Chem 116 POGIL Worksheet - Week 10 Weak Bases, Acid Strength and Structure, Common Ion Effect, and Buffers

Why?

We have seen that the calculation of $[H_3O^+]$ and pH for a solution of a pure weak acid in water requires solving the K_a equilibrium expression for the acid. In similar fashion, calculating the concentrations of all species in a solution of a weak base in water requires solving the equilibrium expression for the bases's hydrolysis, called K_b . In basic solutions we concentrate on finding $[OH^-]$ and pOH, instead. Some weak bases are the conjugate bases of weak acids. These are generally the anions produced by the acid's hydrolysis. Like molecular bases, these conjugate bases have base hydrolysis equilibria with associated K_b values. The relationship between K_a and K_b for a conjugate acid-base pair allows us to calculate the pH of a solution of either species.

The strengths of acids and their conjugate bases are related to their molecular structure. Knowing the trends allows us to predict whether an acid is strong or weak, and if weak how it compares in strength to other similar weak acids.

Beyond solutions of pure acid or base in water, we need to look at the effect of adding extra amounts of the conjugate base or acid to the solution. The shift in the position of the equilibrium, called the *common ion effect*, changes the pH and imbues the solution with certain properties that are the basis for formulating a *buffer*. Buffer solutions are important for regulating pH in many chemical and biological systems.

Learning Objectives

- Understand the weak base hydrolysis constant, K_b , and its application to calculating the concentrations of all species in the solution.
- Know the relationship between K_a and K_b for a conjugate acid-base pair
- Know the relationships between structure types and acid strength
- Understand the effect of adding the conjugate to a solution of a weak acid or weak base
- Understand the principles of buffer solutions

Success Criteria

- Be able to calculate the concentrations of all species and pOH or pH of a solution of a pure weak base
- Be able to determine and use K_b for a conjugate base, given K_a of its conjugate acid, and vice versa.
- Be able to predict relative strengths of acids or their conjugate bases from structure considerations
- Be able to predict the effect of adding additional amounts of conjugate base or acid to a solution
- Be able to calculate the pH of a solution subject to the common ion effect
- Be able to calculate the pH of a buffer solution and to calculate the ratio of conjugate pair concentrations needed to achieve a certain pH

Prerequisite

Have read all of Chapter 16 and Sections 17.1-17.2

Information (Weak Base Hydrolysis)

When a weak base like ammonia is added to water it hydrolyzes to give small amounts of hydroxide ion and its conjugate acid in water. If we symbolize weak bases as B, then the general hydrolysis equilibrium is

$$B + H_2O \Rightarrow BH^+ + OH^-$$

for which we can write the equilibrium constant expression

$$K_b = \frac{[\mathrm{BH}^+][\mathrm{OH}^-]}{[\mathrm{B}]}$$

We can use K_b to calculate the concentrations of all species in the solution in a manner analogous to the way we used K_a for weak acid solutions. However, with base solutions we focus on determining [OH⁻] first, rather than [H₃O⁺]. Once we have determined [OH⁻], we can use $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ to calculate [H₃O⁺] and pH.

For a solution of a pure weak base in water with a moderate analytical concentration, $C_{\rm B}$, we would have the following concentrations initially and at equilibrium:

	$B + H_2O$	\Rightarrow BH ⁺	+ OH
Initial	$C_{ m B}$	0	~0
At equilibrium	$C_{\rm B}-x$	x	x

Substituting into the K_b expression, we obtain

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{C_B - x}$$

This is a quadratic equation of the form $x^2 + K_b x - K_b C_B = 0$. Notice that this is virtually the same equation we obtained in the weak acid case, except here $x = [BH^+] = [OH^-]$. As with the acid case, if the analytical concentration of the base is relatively large $(C_B >> K_b)$, hydrolysis may be minimal and we can ignore x in the expression for [B]. Then, the equation above simplifies to $K_b = x^2/C_B$ or

$$x = \sqrt{C_{\rm B}K_b} = [\rm OH^{-}] = [\rm BH^{+}]$$

Analogous to the acid case, if $C_B \gg K_b$ by two or more powers of 10, then this simplified equation probably can be used. If $C_B \approx K_b$, within two powers of 10, then the quadratic equation will probably need to be solved. If the simplified equation is used, check its validity by calculating the percent hydrolysis of the base:

% hydrolysis =
$$\frac{[OH^{-}]}{C_{B}} \times 100\%$$

If this calculation gives 5% or greater, use the more exact expression $[B] = C_B - x$ and solve the quadratic equation. By either method, once $[OH^-]$ has been calculated, use $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ to calculate $[H_3O^+]$, and pH + pOH = 14.00 to calculate pH.

Key Questions

1. What is the pH of a 0.120 M solution of $NH_3(aq)$? For ammonia, $K_b = 1.77 \times 10^{-5}$. Is it necessary to solve the quadratic equation? Justify the approach you took, either way.

Information (K_b of Conjugate Bases and K_a of Conjugate Acids)

The conjugate base of a strong acid has little tendency to acquire H⁺ and reform the acid. Thus, Cl⁻, the conjugate base of HCl, has virtually no real base strength. But the conjugate bases of weak acids do have a tendency to acquire H⁺, and so they are real weak bases. Like any other weak base, they have a base hydrolysis equilibrium and a related K_b . For example, consider a weak acid HA and its conjugate base A⁻. The two are related to each other by the acid's hydrolysis equilibrium:

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

But they are also related to each other by the conjugate base's hydrolysis equilibrium:

$$A^- + H_2O \Rightarrow HA + OH^ K_b = \frac{[HA][OH^-]}{[A^-]}$$

How is the value of K_a of HA related to the value of K_b of A⁻? The larger the value of K_a for an acid, the smaller the value of K_b will be for its conjugate base, and vice versa. Recall that when two equilibria are added together the equilibrium constant for the sum is the product of the individual equilibrium constants. If we add the acid hydrolysis equilibrium of HA and the base hydrolysis equilibrium of A⁻, the sum is 2 H₂O \Rightarrow H₃O⁺ + OH⁻, which is water's autoprotolysis equilibrium, governed by K_w :

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

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

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

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

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

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

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

Therefore, in general we can write

$$K_a^{\rm HA}K_b^{\rm A^-} = K_{\rm w}$$

Similarly, if we have a molecular base B with known K_b , its conjugate acid BH⁺ would have a K_a given by $K_b^{\mathbf{B}} K_a^{\mathbf{BH}^+} = K_w$

Conjugate bases of weak acids are true bases. For example, the acetate ion (often abbreviated OAc⁻⁾, which is the conjugate base of acetic acid (often abbreviated HOAc), can make a basic solution as a result of its base hydrolysis. The K_b value for the acetate ion can be calculated from acetic acid's $K_a = 1.78 \times 10^{-5}$, using $K_a^{\text{HA}} K_b^{\text{A}^-} = K_w$:

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

 $K_b^{OAc^-} = \frac{K_w}{K_a^{HOAc}} = \frac{1.00 \times 10^{-14}}{1.78 \times 10^{-5}} = 5.62 \times 10^{-10}$

But we cannot simply add acetate ions to a solution. They must be supplied in the form of an ionic salt, such as sodium acetate, which dissociates completely in water to give an equivalent amount of acetate ion and sodium ion in solution. Sodium ion has no acid-base character, so the pH of the solution is the result of the acetate ion's base hydrolysis:

$$NaOAc \rightarrow Na^+ + OAc^-$$

 $OAc^- + H_2O \rightleftharpoons HOAc + OH^ pH > 7$

In similar manner, we can create a solution of the conjugate acid of a molecular weak base by adding one of its soluble salts, such as a chloride. For example, ammonium chloride, NH_4Cl , when dissolved in water supplies an equivalent amount of ammonium ion, NH_4^+ , the conjugate acid of ammonia, and chloride ion. The chloride ion, being the conjugate base of a strong acid (HCl) has no real acid-base character, so the pH of the solution is the result of the ammonium ion's acid hydrolysis:

$$\begin{array}{ll} \mathrm{NH_4Cl} \rightarrow \mathrm{Cl^-} + \mathrm{NH_4^{++}} \\ \mathrm{NH_4^{+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_3} + \mathrm{H_3O^{+}} \end{array} \qquad \qquad \mathrm{pH} < 7 \end{array}$$

The K_a for the ammonium ion can be calculated from $K_b = 1.77 \times 10^{-5}$ for ammonia.

$$NH_4^+ + H_2O \Rightarrow NH_3 + OH^- \qquad K_a^{NH_4^+} = \frac{K_w}{K_b^{NH_3}} = \frac{1.00 \times 10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}$$

Key Questions

- 2. Sodium hypochlorite, NaOCl, is the active ingredient in chlorine bleach (e.g., Chlorox[©]). For hypochlorous acid, HOCl, $K_a = 3.0 \times 10^{-8}$.
 - a. Write the equation for the base hydrolysis equilibrium of the hypochlorite ion.
 - b. What is the value of K_b for the hypochlorite ion?
 - c. What is the pH of a 0.10 M solution of sodium hypochlorite?
- 3. Trimethylamine, $(CH_3)_3N$, is a weak base $(K_b = 6.4 \times 10^{-5})$ that hydrolyzes by the following equilibrium:

 $(CH_3)_3N + H_2O \Rightarrow (CH_3)_3NH^+ + OH^-$

- a. Write the equation for the acid hydrolysis equilibrium of trimethylammonium ion, $(CH_3)_3NH^+$.
- b. What is the value of K_a for the trimethylammonium ion, $(CH_3)_3NH^+$?
- c. What is the pH of a 0.12 M solution of trimethylammonium chloride, $((CH_3)_3NH)Cl?$

Information (Acid Strength and Structure)

The tendency of an acid to lose a proton to solvent water, as indicated by its K_a value, depends upon two principal factors:

- The strength of the H–A bond. The weaker the bond, the greater is the tendency to lose protons, and the larger K_a will be.
- The stability of the conjugate base in solution. The more stable the conjugate base A^- , the greater is the tendency of HA to lose protons, and the larger K_a will be.

For simple inorganic acids, the first factor is more important. The second factor is often important in comparisons among organic acids.

Acid strengths of *binary acids*, with the general formula H_nX , increase as the H–X bond weakens. This results in the following trends:

• The larger the X atom, the weaker the H–X bond is and the stronger the acid is.

HF < HCl < HBr < HI

$$H_2O < H_2S < H_2Se < H_2Te$$

• Among acids with similar H–X bond strengths, the more electronegative the X atom, the more polar the H–X bond will be. This makes the H atom more positive, facilitating its removal by solvent water. Thus, across a period,

$$NH_3 < H_2O < HF$$

One of the most studied groups of acids is the family of *oxyacids*, with the general formula $HOXO_n$, where X is a central atom. In these acids, the acidic hydrogen is always bonded to an oxygen atom, with a linkage of the type X–O–H. Any hydrogen atoms bonded directly to the central X atom (i.e., X–H) are *not* acidic. These acids may also have one or more terminal oxygen atoms, bonded directly to X but not bearing a hydrogen atom (i.e. X–O). In most oxyacids (with some exceptions) there are no X–H bonds, so the number of terminal oxygen atoms is just the total number of oxygen atoms minus the number of hydrogen atoms in the formula. Thus, $HCIO_3$ has two terminal oxygen atoms, with the third oxygen atom bonded to the acidic hydrogen atom. The number of these terminal oxygen atoms affects the acid's strength. In general, two factors are important in judging the strengths of oxyacids:

• Among acids of the same structure type, acid strength increases with the electronegativity of the central X atom. For example,

HOI < HOBr < HOCl

 $H_2SeO_4 < H_2SO_4$

As electronegativity of X increases, the polarity of the -O-H bond increases, making removal of H^+ by solvent water more favorable.

• Acidity increases as the number of terminal oxygen atoms (those without H attached to them) increases. For example,

HOCl < HOClO < HOClO₂ < HOClO₃

The electron withdrawing ability of the terminal –O atoms increases the formal charge on the central X atom, decreasing electron density in the –O–H bond, thereby weakening it. This is an example of an *inductive effect*.

The number of terminal oxygen atoms in the oxyacids bears a strong correlation to K_a .

–O atoms	K_a range	Strength
0	$10^{-7} - 10^{-10}$	very weak
1	$10^{-1} - 10^{-4}$	weak
2	>10 ⁻¹	strong
3	>>1	very strong

An important group of organic acids contains the *carboxyl group*, $-CO_2H$. Accordingly, such acids are called *carboxylic acids*.

HCO ₂ H	CH_3CO_2H	$CH_3CH_2CO_2H$	$CH_{3}CH_{2}CH_{2}CO_{2}H$	HO_2CCO_2H
formic	acetic	propionic	butyric	oxolic (diprotic)

The acidity of the carboxyl group is partly due to the electronegativity of the double-bonded oxygen, which withdraws electron density from the -O-H bond, thereby facilitating the loss of H⁺ to solvent water. Furthermore, when a carboxyl group loses H⁺, it forms a resonance stabilized anion, called a *carboxylate ion*:



(The symbol R represents the rest of the organic molecule.) The acidity of a carboxylic acid can be enhanced by adding electronegative atoms to the rest of the molecule. The electron-withdrawing ability of such atoms weakens the -O-H bond (inductive effect), thereby enhancing the ability of solvent water to remove H⁺. For example, Cl₃CCO₂H is a much stronger acid than CH₃CO₂H.

Key Questions

- 4. Explain the following observations:
 - a. H_2 Se is a stronger acid than H_2 S
 - b. HNO_2 is a weak acid, but HNO_3 is a strong acid
 - c. H_3PO_4 is a stronger acid than H_3AsO_4
 - d. FCH_2CO_2H is a stronger acid than CH_3CO_2H

Information (Common Ion Effect)

Thus far we have only considered the equilibrium of a pure acid or base in water, with no other source for its conjugate but the dissociation itself. What would happen if we were to add a significant amount of the conjugate? Suppose we consider the dissociation of a 0.100 M solution of acetic acid, HOAc, for which $K_a = 1.76 \times 10^{-5}$. What are the concentrations of H₃O⁺ and OAc⁻ in this solution, and what is the pH. We would have the following algebraic expressions for the principal species at equilibrium:

$$\begin{array}{rcl} \mathrm{HOAc} + & \mathrm{H_2O} & \Rightarrow & \mathrm{H_3O^+} & + & \mathrm{OAc^-} \\ 0.100 - x & & x & x \end{array}$$

But $C_{\text{HOAc}} >> K_a$, so we can assume [HOAc] = 0.100 M, and $[\text{H}_3\text{O}^+] = [\text{OAc}^-] = x$. As we have seen, this leads to the simple solution

$$x = \sqrt{C_{\text{HOAc}}K_a^{\text{HOAc}}} = \sqrt{(0.100)(1.76 \times 10^{-5})} = 1.33 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OAc}^-]$$

From this it follows

pH = 2.877

Suppose we added sodium acetate, NaOAc, equivalent to 0.200 mole per liter of this solution. Being a strong electrolyte, the sodium acetate will dissociate completely to give 0.200 mole per liter of OAc⁻, in addition to any acetate ion provided by acetic acid's hydrolysis. Now we have the following algebraic expressions for the principal species at equilibrium:

 $\begin{array}{rcrcrcr} \mathrm{HOAc} + & \mathrm{H_2O} & \Rightarrow & \mathrm{H_3O^+} & + & \mathrm{OAc^-} \\ 0.100 - x & & x & & 0.200 + x \end{array}$

Notice that in this solution, unlike the pure acid case, the concentration of hydronium ion *does* not equal the concentration of conjugate base. By LeChatelier's Principle, the added OAc⁻ will drive the equilibrium to the left, removing some of the H₃O⁺ ion and OAc⁻ ion to reform molecular HOAc and H₂O. Put another way, adding conjugate base to the solution will make the pH go up. From our previous calculation for 0.100 M HOAc, we saw that $x = 1.33 \times 10^{-3}$ M, but now this number will be even smaller, due to the left shift in the equilibrium position. Compared to the analytical concentration of HOAc ($C_{HOAc} = 0.100$ M) and the analytical concentration of NaOAc ($C_{NaOAc} = 0.200$ M), this small value of x is now insignificant, actually falling beyond the significant digits of those concentrations. Therefore, we can simplify the calculation of [H₃O⁺] by assuming that [HOAc] = $C_{HOAc} = 0.100$ M and [OAc⁻] = $C_{NaOAc} = 0.200$ M.

$$\begin{array}{rcl} \text{HOAc} + & \text{H}_2\text{O} & \Rightarrow & \text{H}_3\text{O}^+ & + & \text{OAc}^- \\ \sim 0.100 & & x & \sim 0.200 \end{array}$$

All we have to do is plug these values into the K_a expression and solve for $[H_3O^+]$. (No quadratic equation and not even a square root!)

$$K_a = \frac{[\text{H}_3\text{O}^+][[\text{OAc}^-]]}{[\text{HOAc}]} = \frac{x(0.200)}{0.100} = 1.76 \times 10^{-5}$$
$$x = [\text{H}_3\text{O}^+] = 8.80 \times 10^{-6} \text{ M}$$
$$\text{pH} = 5.056$$

As expected, the pH has gone up, compared to the pure acid solution. Also, note that the value of $x = [H_3O^+]$ that we obtain is, indeed, beyond the significant digits of the analytical concentration values of HOAc and OAc⁻. In other words, we were justified in ignoring *x* in our algebraic expressions for the concentrations of those species.

In general, for a solution of an acid with added amounts of conjugate base, except at extreme dilution, we can assume

$$[\text{HA}] \approx C_{\text{HA}} \qquad [\text{A}^{-}] \approx C_{\text{A}}$$
$$K_{a} = \frac{[\text{H}_{3}\text{O}^{+}][\text{A}^{-}]}{[\text{HA}]} \approx \frac{[\text{H}_{3}\text{O}^{+}]C_{\text{A}}}{C_{\text{HA}}}$$
$$[\text{H}_{3}\text{O}^{+}] \approx K_{a} \times \left(\frac{C_{\text{HA}}}{C_{\text{A}}}\right)$$

By a similar reasoning, for a solution of a base B with added amounts of its conjugate acid, BH⁺, except at extreme dilution, we can assume

$$[B] \approx C_{B} \qquad [BH^{+}] \approx C_{BH^{+}}$$
$$K_{b} = \frac{[OH^{-}][BH^{+}]}{[B]} \approx \frac{[OH^{-}]C_{BH^{+}}}{C_{B}}$$
$$[OH^{-}] \approx K_{b} \times \left(\frac{C_{B}}{C_{BH^{+}}}\right)$$

If we take base-10 logarithms of both of these equations, we can obtain equations for the pH and pOH for these kinds of solutions in terms of K_a and K_b . These are called the **Henderson-Hasselbalch equations**. For the HA/A⁻ case:

$$\log[H_{3}O^{+}] = \log K_{a} + \log \left(\frac{C_{HA}}{C_{A^{-}}}\right)$$
$$pH = pK_{a} - \log \left(\frac{C_{HA}}{C_{A^{-}}}\right)$$

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

For the B/BH⁺ case:

$$\log[OH^{-}] = \log K_{b} + \log\left(\frac{C_{B}}{C_{BH^{+}}}\right)$$
$$pOH = pK_{b} - \log\left(\frac{C_{B}}{C_{BH^{+}}}\right)$$
$$pOH = pK_{b} + \log\left(\frac{C_{BH^{+}}}{C_{B}}\right)$$

These equations are useful if caring out a series of calculations for the same conjugate pair (e.g., using Excel), but for a single calculation it is just as quick to plug the numbers into the appropriate K_a or K_b expression and take the base-10 logarithm of the result, as shown in the example above.

Key Questions

- 5. What is the pH of a solution prepared by adding 0.20 mole of formic acid, HCO₂H, and 0.25 mole of sodium formate, NaHCO₂? The K_a of formic acid is 1.8×10^{-4} .
- 6. What is the pH of a solution prepared by adding 0.60 mole of formic acid and 0.75 mole of sodium formate in enough water to make a liter of solution? How does your answer compare to the answer you obtained in Key Question 5? Explain.
- 7. The solution prepared in Key Question 6 was diluted with enough water to make ten liters of solution. What is the pH of the dilute solution? How does it compare to the previous two solutions? Explain.

Information (Buffers)

The solutions we have just examined, in which significant amounts of both weak acid and its conjugate base or weak base and its conjugate acid have been mixed together, are buffer solutions. Buffer solutions have two key properties that make them useful in a wide variety of applications, including biological systems:

- The pH of a buffer does not change with moderate dilution.
- The pH of a buffer changes only slightly with addition of small amounts of acid or base.

We can understand the first property from having worked Key Questions 5 through 7. As those problems show, it is not really the actual concentrations of the acid-base conjugate pair that fix the hydronium ion concentration, but rather the ratio between those concentrations. Diluting a buffer solution does not alter the ratio of the numbers of moles of each component, and so the concentration ratio remains constant. (This breaks down, however, at extreme dilution.)

If we want to make a buffer with a certain pH from a given acid-base conjugate pair, we simply add the ingredients in the proper ratio, as required by the acid's K_a or bases's K_b , to achieve the hydronium ion that corresponds to the desired pH. The ability of a buffer to resist changing pH with small amounts of acid or base depends on how little this concentration ratio is altered by the additions. Adding small amounts of a strong acid (e.g., HCl) will neutralize an equivalent amount of the conjugate base and form an equivalent amount of the weak acid. Conversely, adding small amounts of a strong base (e.g., NaOH) will neutralize an equivalent amount of the weak acid and form an equivalent amount of the conjugate base. In both scenarios the ratio between the conjugate pair will be altered, but if the change is small the pH will be virtually unaffected. The **buffer capacity** is the amount of added acid or base the buffer can tolerate before the pH changes significantly. This depends on minimizing the change in the conjugate pair ratio. For this reason, it is a good idea to make the concentrations of the two components fairly strong, so that numerically small changes in either component from added acid or base will cause relatively insignificant changes in the ratio.

To illustrate, suppose we wish to make up a buffer that has a pH of 5.00, using acetic acid and sodium acetate. A pH of 5.00 means $[H_3O^+] = 1.0 \times 10^{-5}$. We can plug this value into the K_a expression and solve for the ratio $[OAc^-]/[HOAc]$.

$$K_{a} = \frac{[\text{H}_{3}\text{O}^{+}][\text{OAc}^{-}]}{[\text{HOAc}]} = \frac{(1.0 \times 10^{-5})[\text{OAc}^{-}]}{[\text{HOAc}]} = 1.76 \times 10^{-5}$$
$$\frac{[\text{OAc}^{-}]}{[\text{HOAc}]} = \frac{1.76 \times 10^{-5}}{1.0 \times 10^{-5}} = 1.76$$

Any moderate concentrations that have the ratio $[OAc^-]/[HOAc] = 1.76$ will achieve a pH of 5.00. Furthermore, notice that this is really a ratio of moles of sodium acetate to acetic acid, because the volume is the same for both. Any specific concentrations in this ratio will achieve the desired pH, but in order to achieve a good buffer capacity we should use relative high concentrations. Suppose we chose to make a buffer solution that has $[OAc^-] = 1.76$ M and [HOAc] = 1.00 M. At equilibrium we would have the following concentrations.

$$\begin{array}{rcl} HOAc + & H_2O & \rightleftharpoons & H_3O^+ & + & OAc^- \\ 1.00 \text{ M} & & 10^{-5} \text{ M} & 1.76 \text{ M} \end{array}$$

Now suppose we add a small amount of strong acid (e.g., HCl) to supply an additional 0.01 mol/L of H_3O^+ . This additional hydronium ion, which is much greater than that provided from the acetic acid's hydrolysis, will shift the HOAc/OAc⁻ equilibrium to the left to consume the extra H_3O^+ , thereby forming an equivalent amount of HOAc. This is essentially the same as neutralizing an equivalent amount of the base OAc⁻. The changes and new equilibrium are summarized below:

	$HOAc + H_2O$	\Rightarrow H ₃ O ⁺ +	OAc^{-}
Original equilibrium	1.00 M	$10^{-5} {\rm M}$	1.76 M
Add		0.01 M	
Change	+0.01 M	-0.01 M	-0.01 M
New equilibrium	1.01 M	?	1.75 M

To find the new $[H_3O^+]$, substitute into the K_a expression:

$$K_{a} = \frac{[\text{H}_{3}\text{O}^{+}][\text{OAc}^{-}]}{[\text{HOAc}]} = 1.76 \times 10^{-5} = \frac{[\text{H}_{3}\text{O}^{+}](1.75)}{1.01}$$
$$[\text{H}_{3}\text{O}^{+}] = \frac{(1.76 \times 10^{-5})(1.01)}{1.75} = 1.02 \times 10^{-5} \text{ M}$$
$$\text{pH} = 4.99_{3} = 4.99$$

As this shows, the small addition of H_3O^+ has negligible effect on the pH because the shift in the equilibrium makes only a minor change in the ratio $[OAc^-]/[HOAc]$. This would not be the case if the concentrations of HOAc and OAc⁻ were small numbers. Therefore, the buffer's ability to resist a pH change from small addition of acid depends upon having high concentrations of the acid-base pair. In other words, high concentrations of acid and conjugate base result in a high buffer capacity.

Suppose, instead, that we add a small amount of a strong base (e.g., NaOH) to our pH 5.00 buffer to supply an additional 0.01 mol/L of OH⁻. The addition of hydroxide ion will neutralize an equivalent amount of HOAc, driving the acid hydrolysis equilibrium to the right. In this case, $[OAc^-]$ will increase by 0.01 mol/L and [HOAc] will decrease by 0.01 mol/L. Substituting into the K_a expression, we can obtain the new pH as follows:

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.76 \times 10^{-5} = \frac{[H_3O^+](1.77)}{0.99}$$
$$[H_3O^+] = \frac{(1.76 \times 10^{-5})(0.99)}{1.77} = 9.8_4 \times 10^{-6} M$$
$$pH = 5.00_7 \approx 5.01$$

In both cases, the small shift in pH occurs because the amounts of added acid or base are insignificant relative to the large amounts of the conjugate acid-base pair.

If the concentration of the conjugate base is small, a buffer will not have good resistance to pH change with added H_3O^+ . Likewise, if the concentration of the acid of the conjugate pair is small, a buffer will not have good resistance to pH change with added OH^- . If we want to make an ideal buffer, with equal resistance to pH changes from added H_3O^+ or OH^- , we should have the concentrations of both the acid and conjugate base be high and equal. By substitution into either K_a or the Henderson-Hasselbalch equation, we can see that a buffer for which $C_{HA} = C_{A^-}$ would have $[H_3O^+] = K_a$ and $pH = pK_a$.

It is not always necessary to have equal buffering capacity against both acid or base challenges. For example, the goal may be simply to make a solution with a particular pH to use as a standard for instrument calibration. If a particular pH is desired for a buffer from a given acid-base pair, the concentrations of the two components may need to be unequal. But not all ratios are possible for a given pair. The possible limits are set by the ratio achieved when the pure acid or the pure base hydrolyzes to give the amount of conjugate dictated by its K_a or K_b . When trying to make a buffer with a certain pH, the following guidelines should be followed in selecting the acid-base pair and choosing the concentration ratios:

- ① Try to choose a conjugate pair whose $pK_a \approx pH$.
- ⁽²⁾ Adjust the ratio $[A^-]/[HA]$ or $[BH^+]/[B]$ to achieve the desired pH.
- ③ The practical limit on the choice of conjugate acid-base pair is $pH \approx pK_a \pm 1$

Otherwise, one member of the pair is present in too small an amount to make an effective buffer.

Key Questions

- 8. A student wishes to prepare a buffer with a pH of 4.52. She starts by preparing one liter of 0.10 M formic acid, HCO₂H. How many grams of sodium formate, NaHCO₂, must she add to the solution to achieve the desired pH? $K_a = 1.8 \times 10^{-4}$ for formic acid. The formula weight of sodium formate is 68.00 u.
- 9. A buffer solution is made by adding an equal number of moles of the base pyradine, C_5H_5N , and the chloride salt of it conjugate base, C_5H_5NHCl . What is the pH of the buffer solution? The K_b of C_5H_5N is 1.7×10^{-9} .