

CHEM 1332

HOW TO SOLVE EQUILIBRIUM PROBLEMS

An Approach Based on Stoichiometry

Part II, Acid-Base Reactions

Introduction.

Part II of the handout will apply the approach introduced in Part I to acid-base chemistry. We shall focus on two cases where the application of stoichiometry leads to great simplifications: strong acids which are essentially 100% dissociated and weak acids with $K_a < 0.001$. These cases cover most mineral acids which are commonly used in the lab and in industry and acids normally encountered in organic and biochemistry. For example, most acids of biological importance are derivatives of acetic acid for which $K_a = 1.76 \times 10^{-5}$ at 25.0°C.

The approach to ionic equilibrium will be demonstrated by considering the titration of a monoprotic acid with a base. Not only are titrations important in their own right, other problems can be solved using the same techniques. All the examples in this handout occur in dilute aqueous solution at 25.0°C.

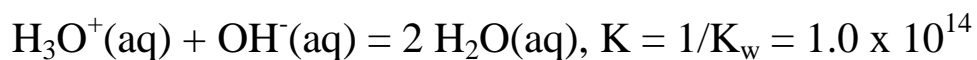
Steps in Solving an Equilibrium Problem. The steps outlined in Part I are worth repeating.

1. *Identify the problem to be solved.*
2. *Summarize the available chemistry with balanced equations. Net ionic equations are expected as charged species are involved.*
3. *Write down the equilibrium expressions for the reactions.*
4. *Assemble numerical data such as initial concentrations and equilibrium constants which are required to solve the problem.*
5. *This is the important step! Use stoichiometry and common sense to obtain values of as many concentrations as possible. Use your qualitative understanding of chemical equilibrium guide your use of stoichiometry. Approximations with a 10% or less error are acceptable because equilibrium constants are rarely known this well. Furthermore, although we are assuming ideal-solution behavior in our calculations, the consequences of non-ideality are quite large since ions are involved. There is no point in worrying about errors at the level of 10% when we casually ignore errors that are much larger.*
6. *Identify the concentrations which are not known. These are the unknowns in the problem. If there is more than one unknown, check to see if there is a stoichiometric relationship between the unknowns.*

7. *If you follow the above steps, you usually have one equation in one unknown which can be easily solved.*
8. *Check your answer at the end to confirm that any approximations made lead to reasonable results.*

Titration of a Strong Acid with a Strong Base.

Consider reacting 50.0 ml of 0.100 M hydrochloric acid with varying volumes of 0.0500 M sodium hydroxide. Stoichiometry is particularly useful as hydrochloric acid is a very strong acid and is essentially 100% dissociated in dilute aqueous solution and the reaction between hydronium ion and hydroxide ion has a very large equilibrium constant.



1) **Pure Hydrochloric Acid in Water.** This is the situation before any base has been added. Because the hydrochloric acid is 100% dissociated, the hydronium ion concentration equals the molar concentration of the acid, 0.100 M.

This yields a pH of 1.00 and $[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = 1.00 \times 10^{-13}$ M.

2) **Intermediate Point in the Titration.** Suppose 50.0 ml of the base solution is added to the 50.0 ml of the acid solution. Since the solutions are dilute, we can assume that the volumes add. The equilibrium constant for the acid-base reaction is so large that the reaction goes virtually 100% except in very dilute solution. *The*

base is the limiting reagent and the final hydronium ion concentration is the amount in excess. The total volume of the combined solution is 100.0 ml and the number of moles of hydronium ion at equilibrium is :

$$(0.100 \text{ M})(0.050 \text{ l}) - (0.050 \text{ M})(0.050 \text{ l}) = 0.0025 \text{ mole.}$$

$$[\text{H}_3\text{O}^+] = (0.0025 \text{ mole})/(0.100 \text{ liter}) = 0.0250 \text{ M}$$

$$\text{pH} = -\log_{10}(0.0250) = 1.60$$

$$[\text{OH}^-] = 1.0 \times 10^{-14}/0.025 = 4.0 \times 10^{-13}$$

3) **The Equivalence Point.** The *equivalence point* occurs when one mole of acid is added to one mole of base, e.g. 50.0 ml of 0.1000 M acid with 100.0 ml of 0.0500 M base. With the proper choice of indicator, this is the same as the *end point*. *The hydronium ions react completely with the hydroxide ions but the equilibrium concentrations of the two species are not zero as the product water is a weak acid and base and the dissociation of water must be considered.*

Recall that one hydronium ion is produced per hydroxide ion and consequently $[\text{OH}^-] = [\text{H}_3\text{O}^+]$ so $K_w = [\text{H}_3\text{O}^+]^2$. These relations yield a pH of 7.00. The solution is neutral.

Note: *The pH of the equivalence point for the titration of a strong base with a strong acid is independent of the nature of the acid and base and their concentrations. This is not the case when either the base or the acid is weak!*

4) **Past the Equivalence Point.** Here an excess of base is added and the hydrochloric acid is the limiting reagent. Suppose, for example, that 150.0 ml of 0.05 M base is mixed with 50.0 ml of 0.100 M acid. In this case, the concentration of the hydroxide ion is yielded directly by stoichiometry.

$$\text{moles of base} = (0.150)(0.0500) - (0.050)(0.100) = 0.0025 \text{ mole}$$

Consequently,

$$[\text{OH}^-] = 0.0025/0.200 = 0.0125 \text{ M.}$$

The concentration of hydronium ion is obtained from the expression for K_w :

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-14}/0.0125 = 8.00 \times 10^{-13} \text{ M (pH} = 12.10\text{)}.$$

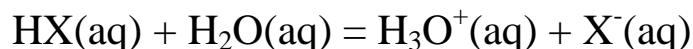
Note in all these examples that the application of stoichiometry has greatly simplified the problem. More effort is required in the reaction of a weak acid with a strong base.

Titration of a Weak Acid with a Strong Base.

The problem will be illustrated with the titration of a 50.0 ml of a 0.100 M solution of a hypothetical weak acid, HX, for which $K_a = 1.00 \times 10^{-5}$. The discussion will develop a problem-solving strategy and point out ties to related problems.

1) **Pure Acid in Water**. *Apply stoichiometric principles first!* The acid is weak so relatively few of the acid molecules dissociate. Consequently, [HX] is *ca.* 0.1 M.

The stoichiometry of the dissociation reaction,



dictates that one hydronium ion is formed per X^- ion and consequently $[\text{H}_3\text{O}^+] = [\text{X}^-]$.

The equilibrium expression simplified to one equation in one unknown which is easily solved.

$$K_a = [\text{H}_3\text{O}^+][\text{X}^-]/[\text{HX}] = [\text{H}_3\text{O}^+]^2/0.1$$

$$[\text{H}_3\text{O}^+] = ([\text{HX}]K_a)^{0.5} = 0.00100 \text{ M and pH} = 3.00$$

Note: The final result depends on both the value of K_a as well as the concentration of weak acid. It is useful to confirm that the initial simplifying approximation is valid. 0.001 is a small fraction of 0.1 so the approach is internally consistent and the final result is acceptable.

2) **Intermediate Point in the Titration.** Suppose 50.0 ml of 0.100 M HX is mixed with 75.0 ml of 0.0500 M NaOH. *The base is the limiting reagent so only a portion of the weak acid is converted into its conjugate base.* NaOH is a strong base and virtually every hydroxide ion yields an X^- ion. We are then able to draw the following stoichiometric conclusions:

$$\text{moles of } X^- = (0.075 \text{ l})(0.0500 \text{ M}) = 0.00375 \text{ mole } [X^-] = (0.0375 \text{ mole}) / (0.075 + 0.050 \text{ l}) = 0.0300 \text{ M}$$

$$\text{moles of HX} = (0.050)(0.100) - 0.00375 = 0.00125$$

$$[\text{HX}] = 0.00125 / 0.125 = 0.0100 \text{ M}$$

We have one unknown, $[\text{H}_3\text{O}^+]$, which can be obtained by substituting the known quantities into the equilibrium constant expression.

$$1.00 \times 10^{-5} = [\text{H}_3\text{O}^+](0.0300) / (0.0100)$$

The above equation yields

$$[\text{H}_3\text{O}^+] = 3.33 \times 10^{-6} \text{ and pH } 5.47.$$

The end result can be obtained in several ways. The titration protocol is outlined above.

One could also transfer 0.0100 mole of HX and 0.0300 mole of NaX to a 1.000 liter volumetric flask (How much if you used a 0.100 liter flask?) and add water to the 1.000 liter mark. This would generate a solution which is 0.0100 M in HX and 0.0300 M in NaX and would have the same pH, 5.47.

Note: The pH depends on the ratio $[\text{X}^-]/[\text{HX}]$ which is equal to the ratio of the number of moles so that the pH is independent of the total volume of water. Furthermore, the pH depends logarithmically on the concentration of hydronium ion and an order-of-magnitude (i.e. factor of ten) change in the ratio $[\text{X}^-]/[\text{HX}]$ is required to change $[\text{H}_3\text{O}^+]$ by 10 or the pH by one unit. Consequently, the pH of the solution is resistant to a change in pH (*becomes a buffer*). That is, large variations in the volume of base or equivalently in the ratio $[\text{X}^-]/[\text{HX}]$ lead to small changes in the pH. This condition prevails as long as X^- and HX have comparable concentrations, i.e. within an order of magnitude. The buffering

property of a solution of a weak acid and its conjugate base is illustrated by the full titration curve. After an initial jump, the pH changes slowly with addition of base until the equivalence point. Then the ratio $[X^-]/[HX]$ changes by orders of magnitude as $[HX]$ drops precipitously.

The dependence of the pH on the ratio $[X^-]/[HX]$ is useful in the experimental determination of K_a . At the halfway point in the titration (e.g. 50.0 ml of 0.1 M HX plus 50.0 ml of 0.05 M NaOH), the ratio is exactly one and K_a equals $[H_3O^+]$. Hence the pH at the point where half the volume of strong base required to reach the equivalence point has been added equals the pKa of the weak acid being titrated.

A solution with these desirable characteristics is called a buffer.

Buffering is very important as pH controls the rate and direction of many reactions, particularly reactions in living organisms. The student is advised to master buffer problems as they are frequently encountered in chemical systems.

3) **The equivalence point.** In our example, 50.0 ml of 0.100 M HX has been mixed with 100.0 ml of 0.0500 M NaOH. *Neither reactant is in excess and the product is the conjugate base X.*

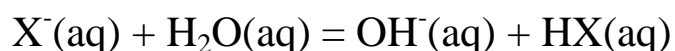
In many cases and certainly in the cases we shall consider, the values of K_a and K_w are such that HX is a weak acid and X^- is also a weak base. Hence, at the equivalence point we have the problem of the solution of a weak base in water. This is the mirror image of the problem at the start of the titration.

The molar concentration of the weak base X^- is given by

$$[(0.050 \text{ l})(0.100\text{M})]/(0.050 \text{ l} + 0.100 \text{ l}) = 0.0333 \text{ M}$$

One could achieve the same result by preparing a 0.0333 M solution of NaX.

The reaction defining the properties of X^- as a base is



$$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.0 \times 10^{-5} = 1.0 \times 10^{-9} \ll 1$$

Some texts also refer to the above reaction as a *hydrolysis reaction*.

Since K_b is so small, very little of the base is converted to its conjugate acid and

$$[X^-] \text{ at equilibrium} = 0.0333 \text{ M.}$$

The stoichiometry dictates that $[\text{OH}^-] = [\text{HX}]$.

Note that we are neglecting any contributions from the weak base water. We can therefore conclude that

$$K_b = [\text{OH}^-][\text{HX}]/[\text{X}^-] = [\text{OH}^-]^2/[\text{X}^-]$$

$$[\text{OH}^-] = (K_b[\text{X}^-])^{0.5} = [(1.0 \times 10^{-9})(0.0333)]^{0.5} = 5.8 \times 10^{-6} \text{ M}$$

$[\text{OH}^-]$ is very small compared with $[\text{X}^-]$ and the simplifying approximation is valid.

The concentration of hydronium ion is easily calculated from the ion-product of water expression:

$$[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-] = 1.0 \times 10^{-14}/5.8 \times 10^{-6} = 1.7 \times 10^{-9} \text{ M}.$$

This yields a pH of 8.76.

Note: The solution at the equivalence point of the titration of a weak acid with a strong base is basic and that the value of the pH depends on the concentration of the solution as well as the value of K_b (K_a).

4) **Past the equivalence point**. An excess of base has been added. Since OH^- is a much stronger base than X^- , one can ignore the small contributions that X^- makes to the pH. Consequently, this

portion of the titration curve is identical to that obtained in the titration of a strong acid with a strong base.

Variations on a Theme.

We have focused primarily on the titration of a weak acid with a strong base.

The parallel problem, the titration of a weak base with a strong acid, is handled similarly. The start of the titration is a solution of the pure base in water. This is handled identically to the equivalence point in the titration of a weak acid with a strong base. The region between the start and the equivalence point is the buffer region and all buffer problems are identical. The pH is determined by the ratio of the concentrations of the base and its conjugate acid or depending on your perspective the conjugate base and its acid. The solution at the equivalence point is a solution of a weak acid in water. Finally, beyond the equivalence point, the strong acid is in excess and the pH is dominated by the concentration of excess acid, a quantity readily determined from stoichiometry.

The case of the titration of a polyprotic acid with n ionizable protons. The problem can be divided into n cases of the titration of a monoprotic acid. That is the titration of phosphoric acid with

sodium hydroxide can be simplified by separately considering the removal of one proton from H_3PO_4 , H_2PO_4^- , and HPO_4^{2-} .

There is one qualification to this simplification. The first and second equivalence points (in general the first through $n-1$ 'th equivalence points) must be handled differently as multiple equilibria that are involved.

Solution of Difficult Problems. A difficult problem is one in which the simplifying approximations are not justified or several reactions occur simultaneously. Therefore, a systematic approach is required.

For a system involving n species, n equations are required. These are generated by 1) equilibrium constant expression(s), 2) mass balances, and 3) a charge balance.

The charge balance is required because charged species are involved in acid-base equilibria. The system of equations is solved numerically. However, estimates of the equilibrium concentrations are required. Hence, in cases in which the equilibrium constants are either very large or very small, the approach of making simplifying assumptions and hence converting an intractable problem into a tractable one is necessary and sufficient. In the

difficult cases, it is not sufficient but is still necessary as a step towards a full solution.

Difficult problems will not be addressed in this course. The interested student should consult the classic treatise by Butler.(J. N. Butler, Ionic Equilibrium: A Mathematical Approach, Addison-Wesley, Reading, MA, 1964.)