans: 11.97.

2-18) Calculate the pH of a 0.00100 F solution of KCN (potassium cyanide). Ans: 10.08.

Sections 2.5 to 2.7: Acid-Base Mixtures and Titrations

2-19) What is the $[H^+]$ in a solution prepared by mixing 50.0 mL of 0.0100 F NH_3 and 50.0 mL of 0.100 F NH_4Cl? Ans: 5.75×10^{-9} M.

2-20) Calculate the pH of a solution obtained by mixing 10.0 mL of reagent HCl (density = 1.19 g/mL, 37.0% by wt. HCl) and 100.0 mL of 1.00 F NaOH and diluting to 1.00 L. Ans: 1.68.

2-21) What is the $[H_3O^+]$ in a solution formed by mixing 40.0 mL of 0.0200 F HCl and 25.00 mL of 0.0320 F ethylamine. Ans: 5.37×10^{-7} M.

2-22) When 100 mL of 0.0500 F KOH are mixed with 50.0 mL of 0.200 F trichloroacetic acid, what is the resulting solution pH? Ans: 1.58.

2-23) What is the $[OH^-]$ in a solution prepared by adding 50.0 mL of 0.100 F HNO_3 to 75.0 mL of 0.0500 F trimethyl amine? Ans: 1.00×10^{-12}.

2-24) Calculate the pH of the solution in the titration flask after 30.0 mL of 0.0500 F NaOH have been added to 50.0 mL of 0.0500 F HCl. Ans: 1.90.

2-25) Calculate the change in pH that occurs between the 20% and 80% titrated point in the titration of 50.0 mL of 0.100 F weak acid (pK_a = 5.00) with 0.100 F NaOH. Ans: 1.20.

2-26) Calculate the pH of the solution in the titration flask after 20.0 mL of 0.0300 F HCl have been added to 50.0 mL of 0.0450 F NaOH. Ans: 12.37.

2-27) What is the pH at the equivalence point in the titration of 50.00 mL of 0.100 F NH_3 with 0.200 F HCl? Ans: 5.21.

2-28) 50.0 mL of 0.100 F dichloroacetic acid are titrated with 0.100 F NaOH. When exactly 25.0 mL of the base have been added, the $[H^+]$ is found to be 1.74×10^{-2} M. What is the value of K_a for the acid? Ans: 5.54×10^{-2}.

2-29) What is the pH in the titration flask after 0.500 mL of 0.100 F NaOH have been added to 50.0 mL of 0.100 F acetic acid? Ans: 3.05.

Sections 2-5 to 2-6: Acid-Base Mixtures and Titrations

2-30) Consider the titration of 50.0 mL of 0.100 F formic acid with 0.100 F NaOH. At what volume of NaOH added will the pH be 7.00? Ans: 49.97 mL.

2-31) What volume of 0.100 F LiOH must be added to 50.0 mL of 0.100 F propionic (propanoic) acid to bring the resulting solution to pH 11.00? Ans: 51.01 mL.

2-32) It has been suggested that the weakest acid which should be titrated with a strong base has a pK_a of 7.00. Select from the following indicators the proper one for the titration of such an acid at 0.100 F with 0.100 F NaOH: phenolphthalein, *m*-nitrophenol, *p*-nitrophenol, chlorophenol red, methyl red. (Assume an initial volume of 50 mL if you wish.) Ans: phenolphthalein.

2-33) The molecular masses of amines are often determined by titration with a strong acid such as HCl. The pK_b of most aliphatic amines is about 4.0. If the amines and the HCl are both assumed to be about 0.0500 F, select the proper indicator for the titration from those you have available - methyl orange, chlorophenol red, *p*-nitrophenol, phenol red, thymol blue. Ans: chlorophenol red.

2-34) The following indicators are available: bromophenol blue, methyl red, bromocresol purple, *p*-nitrophenol, phenol red, and thymol blue. Which indicator would you choose in the titration of 50.0 mL of 0.100 F ammonia with 0.100 F HCl? Ans: methyl red.

Section 2.8: Buffers

2-35) A chemist wishes to prepare a buffer of pH 5.00 using sodium acetate and acetic acid in which the formality of the conjugate base is 0.0100 F. However, no sodium acetate is available. Calculate the weights of sodium hydroxide and acetic acid needed to prepare 1.00 L of the buffer. Ans: 0.400 and 0.946 g.

2-36) A buffer of pH 10.00 can be readily prepared from trimethylammonium chloride and trimethylamine. Calculate the initial concentrations of the weak acid and base necessary to prepare a buffer which will not change pH by more than 0.20 units on addition of 0.00100 mol of strong base to 100 mL of the buffer. Ans: 0.0379 and 0.0600 mol/L.

2-37) You wish to study the saponification of an ester at pH 10.00:

$$RCOOR' + OH^- \rightarrow RCOO^- + HOR'$$

You choose a buffer containing ammonia and ammonium chloride. What must the formalities of these substances be to hold the pH constant to within 0.10 unit if the formality of the ester (RCOOR') at the start of the reaction is 0.0500? You may choose a specific volume for the reaction if you wish. Ans: 1.35 and 0.235 mol/L.

2-38) Calculate the masses of trimethylammonium chloride and sodium hydroxide needed to form 1.00 L of a buffer of pH 10.00 such that the addition of 50.00 mL of buffer to 50.00 mL of another solution containing up to 0.0200 F H^+ or OH^- causes the pH to change no more than 0.02 units. Ans: 45.1 g NaOH, 175.9 g of TMAC.

Section 2.9: Polyfunctional Acids and Bases

2-39) Write mass balance, charge balance, and proton balance equations for solutions containing the following pure substances: phosphoric acid, sodium dihydrogen phosphate, potassium monohydrogen phosphate, and trisodium phosphate.

2-40) What is the pH of a 0.0500 F solution of Maleic acid? Ans: 1.72.

2-41) Determine the pH of the solution that results from the mixture of 50.0 mL of 0.0200 F trisodium phosphate and 50.0 mL of 0.0100 F HCl. Ans: 11.50.

2-42) What is the pH of a solution formed by addition of 30.0 mL of 0.200 F HCl to 25.0 mL of 0.100 F disodium maleate? Ans: 1.51.

2-43) Trisodium phosphate is often recommended as a strong cleaning agent. Calculate the pH of a 0.100 F solution of this material. Ans: 12.49.

2-44) What is the pH of a mixture of 100.0 mL of 0.0500 F Na_3PO_4 and 100.0 mL of 0.140 F HCl? Ans: 2.14.

2-45) Calculate the pH at the following points in the titration of 50.0 mL of 0.0500 F H_3PO_4 with 0.100 F NaOH: 0.00, 10.0, 20.0, 30.0, 40.0, 60.0, 75.0, and 90.0 mL of base added. Ans: 1.81, 2.22, 2.86, 6.60, 7.38, 11.61, 12.05, 12.27.

2-46) Reagent phosphoric acid has a density of 1.69 g/mL and is 85.0 % by weight pure acid. Calculate the mass of NaOH and the volume of reagent phosphoric acid needed to prepare 1.00 L of a buffer of pH 7.00 in which the sum of the weak acid and conjugate base formalities is 0.100. Ans: 5.55g and 6.82 mL.

2-47) A buffer of pH 2.00 can be prepared from HCl or from a weaker acid such as phosphoric acid and its conjugate base, sodium dihydrogen phosphate. Calculate the moles of HCl or H_3PO_4 (if F_b is assumed to be 0.0100) necessary to prepare 1.00 L of the buffer. Calculate the final pH for each buffer if 50.0 mL of buffer is added to 50.0 mL of a 0.00500 F NaOH solution. Ans: mol HCl = 0.0100, mol H_3PO_4 = 0.0383, final pH of HCl buffer = 2.60, of the phosphate buffer = 2.24.