An Intuitive Approach to Chemical Equilibrium
Second Edition

Sahand Rabbani

Preface

I wrote this instructional text over the course of several months during Mr. James Shannon's AP Chemistry class at Pittsford-Mendon High School (2002-2003). In an attempt to help my fellow students better understand the analysis of buffered systems, I decided to write out a few example problems and walk them through it, making sure to emphasize some of what I considered to be the more subtle points.

I had always been warned by former AP Chemistry students of the mystical topic of "buffers." For some reason, calculations involving buffered systems had always been a challenging topic in AP Chemistry. Mr. Shannon always insisted that practice made perfect and allowed us to recognize the critical patterns that would help us solve problems. Indeed, after many calculations and examples, the mystic aura of buffers dissolved away.

Here, I endeavor to implement Mr. Shannon's unparalleled teaching philosophy. I have tried to provide a short collection of problems dealing with a variety of equilibrium systems. This piece is not meant to stand on its own as an introduction to chemical equilibrium; rather, it is meant to help the student further develop the skills and intuition that are needed to form a strong fundamental understanding of the quantitative analysis of equilibrium systems.

This text should always be freely available to motivated students who wish to supplement their learning. It would be my greatest reward if even one student picked up this text and could say that he or she found a better grasp of chemical equilibrium because of it.

Sahand Rabbani
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Chapter 1

Introduction

In this text, we will consider quantitative calculations for chemical systems in equilibrium. We will deal primarily with equilibrium systems involving Bronsted-Lowery acids and bases. Such systems are often called *buffers*.

In order to perform quantitative buffer calculations, we must first understand the nature of these buffered systems. Buffered systems, so called because they resist large pH changes with the addition of acids or bases, consist of an equilibrium mixture of a weak acid and a strong base or a weak base and a strong acid.

In the next chapter, we will deal only with the former. In the following three chapters, we will extend our analysis to cover many permutations of acids and bases, weak and strong. We will conclude with a discussion of other topics in chemical equilibrium: a brief review of gaseous equilibrium and a few examples on salt solubility.

Chapter 2

Weak Acids and Strong Bases

2.1 Introduction

We can classify problems that involve weak acids and strong bases into five categories. In this chapter, we consider a systematic analysis of each.

2.2 The Simple Dissociation of a Weak Acid

In the first case, we deal only with the acid, before any base has been added. To demonstrate, we will answer this question:

> What is the pH of a 0.30-M solution of nitrous acid?

We must first write the dissociation reaction for this weak acid, including all charges and phases:

$$HNO_2(aq) + H_2O(l) = H_3O^+(aq) + {NO_2}^-(aq) \tag{2.1}$$

which is a specific instance of the more general formula for the dissociation of a weak acid:

$$HA(aq) + H_2O(l) = H_3O^+(aq) + A^-(aq) \tag{2.2}$$

The mass action expression is

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{[{NO_2}^-][H_3O^+]}{[HNO_2]} = 4.5 \times 10^{-4} \tag{2.3}$$

where the last value is a tabulated constant. To find the pH, we must first know the hydronium ion concentration. We shall call this unknown equilibrium concentration x and work from there.

$$\begin{array}{ccccccc} HNO_2(aq) & + & H_2O(l) & = & H_3O^+(aq) & + & {NO_2}^-(aq) \\ 0.30\text{ M} - x & & & & 0.00\text{ M} + x & & 0.00\text{ M} + x \end{array} \tag{2.4}$$

Plugging these new concentrations into the equilibrium expression, we have

$$K_a = \frac{(x)(x)}{0.30\text{ M} - x} = 4.5 \times 10^{-4} \tag{2.5}$$

Since x is small compared to 0.30 M, we eliminate it and rewrite Eq. 2.5:

$$K_a = \frac{x^2}{0.30\text{ M}} = 4.5 \times 10^{-4} \tag{2.6}$$

Solving for x yields 0.0116 M. We may now calculate the pH:

$$pH = -\log x = -\log(0.0116 \text{ M}) = 1.93 \tag{2.7}$$

But, of course, on a multiple-choice test, where no work needs to be shown, we simply plug the numbers into this convenient equation:

$$pH = -\log\sqrt{K_a C_a} = -\log\sqrt{4.5 \times 10^{-4} \times 0.30 \text{ M}} = 1.93 \tag{2.8}$$

where C_a is the initial concentration of the acid.

2.3 A Solution of a Weak Acid and a Strong Base

The second category, which seems to conjure the most confusion, is only slightly more complicated. The difference between this case and the former is that there is an initial concentration on the right side of the dissociation equation. To demonstrate:

> What is the pH of a solution containing 20.0 mL of 0.40-M nitrous acid and 15.0 mL of 0.20-M sodium hydroxide?

Let us return to the acid dissociation equation, Eq. 2.1:

$$HNO_2(aq) + H_2O(l) = H_3O^+(aq) + NO_2{}^-(aq)$$

and the equilibrium expression Eq. 2.3:

$$K_a = \frac{[NO_2{}^-][H_3O^+]}{[HNO_2]} = 4.5 \times 10^{-4}$$

The nitrite ($NO_2{}^-$) does *not* have an initial concentration of 0.00 M because of the addition of the base; therefore, we must solve for it through an equation that relates $NaOH$ to $NO_2{}^-$. Here it is:

$$Na^+ + OH^- + HNO_2 = Na^+ + H_2O + NO_2{}^- \tag{2.9}$$

Since Na^+ is a spectator ion, it drops out, leaving:

$$OH^- + HNO_2 \rightarrow H_2O + NO_2{}^- \tag{2.10}$$

Notice that this is not an equilibrium equation: the reaction goes to completion. Since the hydroxide and nitrite ions react in a one-to-one ratio, we know that the new number of moles of $NO_2{}^-$ is identical to the initial number of moles of OH^-:

$$n_B = M_B V = (0.015 \text{ L})(0.20 \text{ M}) = 0.0030 \text{ mol} \tag{2.11}$$

This, divided by the total volume (20.0 mL + 15.0 mL = 0.035 L), yields 0.0857 M of $NO_2{}^-$. The same number of moles are also subtracted from $[HNO_2]$:

$$\begin{aligned} n_A &= M_A V - n_B \\ &= (0.020 \text{ L})(0.40 \text{ M}) - 0.0030 \text{ mol} = 0.0050 \text{ mol} \end{aligned} \tag{2.12}$$

This, divided by the total volume (0.035 L), yields 0.143 M of HNO_2. Solving the equilibrium expression for $[H_3O^+]$ gives us

$$\begin{aligned} [H_3O^+] &= \frac{K_a[HNO_2]}{[NO_2{}^-]} \\ &= \frac{(4.5 \times 10^{-4})(0.143 \text{ M})}{0.0857 \text{ M}} = 7.5 \times 10^{-4} \text{ M} \end{aligned} \tag{2.13}$$

We take the negative logarithm and find the pH to be 3.12.

2.4 The Half Equivalence Point

Let us consider, now, what happens at the half equivalence point.

> What is the pH of solution containing 20.0 mL of 0.40-M nitrous acid and 20.0 mL of 0.20-M sodium hydroxide?

At this point, the moles of base are half the moles of acid, and the new problem can be solved just as above. But on a multiple-choice test, there is a quick formula that will immediately yield the pH:

$$pH = pK_a = -\log(4.5 \times 10^{-4}) = 3.35 \tag{2.14}$$

This equation is only valid at the half equivalence point. Notice the relatively small change in pH from the previous problem. At the half equivalence point, the solution is said to be a *perfect buffer* because it best resists changes in pH.

2.5 The Equivalence Point

Next, we analyze the solution at the equivalence point.

> What is the pH of a solution containing 20.0 mL of 0.40-M nitrous acid and 40.0 mL of 0.20-M sodium hydroxide?

Eq. 2.10 shows us that the equal moles of acid and base will fully combine to yield only products; no reactants are left over. But we are left with $NO_2{}^-$, which hydrolyzes:

$$NO_2{}^- + H_2O = OH^- + HNO_2 \tag{2.15}$$

We need to find the OH^- concentration. We resort to the equilibrium expression of the base reaction:

$$\begin{aligned} K_b &= \frac{K_w}{K_a} = \frac{[HNO_2][OH^-]}{[NO_2{}^-]} \\ &= \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11} \end{aligned} \tag{2.16}$$

Since OH^- and HNO_2 react in a one-to-one ratio, they are produced in the same number of moles. We shall call their equilibrium concentration x.

$$\frac{K_w}{K_a} = \frac{(x)(x)}{[NO_2{}^-]} \tag{2.17}$$

We are left to find the equilibrium molarity of $NO_2{}^-$. Upon consulting Eq. 2.10, we realize that the moles of $NO_2{}^-$ can be equated to the original number of moles of OH^- or HNO_2:

$$n = MV = (0.040\ \text{L})(0.20\ \text{M}) = 0.0080\ \text{mol} \tag{2.18}$$

Dividing by the total volume ($20.0\ \text{mL} + 40.0\ \text{mL} = 0.060\ \text{L}$), yields 0.133 M. We can now solve for $[OH^-]$:

$$\begin{aligned} x &= [OH^-] = \sqrt{\frac{K_w}{K_a}[NO_2{}^-]} \\ &= \sqrt{2.2 \times 10^{-11} \times 0.133\ \text{M}} = 1.72 \times 10^{-6}\ \text{M} \end{aligned} \tag{2.19}$$

To find pH:

$$\begin{aligned} pH &= 14 - pOH = 14 + \log[OH^-] \\ &= 14 + \log(1.72 \times 10^{-6}\ \text{M}) = 8.24 \end{aligned} \tag{2.20}$$

On a multiple-choice test, we can simply use

$$pH = 14 + \log\sqrt{\frac{K_w}{K_a}C_s} = 8.24 \tag{2.21}$$

where C_s is the initial concentration of the salt.

2.6 Beyond the Equivalence Point

What happens when even more base is added? Let's take a look.

> What is the pH of solution containing 20.0 mL of 0.40-M nitrous acid and 45.0 mL of 0.20-M sodium hydroxide?

The pH of solutions titrated with a strong base beyond the equivalence point are easy to calculate, for we need only deal with the unreacted base:

$$HNO_2 + OH^- = H_2O + NO_2{}^- \tag{2.22}$$

The moles of nitrous acid is 0.0080 mol and the moles of hydroxide is 0.0090 mol. The remaining moles of hydroxide, therefore, is the difference, 0.0010 mol. When divided by the total volume, 0.065 L, we find the molarity to be 0.0153 M. The negative logarithm, subtracted from 14, yields a pH of 12.19.

Chapter 3

Weak Bases and Strong Acids

3.1 Introduction

Now that we have explored the behavior of a weak acid in the presence of a strong base, we will take a closer look at the reverse scenario: a solution of a weak base and a strong acid. As in the analysis of the former, we can think of five different categories of problems that involve weak bases and strong acids. We will engage, again, in a systematic analysis of each.

3.2 The Simple Dissociation of a Weak Base

In the simplest case, where no acid has been added, there is only weak base. To demonstrate:

> What is the pH of a 0.50-M solution of dimethylamine?

We must write the dissociation reaction for this weak base:

$$(CH_3)_2NH(aq) + H_2O(l) = OH^-(aq) + (CH_3)_2NH_2{}^+(aq) \tag{3.1}$$

The mass action expression is, therefore,

$$K_b = \frac{[(CH_3)_2NH_2{}^+][OH^-]}{[(CH_3)_2NH]} = 9.6 \times 10^{-4} \tag{3.2}$$

where the last value is a tabulated constant. To find the pH, we must first know the hydroxide ion concentration. We shall call this unknown equilibrium concentration x and work from there.

$$\begin{array}{ccccccc} (CH_3)_2NH(aq) & + & H_2O(l) & = & OH^-(aq) & + & (CH_3)_2NH_2{}^+(aq) \\ 0.50\text{ M} - x & & & & 0.00\text{ M} + x & & 0.00\text{ M} + x \end{array} \tag{3.3}$$

At equilibrium, we have

$$K_b = \frac{(x)(x)}{0.50\text{ M} - x} = 9.6 \times 10^{-4} \tag{3.4}$$

Because x is small compared to 0.50 M, we are justified in eliminating it. Eq. 3.4, thus rewritten, is

$$K_b = \frac{x^2}{0.50\text{ M}} = 9.6 \times 10^{-4} \tag{3.5}$$

Solving for x yields 0.0219 M. Solving for pH is now easy:

$$pH = 14 - pOH = 14 + \log x = 14 + \log(0.0219 \text{ M}) = 12.34 \tag{3.6}$$

Since x represents the OH^- concentration, pH must be derived from pOH, as above. On a multiple-choice test, however, we use this convenient equation:

$$\begin{aligned} pH &= 14 + \log \sqrt{K_b C_b} \\ &= 14 + \log \sqrt{9.6 \times 10^{-4} \times 0.50 \text{ M}} = 12.34 \end{aligned} \tag{3.7}$$

where C_b is the initial concentration of the weak base.

3.3 A Solution of a Weak Base and a Strong Acid

Let's add a strong acid.

> What is the pH of a solution containing 10.0 mL of 0.30-M dimethylamine and 10.0 mL of 0.10-M hydrochloric acid?

We return to the base dissociation expression, Eq. 3.1:

$$(CH_3)_2NH(aq) + H_2O(l) = OH^-(aq) + (CH_3)_2NH_2{}^+(aq)$$

and the mass action expression, Eq. 3.2:

$$K_b = \frac{[(CH_3)_2NH_2{}^+][OH^-]}{[(CH_3)_2NH]} = 9.6 \times 10^{-4}$$

In this scenario, $(CH_3)_2NH_2{}^+$ does not have an initial concentration of 0.00 M because of the addition of the strong acid (HCl); to find the initial concentration, we must solve for it through an equation that relates HCl to $(CH_3)_2NH_2{}^+$:

$$(CH_3)_2NH + H^+ + Cl^- + H_2O \rightarrow Cl^- + H_2O + (CH_3)_2NH_2{}^+ \tag{3.8}$$

Since Cl^- is a spectator ion, it is not included in the net ionic equation:

$$(CH_3)_2NH + H_3O^+ \rightarrow H_2O + (CH_3)_2NH_2{}^+ \tag{3.9}$$

Notice that this is not an equilibrium equation; the reaction goes to completion. Since H_3O^+ and $(CH_3)_2NH_2{}^+$ react in a one-to-one ratio, we know that the latter's quantity after the reaction is identical to the former's before the reaction:

$$n_A = M_A V = (0.010 \text{ L})(0.10 \text{ M}) = 0.0010 \text{ mol} \tag{3.10}$$

This, divided by the total volume (10.0 mL + 10.0 mL = 0.020 L), yields 0.050 M $(CH_3)_2NH_2{}^+$. The same number of moles are also subtracted from $[(CH_3)_2NH]$:

$$\begin{aligned} n_B &= M_B V - n_A \\ &= (0.010 \text{ L})(0.30 \text{ M}) - 0.0010 \text{ mol} = 0.0020 \text{ mol} \end{aligned} \tag{3.11}$$

This, divided by the total volume (0.020 L), yields 0.10 M HNO_2. Solving the equilibrium expression for $[OH^-]$ gives us

$$\begin{aligned}[OH^-] &= \frac{K_b[(CH_3)_2NH]}{[(CH_3)_2NH_2{}^+]} \\ &= \frac{(9.6 \times 10^{-4})(0.10 \text{ M})}{(0.50 \text{ M})} = 1.92 \times 10^{-3} \text{ M} \qquad (3.12)\end{aligned}$$

Finally, to solve for pH:

$$\begin{aligned}pH &= 14 - pOH = 14 + \log[OH^-] \\ &= 14 + \log(1.92 \times 10^{-3} \text{ M}) = 11.28 \qquad (3.13)\end{aligned}$$

3.4 The Half Equivalence Point

At the half equivalence point, Eq. 3.12 simplifies to a convenient identity. Let's take a look.

> What is the pH of a solution containing 20.0 mL of 0.30-M dimethylamine and 15.0 mL of 0.20-M hydrochloric acid?

At this point, the moles of acid are half the moles of base, and the new problem can be solved just as above. On a multiple-choice test, however, we can take a short cut:

$$\begin{aligned}pH &= 14 - pOH = 14 + pK_b \\ &= 14 + \log(9.6 \times 10^{-4}) = 10.98 \qquad (3.14)\end{aligned}$$

This equation is only valid at the half equivalence point.

3.5 The Equivalence Point

Now, let us consider what happens at the equivalence point.

> What is the pH of a solution containing 20.0 mL of 0.30-M dimethylamine and 15.0 mL of 0.40-M hydrochloric acid?

Eq. 3.9 shows us that the equal moles of acid and base will fully combine to yield only products. No reactants remain. But we are left with $(CH_3)_2NH_2{}^+$, which hydrolyzes:

$$(CH_3)_2NH_2{}^+(aq) + H_2O(l) = H_3O^+(aq) + (CH_3)_2NH(aq) \qquad (3.15)$$

We need to find the H_3O^+ concentration; we turn, therefore, to the equilibrium expression for the dissociation of the conjugate acid:

$$\begin{aligned}K_a &= \frac{K_w}{K_b} = \frac{[(CH_3)_2NH][H_3O^+]}{[(CH_3)_2NH_2{}^+]} \\ &= \frac{1.0 \times 10^{-14}}{9.6 \times 10^{-4}} = 1.0 \times 10^{-11} \qquad (3.16)\end{aligned}$$

Since H_3O^+ and $(CH_3)_2NH$ react in a one-to-one ratio, they are produced in the same number of moles. We shall call their equilibrium concentration x:

$$\frac{K_w}{K_b} = \frac{(x)(x)}{[(CH_3)_2NH_2{}^+]} \tag{3.17}$$

We must now to find the equilibrium molarity of $(CH_3)_2NH_2{}^+$. Eq. 3.9 shows that the moles of $(CH_3)_2NH_2{}^+$ is equal to the original moles of H_3O^+ or $(CH_3)_2NH$:

$$n = MV = (0.020 \text{ L})(0.30 \text{ M}) = 0.0060 \text{ mol} \tag{3.18}$$

Dividing by the total volume (20.0 mL + 15.0 mL = 0.035 L), yields 0.171 M. We can now solve for $[H_3O^+]$:

$$\begin{aligned} x &= [H_3O^+] = \sqrt{\frac{K_w}{K_b}[(CH_3)_2NH_2{}^+]} \\ &= \sqrt{1.0 \times 10^{-11} \times 0.171 \text{ M}} = 1.34 \times 10^{-6} \text{ M} \end{aligned} \tag{3.19}$$

For pH, we take the negative logarithm of the hydronium ion concentration, which yields 5.87. On a multiple-choice test, we can simply use

$$pH = -\log\sqrt{\frac{K_w}{K_b}C_s} = 5.87 \tag{3.20}$$

where C_s is the initial concentration of the salt.

3.6 Beyond the Equivalence Point

When additional acid is added, the problem simplifies.

> What is the pH of a solution containing 20.0 mL of 0.30-M dimethylamine and 20.0 mL of 0.40-M hydrochloric acid?

The pH of solutions titrated with a strong acid beyond the equivalence point is easy to calculate, for we need only deal with the unreacted acid:

$$(CH_3)_2NH + H_3O^+ \rightarrow H_2O + (CH_3)_2NH_2{}^+ \tag{3.21}$$

The moles of base are 0.0060 mol and the moles of hydronium are 0.0080 mol. The remaining moles of hydronium, therefore, is the difference, 0.0020 mol. When divided by the total volume, 0.040 L, we find the molarity to be 0.050 M. The negative logarithm yields a pH of 1.30.

Chapter 4

Weak Polyprotic Acids

4.1 Introduction

We have already analyzed the titration of weak monoprotic acids and weak monohydroxy bases. We turn, now, to study the behavior of weak polyprotic acids, first, in the presence of strong acids and, second, when titrated with strong monohydroxy bases. In our examples, we consider citric acid, whose three ionization constants are

$$\begin{aligned} K_{a1} &= 7.1 \times 10^{-4} && (4.1) \\ K_{a2} &= 1.7 \times 10^{-5} && (4.2) \\ K_{a3} &= 6.3 \times 10^{-6} && (4.3) \end{aligned}$$

There are three equivalence and three half equivalence points for this triprotic acid. Before we become too concerned with them, we will first look at the simple dissociation of the acid when no base is present.

4.2 The Simple Dissociation of a Weak Polyprotic Acid

Our objective is to find the concentration of all ions and molecules present in the solution. For example's sake, we will deal with a 2.0-M solution of citric acid. First, we must write the three dissociation reactions:

$$\begin{aligned} H_3C_6H_5O_7(aq) + H_2O(l) &= H_3O^+(aq) + H_2C_6H_5O_7{}^-(aq) && (4.4) \\ H_2C_6H_5O_7{}^-(aq) + H_2O(l) &= H_3O^+(aq) + HC_6H_5O_7{}^{2-}(aq) && (4.5) \\ HC_6H_5O_7{}^{2-}(aq) + H_2O(l) &= H_3O^+(aq) + C_6H_5O_7{}^{3-}(aq) && (4.6) \end{aligned}$$

The mass action expression for the first dissociation is

$$K_{a1} = \frac{[H_2C_6H_5O_7{}^-][H_3O^+]}{[H_3C_6H_5O_7]} = 7.1 \times 10^{-4} \qquad (4.7)$$

Let us analyze this system in equilibrium by calling the amount reacted x:

$$\begin{array}{ccccccccc} H_3C_6H_5O_7(aq) & + & H_2O(l) & = & H_3O^+(aq) & + & H_2C_6H_5O_7{}^-(aq) \\ 2.0\text{ M} - x & & & & 0.0\text{ M} + x & & 0.0\text{ M} + x \end{array} \qquad (4.8)$$

Plugging these new concentrations into the equilibrium expression, we have

$$K_{a1} = \frac{(x)(x)}{2.0 \text{ M} - x} = 7.1 \times 10^{-4} \tag{4.9}$$

Since x is small compared to 2.0 M (ionization is less than 5%), we eliminate it and rewrite Eq. 4.9:

$$K_{a1} = \frac{x^2}{2.0 \text{ M}} = 7.1 \times 10^{-4} \tag{4.10}$$

Solving for x yields 0.0377 M. Since the only significant hydronium ions result from the first reaction, we can safely declare the pH to be the negative logarithm of this value:

$$pH = -\log x = -\log(0.0377 \text{ M}) = 1.42 \tag{4.11}$$

But, of course, on a multiple-choice test, where no work needs to be shown, we can use this familiar equation, assuming ionization is less than 5%:

$$\begin{aligned} pH &= -\log \sqrt{K_{a1} C_a} \\ &= -\log \sqrt{7.1 \times 10^{-4} \times 2.0 \text{ M}} = 1.42 \end{aligned} \tag{4.12}$$

where C_a is the initial concentration of the acid. Also, knowing $[H_3O^+]$, we can easily find $[OH^-]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.0377 \text{ M}} = 2.7 \times 10^{-13} \text{ M} \tag{4.13}$$

As we know the original molarity of citric acid and the amount that reacts, we can calculate the new molarity, which is their difference:

$$\begin{aligned} [H_2C_6H_5O_7{}^-] &= [H_2C_6H_5O_7{}^-]_0 - x \\ &= 2.0 \text{ M} - 0.0377 \text{ M} = 2.0 \text{ M} \end{aligned} \tag{4.14}$$

Next, we look at the second mass action expression:

$$K_{a2} = \frac{[HC_6H_5O_7{}^{2-}][H_3O^+]}{[H_2C_6H_5O_7{}^-]} = 1.7 \times 10^{-5} \tag{4.15}$$

Letting an amount x react, we can plug in some numbers that we have already calculated and make appropriate approximations:

$$K_{a2} = \frac{(x)(2.0 \text{ M} + x)}{2.0 \text{ M} - x} = x = [HC_6H_5O_7{}^{2-}] = 1.7 \times 10^{-5} \text{ M} \tag{4.16}$$

In fact, when no other acid or base is added, the concentration of the ion from the second dissociation will always be approximately equal to K_{a2}. Finally, to find $[C_6H_5O_7{}^{3-}]$:

$$K_{a3} = \frac{[C_6H_5O_7{}^{3-}][H_3O^+]}{[HC_6H_5O_7{}^{2-}]} = 6.3 \times 10^{-6} \tag{4.17}$$

This is an instance of the convenient equation:

$$[A^{3-}] = \frac{K_{a2} K_{a3}}{\sqrt{K_{a1} C_a}} \tag{4.18}$$

In Eq. 4.17, dropping the x where appropriate and solving for $[C_6H_5O_7{}^{3-}]$ gives us 2.8×10^{-9} M.

4.3 A Solution of a Weak Polyprotic Acid and a Strong Acid

Before we begin to titrate, let us add a strong acid to this solution so that we have 2.0 M of citric acid and 1.0 M of HCl. Eq. 4.8 will look a little different, with an initial hydronium ion concentration:

$$\begin{array}{ccccccc} H_3C_6H_5O_7(aq) & + & H_2O(l) & = & H_3O^+(aq) & + & H_2C_6H_5O_7{}^-(aq) \\ 2.0\text{ M} - x & & & & 1.0\text{ M} + x & & 0.0\text{ M} + x \end{array} \tag{4.19}$$

After taking a look at the mass action expression for the first dissociation, we can find $[H_2C_6H_5O_7{}^-]$:

$$\begin{aligned} K_{a1} &= \frac{[H_2C_6H_5O_7{}^-][H_3O^+]}{[H_3C_6H_5O_7]} \\ &= \frac{(x)(1.0\text{ M} + x)}{2.0\text{ M} - x} = 7.1 \times 10^{-4} \end{aligned} \tag{4.20}$$

Since x is small relative to 1.0 M and 2.0 M, we can eliminate it and solve for $[H_2C_6H_5O_7{}^-]$: 1.4×10^{-3} M. The hydronium ion concentration, dominated by the dissociation of HCl, is 1.0 M. The other quantities can be found by following the steps detailed in Section 4.2.

4.4 The First and Second Equivalence Points

Since, at these equivalence points, amphiprotic anions (anions that can act as acids or bases) are present, the calculation becomes more complicated. The equations that represent the pH follow:

First equivalence point:

$$pH = \frac{pK_{a1} + pK_{a2}}{2} = -\log\sqrt{K_{a1}K_{a2}} = 3.96 \tag{4.21}$$

Second equivalence point:

$$pH = \frac{pK_{a2} + pK_{a3}}{2} = -\log\sqrt{K_{a2}K_{a3}} = 4.99 \tag{4.22}$$

4.5 The Half Equivalence Points

The pH at the half equivalence points, however, is still given by a variation of the convenient equation discussed in Chapter 2:

First half equivalence point:

$$pH = pK_{a1} = -\log K_{a1} = 3.15 \tag{4.23}$$

Second half equivalence point:

$$pH = pK_{a2} = -\log K_{a2} = 4.77 \tag{4.24}$$

Third half equivalence point:

$$pH = pK_{a3} = -\log K_{a3} = 5.20 \tag{4.25}$$

4.6 The Third Equivalence Point

At the third equivalence point, the citric acid evolves completely into hydronium ions and $C_6H_5O_7{}^{3-}$. We will only deal, therefore, with the first hydrolysis of this ion, given by the equation

$$C_6H_5O_7{}^{3-}(aq) + H_2O(l) = OH^-(aq) + HC_6H_5O_7{}^{2-}(aq) \tag{4.26}$$

We need to find the OH^- concentration; resorting to the equilibrium expression of the above reaction,

$$\begin{aligned} K_{b1} &= \frac{K_w}{K_{a3}} = \frac{[HC_6H_5O_7{}^{2-}][OH^-]}{[C_6H_5O_7{}^{3-}]} \\ &= \frac{1.0\times10^{-14}}{6.3\times10^{-6}} = 1.6\times10^{-9} \end{aligned} \tag{4.27}$$

Let us say that we are titrating 50.0 mL of 3.0-M citric acid with 75.0 mL of 6.0-M sodium hydroxide (the moles of the latter is three times that of the former, for all three hydronium ions of one citric acid molecule must be dissociated). Since $C_6H_5O_7{}^{3-}$ and OH^- are produced in a one-to-one ratio, we can call both of their concentrations x:

$$\frac{K_w}{K_{a3}} = \frac{(x)(x)}{[C_6H_5O_7{}^{3-}]} \tag{4.28}$$

We must find the equilibrium molarity of $C_6H_5O_7{}^{3-}$, which is given by one third of the number of moles of base added:

$$n = \frac{MV}{3} = \frac{(0.075\text{ L})(6.0\text{ M})}{3} = 0.15\text{ mol} \tag{4.29}$$

Dividing by the total volume (50.0 mL + 75.0 mL = 0.125 L) yields 1.2 M. We can now solve for $[OH^-]$:

$$\begin{aligned} x &= [OH^-] = \sqrt{\frac{K_w}{K_{a3}}[C_6H_5O_7{}^{3-}]} \\ &= \sqrt{1.6\times10^{-9}\times1.2\text{ M}} = 4.4\times10^{-5}\text{ M} \end{aligned} \tag{4.30}$$

To find pH:

$$\begin{aligned} pH &= 14 - pOH = 14 + \log[OH^-] \\ &= 14 + \log(4.4\times10^{-5}\text{ M}) = 9.64 \end{aligned} \tag{4.31}$$

On a multiple-choice test, we can use the familiar equation,

$$pH = 14 + \log\sqrt{\frac{K_w}{K_{a3}}C_s} = 9.64 \tag{4.32}$$

where C_s is the initial concentration of the salt.

4.7 Calculating the pH at Any Stage in Titration: The Henderson-Hasselbach Equation

What happens when we are not at a convenient equivalence or half equivalence point? The Henderson-Hasselbach equation allows us to calculate the pH anyway. We are always dealing with some K_a, be it the first, second, or third, so we have, in the general case,

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \tag{4.33}$$

By the rules of logarithms, we derive

$$pK_a = -\log[H_3O^+] - \log\frac{[A^-]}{[HA]} = pH - \log\frac{[A^-]}{[HA]} \tag{4.34}$$

Thus,

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \tag{4.35}$$

where HA is the acid and A^- is its conjugate base.

Chapter 5

Adjusting the *pH* of a Buffer Solution

5.1 Introduction

In this chapter, we will learn how to manipulate the *pH* of buffered solutions. First, we will calculate the *pH* of a buffered solution when we are given the concentrations of the weak acid and its conjugate base. From there, we will proceed to lower the *pH* by adding a strong acid, then increase it by adding a strong base.

5.2 The *pH* of a Buffer Solution

Let us find the *pH* of a buffered solution prepared with 100 mL of 3.0-M hypochlorous acid and 50.0 mL of 1.5-M sodium hypochlorite. The dissociation equation for hypochlorous acid is

$$HOCl(aq) + H_2O(l) = H_3O^+(aq) + OCl^-(aq) \tag{5.1}$$

The mass action expression is, therefore,

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]} = 3.0 \times 10^{-8} \tag{5.2}$$

where the last value is a tabulated constant. To find the initial concentrations of the acid and base, we must find the moles of each and divide by the total volume, 0.150 L:

$$\begin{aligned} M_A &= \frac{n_A}{V} = \frac{(3.0 \text{ M})(0.100 \text{ L})}{0.150 \text{ L})} = 2.0 \text{ M} && (5.3) \\ M_B &= \frac{n_B}{V} = \frac{(1.5 \text{ M})(0.0500 \text{ L})}{0.150 \text{ L})} = 0.50 \text{ M} && (5.4) \end{aligned}$$

Now, let us look at this system in equilibrium by calling the amount reacted x:

$$\begin{array}{ccccccc} HOCl(aq) & + & H_2O(l) & = & H_3O^+(aq) & + & OCl^-(aq) \\ 2.0 \text{ M} - x & & & & 0.0 \text{ M} + x & & 0.5 \text{ M} + x \end{array} \tag{5.5}$$

Plugging these new concentrations into the equilibrium expression, we have

$$K_a = \frac{(0.50 \text{ M} + x)(x)}{0.20 \text{ M} - x} = 3.0 \times 10^{-8} \tag{5.6}$$

Since x is small compared to 2.0 M (ionization is much less than 5%), we eliminate it and rewrite the above equation:

$$K_a = \frac{(0.50\text{ M})(x)}{0.20\text{ M}} = 3.0 \times 10^{-8} \tag{5.7}$$

Solving for x, the hydronium ion concentration, we have 1.2×10^{-7} M. Thus, the pH is

$$pH = -\log x = -\log(1.2 \times 10^{-7}\text{ M}) = 6.92 \tag{5.8}$$

5.3 Decreasing the pH

What would we have to do to this system to obtain a pH of 6.00? Add a strong acid, of course. But how many moles? To answer this question, we revisit Eq. 5.1:

$$HOCl(aq) + H_2O(l) = H_3O^+(aq) + OCl^-(aq)$$

If we should add a strong acid, let us say HCl, it will have an immediate effect on the above system. We can ignore Cl^-, since it is a spectator ion, and consider only the net ionic equation that explains this effect:

$$OCl^- + H^+ \rightarrow HOCl \tag{5.9}$$

This equation tells us that the number of moles by which the hypochlorous acid increases is the same number of moles by which the hypochlorite ion decreases, which is equal to the number of moles of strong acid added. We can call this unknown quantity x:

$$\begin{array}{ccccccc} HOCl(aq) & + & H_2O(l) & = & H_3O^+(aq) & + & OCl^-(aq) \\ 0.30\text{ mol} + x & & & & 0.00\text{ mol} + x & & 0.075\text{ mol} - x \end{array} \tag{5.10}$$

The desired pH is given in the question (6.00), so we know that the hydronium ion concentration at equilibrium is the common antilogarithm of -6.00. Plugging into the mass action expression, we have

$$K_a = \frac{(\frac{0.075\text{ mol}-x}{0.150\text{ L}})(10^{-6}\text{ M})}{\frac{0.30\text{ mol}+x}{0.150\text{ L}}} = 3.0 \times 10^{-8} \tag{5.11}$$

The volumes cancel conveniently, leaving

$$3.0 \times 10^{-8}\text{ M} = \frac{(10^{-6}\text{ M})(0.075\text{ mol} - x)}{0.30\text{ mol} + x} \tag{5.12}$$

After some algebra, we isolate x and find its numerical value:

$$\begin{aligned} x &= \frac{(10^{-6}\text{ M})(0.075\text{ mol}) - (3.0 \times 10^{-8}\text{ M})(0.30\text{ mol})}{(10^{-6}\text{ M}) + (3.0 \times 10^{-8}\text{ M})} \\ &= 6.4 \times 10^{-2}\text{ mol} \end{aligned} \tag{5.13}$$

5.4 Increasing the pH

To increase the pH, we must add a strong base. In this case, the number of moles of the conjugate base will increase while the number of moles of the weak acid will decrease. The difference will be given by the number of moles of strong base added. With this in mind, how many moles of $NaOH$ are necessary to attain a neutral pH?

We know the number of moles of $HOCl$ and of OCl^-, and we also know the molarity of the hydronium ion that will give us a neutral pH, 1.0×10^{-7} M. Letting x represent the number of moles of strong base added, we can resort to the equilibrium expression:

$$K_a = \frac{(\frac{0.075\ \text{mol}+x}{0.150\ \text{L}})(10^{-7}\ \text{M})}{\frac{0.30\ \text{mol}-x}{0.150\ \text{L}}} = 3.0 \times 10^{-8} \tag{5.14}$$

which simplifies to

$$3.0 \times 10^{-8}\ \text{M} = \frac{(10^{-7}\ \text{M})(0.075\ \text{mol} + x)}{0.30\ \text{mol} - x} \tag{5.15}$$

Solving for x, we have

$$\begin{aligned} x &= \frac{(3.0 \times 10^{-8}\ \text{M})(0.30\ \text{mol}) - (10^{-7}\ \text{M})(0.075\ \text{mol})}{3.0 \times 10^{-8}\ \text{M} + 10^{-7}\ \text{M}} \\ &= 1.2 \times 10^{-2}\ \text{mol} \end{aligned} \tag{5.16}$$

5.5 Examples

For further practice, you may solve these examples on your own.

1. Given 0.40 moles of phenol (HC_6H_5O; $K_a = 1.3 \times 10^{-10}$) and 0.60 moles of $C_6H_5O^-$ dissolved in 5.0 L (though we know that this volume is inconsequential), how many moles of HCl must be added to attain a pH of 9.00?

   Answer: 0.48 moles

2. Given 0.90 moles of hydrocyanic acid (HCN; $K_a = 6.2 \times 10^{-10}$) and 0.50 moles of CN^- dissolved in 2.0 L, how many moles of KOH must be added to attain a perfect buffer? *Hint*: We can solve this the long way like the above problems by taking the pH of a perfect buffer to be pK_a, but a simpler case of this question will call for mere mental arithmetic: How many moles of KOH must be added to make the moles of HCN and CN^- equal?

   Answer: 0.20 moles

Chapter 6

Gaseous Equilibrium

Reactions involving gases form an important part of chemical equilibrium. Hitherto, we have considered only acid and base reactions, but we will provide a brief, and by no means sufficient, review of the key ideas and equations for solving problems in gaseous equilibrium.

Key Ideas

1. Exclude liquids and solids from the equilibrium expression.
2. Pressure measurements must always be expressed in atmospheres.
3. There are two equilibrium constants (K_c and K_p) for every gaseous reaction; they have no units and only change with temperature.

Key Equations

1. Generic reaction: $aA + bB = cC + dD$
2. $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
3. $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$
4. $P_n = \chi_n \times P_T$
5. $K_p = K_c(RT)^{\Delta n}$

Chapter 7

Solubility Product and Precipitation

7.1 Introduction

In this chapter, we will deal with solutions prepared by dissolving solids in water and the formation of precipitates. We will begin by laying down some basic definitions essential to our understanding of solubility, then proceed to solve simple problems by using the solubility product equation. After establishing a firm basis for these problems, we will briefly visit *pH* and then introduce the concept of the precipitate, expanding upon it in the final two sections.

7.2 Solubility Product, Molar Solubility, and K_{sp}

Whenever we dissolve a solid in water, we must be concerned with three main quantities: the solubility, the molar solubility, and the solubility constant (K_{sp}). *Solubility* refers to the mass of the solid that dissolves in water and is expressed in units of grams per liter. *Molar solubility* refers to the moles of the solid that dissolve in water and is expressed in moles per liter, or molar. The *solubility product* is the constant that relates the concentrations of the ions present in the solution and only varies with temperature.

If we are given solubility, we can conveniently solve for molar solubility by dividing the former by the gram formula mass of the solid. For instance, if we are told that M_2X_3 (179.3 g/mol) has a solubility of 0.045 g/L, we know that the molar solubility of M_2X_3 is (0.045 g/L)/(179.3 g/mol) = 0.00025 M. The reaction is

$$M_2X_3(s) = 2M^{3+}(aq) + 3X^{2-}(aq) \tag{7.1}$$

and K_{sp} will be

$$K_{sp} = [M^{3+}]^2[X^{2-}]^3 \tag{7.2}$$

If we are given the solubility of the solid, we can easily solve for K_{sp}. Since the solubility product pertains to molarities, we must express all solubility as molar solubility, which we have already done. To save ink, let x equal the molar solubility calculated above (0.00025 M). For every unit x of the solid that is reacted, two units of M^{3+} and three units of X^{2+} are formed, so we can rewrite the solubility product equation:

$$K_{sp} = (2x)^2(3x)^3 = 108x^5 \tag{7.3}$$

When we substitute 0.00025 M for x, we find that K_{sp} is 1.1×10^{-16}.

7.3 Dissolving a Solid in Water

Using the same algorithm in reverse, we can determine the solubility of a solid given its solubility product. For example, let us find the molar solubility and solubility of Ag_2CrO_4 ($K_{sp} = 1.2 \times 10^{-12}$). We will consider, first, the chemical equation

$$Ag_2CrO_4(s) = 2Ag^+(aq) + {CrO_4}^{2-}(aq) \tag{7.4}$$

and the solubility product

$$K_{sp} = [Ag^+]^2[{CrO_4}^{2-}] \tag{7.5}$$

Again, we will let x represent the amount of solid that reacts. Since the chromate ion forms from the salt in a one-to-one ratio, its concentration is x. The silver ion, however, is produced in twice this quantity, so its concentration is $2x$. Plugging into the solubility product equation, we have

$$K_{sp} = (2x)^2(x) = 4x^3 = 1.2 \times 10^{-12} \tag{7.6}$$

Solving for x gives

$$x = \sqrt[3]{\frac{1.2 \times 10^{-12}}{4}} = 6.7 \times 10^{-5} \text{ M} \tag{7.7}$$

which is the molar solubility. The solubility is the product of the molar solubility and the gram formula mass, (332 g/mol): 0.022 g/L.

7.4 Finding pH with Hydroxide Salts

In the case of a hydroxide salt, e.g. $Ca(OH)_2$ ($K_{sp} = 6.5 \times 10^{-6}$), we have yet another quantity for which to solve, the pH. We will forgo the chemical equation in this example, although it is not good practice to do so, and move on to the solubility product expression:

$$K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5 \times 10^{-6} \tag{7.8}$$

Letting x represent the reacted quantity, we have

$$K_{sp} = (x)(2x)^2 = 4x^3 = 6.5 \times 10^{-6} \tag{7.9}$$

We find x to be 1.2×10^{-2} M. To solve for the pH, we need the hydroxide ion concentration, which is given by

$$[OH^-] = 2x = 2(1.2 \times 10^{-2} \text{ M}) = 2.4 \times 10^{-2} \text{ M} \tag{7.10}$$

The pH is then easy:

$$\begin{aligned} pH &= 14 - pOH = 14 + \log[OH^-] \\ &= 14 + \log(2.4 \times 10^{-2} \text{ M}) = 12.37 \end{aligned} \tag{7.11}$$

7.5 Solving for the Concentration of the Unknown Ion

Imagine that instead of dissolving a salt in pure water, an ion is already present. For instance, if we introduce $PbSO_4$ ($K_{sp} = 6.3 \times 10^{-7}$) into a solution containing 0.35 M of Pb^{2+}, what will the sulfate ion concentration be? We resort to the equilibrium expression, calling the unknown quantity x:

$$K_{sp} = [Pb^{2+}][{SO_4}^{2-}] = 6.3 \times 10^{-7} = (0.35\text{ M} + x)(x) \tag{7.12}$$

Since the concentration of the lead ion is large relative to x, we can omit the x. What we are left with, in fact, is simple arithmetic:

$$6.3 \times 10^{-7} = (0.35\text{ M})(x) \tag{7.13}$$

The value of the unknown quantity x is 1.8×10^{-6}.

7.6 Forming a Precipitate: Q_{sp}

Now let us consider the case where we have no initial concentration of salt, only ions. Will these ions bond to form the solid (i.e., the precipitate)? In order to find out, we must understand the concept of Q_{sp}, the solubility product at any given time, not necessarily at equilibrium.

To demonstrate, we have a solution of 0.030-M Pb^{2+} and 0.040-M Cl^-. (K_{sp} for $PbCl_2$ is 1.7×10^{-5}.) Let us look at Q_{sp} for this system:

$$\begin{aligned} Q_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= (0.030\text{ M})(0.040\text{ M})^2 = 4.8 \times 10^{-5} \end{aligned} \tag{7.14}$$

Since Q_{sp} is larger than K_{sp}, the system will shift left to remove some of the ions in order to achieve equilibrium; a precipitate will form. Should Q_{sp} be smaller than K_{sp}, the system would not shift and equilibrium would not be achieved; no precipitate would form.

7.7 Systems Involving Multiple Precipitates

When we have a solution containing two ions and we add a third ion, how do we know which solid will precipitate first? To answer this question, we must know the K_{sp} values for the two corresponding salts; whichever system reaches its K_{sp} value first will begin to precipitate.

Let us consider a solution containing (3.0×10^{-2})-M Pb^{2+} and (7.0×10^{-6})-M Cu^+. As $NaCl$ is gradually added, which will precipitate first: $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) or $CuCl$ ($K_{sp} = 1.9 \times 10^{-7}$)?

Writing the equilibrium expressions for both and substituting the known values, we have

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = (0.030\text{ M})[Cl^-]^2 = 1.7 \times 10^{-5} \tag{7.15}$$

$$K_{sp} = [Cu^+][Cl^-] = (7.0 \times 10^{-6}\text{ M})[Cl^-] = 1.9 \times 10^{-7} \tag{7.16}$$

Solving for the chloride ion concentration in each, we have

$$[Cl^-] = \sqrt{\frac{1.7 \times 10^{-5}}{0.030\text{ M}}} = 0.024\text{ M} \tag{7.17}$$

$$[Cl^-] = \frac{1.9 \times 10^{-7}}{7.0 \times 10^{-6}\text{ M}} = 0.027\text{ M} \tag{7.18}$$

Since fewer moles of the chloride ion are needed to reach equilibrium for $PbCl_2$, this salt will precipitate first.

What will be the concentration of the lead ion when the precipitate $CuCl$ forms? We know the Cl^- concentration (0.027 M) and K_{sp} (1.7×10^{-5}), so we solve for $[Pb^{2+}]$ in the equilibrium expression:

$$[Pb^{2+}] = \frac{K_{sp}}{[Cl^-]^2} = \frac{1.7 \times 10^{-5}}{(0.027\ \mathrm{M})^2} = 0.023\ \mathrm{M} \tag{7.19}$$

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