Experiment 25

pH Measurements—Buffers and Their Properties

One of the more important properties of an aqueous solution is its concentration of hydrogen ion. The H^+ or H_3O^+ ion has great effect on the solubility of many inorganic and organic species, on the nature of complex metallic cations found in solutions, and on the rates of many chemical reactions. It is important that we know how to measure the concentration of hydrogen ion and understand its effect on solution properties.

For convenience the concentration of H^+ ion is frequently expressed as the pH of the solution rather than as molarity. The pH of a solution is defined by the following equation:

$$\text{pH} = -\log[H^+] \tag{1}$$

where the logarithm is taken to the base 10. If $[H^+]$ is 1×10^{-4} moles per liter, the pH of the solution is, by the equation, 4. If the $[H^+]$ is 5×10^{-2} M, the pH is 1.3.

Basic solutions can also be described in terms of pH. In water solutions the following equilibrium relation will always be obeyed:

$$[H^+] \times [OH^-] = K_w = 1 \times 10^{-14} \text{ at } 25°\text{C} \tag{2}$$

In distilled water $[H^+]$ equals $[OH^-]$, so, by Equation 2, $[H^+]$ must be 1×10^{-7} M. Therefore, the pH of distilled water is 7. Solutions in which $[H^+] > [OH^-]$ are said to be acidic and will have a pH < 7; if $[H^+] < [OH^-]$, the solution is basic and its pH > 7. A solution with a pH of 10 will have a $[H^+]$ of 1×10^{-10} M and a $[OH^-]$ of 1×10^{-4} M.

We measure the pH of a solution experimentally in two ways. In the first of these we use a chemical called an indicator, which is sensitive to pH. These substances have colors that change over a relatively short pH range (about two pH units) and can, when properly chosen, be used to determine roughly the pH of a solution. Two very common indicators are litmus, usually used on paper, and phenolphthalein, the most common indicator in acid-base titrations. Litmus changes from red to blue as the pH of a solution goes from about 6 to about 8. Phenolphthalein changes from colorless to red as the pH goes from 8 to 10. A given indicator is useful for determining pH only in the region in which it changes color. Indicators are available for measurement of pH in all the important ranges of acidity and basicity. By matching the color of a suitable indicator in a solution of known pH with that in an unknown solution, one can determine the pH of the unknown to within about 0.3 pH units.

The other method for finding pH is with a device called a pH meter. In this device two electrodes, one of which is sensitive to $[H^+]$, are immersed in a solution. The potential between the two electrodes is related to the pH. The pH meter is designed so that the scale will directly furnish the pH of the solution. A pH meter gives much more precise measurement of pH than does a typical indicator and is ordinarily used when an accurate determination of pH is needed.

Some acids and bases undergo substantial ionization in water, and are called strong because of their essentially complete ionization in reasonably dilute solutions. Other acids and bases, because of incomplete ionization (often only about 1% in 0.1 M solution), are called weak. Hydrochloric acid, HCl, and sodium hydroxide, NaOH, are typical examples of a strong acid and a strong base. Acetic acid, $HC_2H_3O_2$, and ammonia, NH_3, are classic examples of a weak acid and a weak base.

A weak acid will ionize according to the Law of Chemical Equilibrium:

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq) \tag{3}$$

You might wonder why [HB] and [B^-] do not change after the species are mixed. Actually, they do, very very slightly, just enough to generate enough H^+ ion to satisfy the condition imposed by Equation 4a. Ordinarily, however, K_a is small, so [H^+] is also small. If $K_a = 1 \times 10^{-5}$, [H^+] will be 1×10^{-5} M, and so, in our example, where we have 1 L of solution, we will have 1×10^{-5} moles of H^+. This means that 1×10^{-5} moles of HB dissociate, out of 0.050 moles initially present, so only a negligible decrease in [HB] occurs, and only a tiny increase in [B^-] as a result of the reaction to form the equilibrium system.

From the above discussion, we can conclude that the acid and conjugate base in a buffer *do not* react appreciably when mixed, so the relative concentrations can be calculated from the way the buffer was put together.

Another interesting property of a buffer is that its pH does not change appreciably on dilution. If we look again at the buffer in our example, if we increased the volume from 1 L to 5 L by adding water, the ratio of [HB] to [B^-] would not change, and since that ratio fixes [H^+], the pH would not change.

We can adjust the pH of the buffer, within limits, to bring it to some desired value. In our example, if K_a for the buffer is 1.0×10^{-5}, the pH of the buffer solution would be 5.0. If we wish to make a buffer of pH equal to 4.5, we need to simply select volumes of the acid and conjugate base such that the resultant ratio of [HB] to [B^-] would make [H^+] equal to $10^{-4.5}$, or 3.2×10^{-5} M. Then, by Equation 4a,

$$3.2 \times 10^{-5} = 1.0 \times 10^{-5} \times \frac{[HB]}{[B^-]} \qquad \text{and} \qquad \frac{[HB]}{[B^-]} = 3.2$$

So, to make the desired buffer we could use 320 mL 0.10 M HB and 100 mL 0.10 M NaB. Or, if our stock solutions were of different concentrations, we would select reagent volumes such that the number of *moles* of HB used would be 3.2 times as large as the number of *moles* of B^-.

The reason that a buffer has a stable pH is that its two components can "soak up" added H^+ or OH^- ions. If we add a little HCl, a strong acid, to our buffer, the following reaction will occur:

$$H^+(aq) + B^- \longrightarrow HB(aq) + H_2O \qquad \textbf{(7)}$$

If we added a little NaOH, a strong base, it will react with the HB present:

$$OH^-(aq) + HB(aq) \longrightarrow B^-(aq) + H_2O \qquad \textbf{(8)}$$

As a result of these reactions, [HB] and [B^-] will change slightly, but if the amounts of H^+ and OH^- ions that are added are *small* as compared to the amounts of HB and B^- present in the buffer, the effect on the pH will be small since the ratio of [HB] to [B^-] will not change much.

The range over which a buffer is useful is limited to about 2 pH units. In the example we used earlier, if we mixed 500 mL 0.10 M HB with 50 mL 0.10 M NaB, in the buffer [HB]/[B^-] would be 10, and so [H^+] would be 1×10^{-4} M and the pH would be 4.0. This buffer could deal with added NaOH much better than with added HCl, since the amount of available HB is much greater than that of B^-. Indeed, if we add enough HCl to react with all of the B^- present, the buffer would be "exhausted," since it would contain only HB, and any excess HCl would produce a pH with just about the same value as if the HCl were added to water. Similar behavior would occur if we made the buffer in such a way that [HB]/[B^-] were equal to 0.1. Then the pH would be 6, and the buffer would have very little capacity for added NaOH.

In the first part of this experiment you will determine the approximate pH of several solutions by using acid-base indicators. Then you will find the pH of some other solutions with a pH meter. The rest of the experiment will deal with the properties of buffer solutions. You will be working with one acid-conjugate base buffer system. You will note the effect on pH of changing the composition of the buffer, and use the data obtained to find the K_a of the acid. The stability of the pH as we add small amounts of acid and base will be examined. The effect of dilution on the pH will also be noted. We will then exhaust a buffer by adding an excess amount of acid or base. Finally, we will prepare one or two buffers having specific pH values.

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Experimental Procedure

WEAR YOUR SAFETY GLASSES WHILE PERFORMING THIS EXPERIMENT

You may work in pairs on the first three parts of this experiment.

A. Determination of pH by the Use of Acid-Base Indicators

To each of five small test tubes add about 1 mL 0.1 M HCl (about 1/2-inch depth in tube). To each tube add a drop or two of one of the indicators in Table 25.1, one indicator to a tube. Note the color of the solution you obtain in each case. By comparing the colors you observe with the information in Table 25.1, estimate the pH of the solution to within a range of one pH unit, say 1 to 2, or 4 to 5. In making your estimate, note that the color of an indicator is most indicative of pH in the region where the indicator is changing color.

Repeat the procedure with each of the following solutions:

0.1 M NaH_2PO_4 0.1 M $HC_2H_3O_2$ 0.1 M $ZnSO_4$

Record the colors you observe and the pH range for each solution.

Table 25.1

Indicator		Useful pH Range (Approximate) 0	1	2	3	4	5	6	7
Methyl violet	yellow	[	]	violet					
Thymol blue		red	[	]	yellow				
Methyl yellow			red	[	]	yellow			
Congo red				violet	[	]	orange-red		
Bromcresol green				yellow	[		]	blue	

B. Measurement of the pH of Some Typical Solutions

In the rest of this experiment we will use pH meters to find pH. Your instructor will show you how to operate your meter. The electrodes may be fragile, so use due caution when handling the electrode probe. See Appendix IV for a discussion of pH meters.

Using a 25-mL sample in a 150-mL beaker, measure and record the pH of a 0.1 M solution of each of the following substances:

$NaCl$ Na_2CO_3 $NaC_2H_3O_2$ $NaHSO_4$

Rinse the electrode probe in distilled water between measurements. After you have completed a measurement, add a drop or two of bromcresol green to the solution and record the color you obtain.

Some of the solutions are nearly neutral; others are acidic or basic. For each solution having a pH less than 6 or greater than 8, write a net ionic equation that explains qualitatively why the observed pH value is reasonable.

Then write a rationale for the colors obtained with bromcresol green with these solutions.

C. Some Properties of Buffers

On the lab bench we have 0.10 M stock solutions that can be used to make three different common buffer systems. These are

$HC_2H_3O_2$—$C_2H_3O_2^-$	NH_4^+—NH_3	HCO_3^-—CO_3^{2-}
acetic acid–acetate ion	ammonium ion–ammonia	hydrogen carbonate–carbonate

The sources of the ions will be sodium and ammonium salts containing those ions. Select **one** of these buffer systems for your experiment.

1. Using a graduated cylinder, measure out 15 mL of the acid component of your buffer into a 100-mL beaker. The acid will be in one of the following solutions: 0.10 M $HC_2H_3O_2$, 0.10 M NH_4Cl, or 0.10 M $NaHCO_3$. Rinse out the graduated cylinder with distilled water and use it to add 15 mL of the conjugate base of your buffer. Measure the pH of your mixture and record it on the Data page. Calculate K_a for the acid.
2. Add 30 mL water to your buffer mixture, mix, and pour half of the resulting solution into another 100-mL beaker. Measure the pH of the diluted buffer. Calculate K_a once again. Add five drops of 0.10 M NaOH to the diluted buffer and measure the pH again. To the other half of the diluted buffer add 5 drops 0.10 M HCl, and again measure the pH. Record your results.
3. Make a buffer mixture containing 2 mL of the acid component and 20 mL of the solution containing the conjugate base. Mix, and measure the pH. Calculate a third value for K_a. To that solution add 3 mL 0.10 M NaOH, which should exhaust the buffer. Measure the pH.
4. Put 25 mL distilled water into a 100-mL beaker. Measure the pH. Add 5 drops 0.10 M HCl and measure the pH again. To that solution add 10 drops 0.10 M NaOH, mix, and measure the pH.
5. Select a pH different from any of those you observed in your experiments. Design a buffer which should have that pH by selecting appropriate volumes of your acidic and basic components. Make up the buffer and measure its pH.

D. Preparing a Buffer from an Unknown Acid Solution Optional

So far in this experiment we have made buffers by mixing solutions of a weak acid and its conjugate base. It is possible to prepare buffers by adding a strong base to solutions containing a weak acid. Reaction 8 will occur, quantitatively, so we will produce the same number of moles of B^- as we add of NaOH. If we add *half* as many moles of OH^- as we have of HB, the final solution will be half-neutralized, and will be a buffer in which [HB] equals [B^-]. This solution will be completely equivalent to the one we used in our example in which we mixed equal amounts of HB and NaB.

In this part of the experiment we will furnish you with an unknown containing a 0.50 M solution of a weak acid. Using that solution and some 0.10 M NaOH, you will be asked to design and prepare a buffer with a particular pH. The following procedure is suggested:

1. Dilute your unknown to 0.10 M by adding 10 mL of your sample to 40 mL distilled water and mixing thoroughly.
2. Mix 20 mL of your unknown acid with 10 mL of 0.10 M NaOH. Measure the pH of the resulting half-neutralized buffer. Calculate K_a for your unknown acid.
3. Given the pH of the buffer you need to design, and the value of K_a you just found, calculate the value of $\frac{[HB]}{[B^-]}$ that is needed in the buffer.

Noting that $\frac{[HB]}{[B^-]} = \frac{\text{no. moles HB}}{\text{no. moles } B^-}$ in the buffer, find the volumes of 0.10 M NaOH and 0.10 M HB that will produce the required ratio. This is perhaps most easily done by arbitrarily deciding to add 10 mL of the NaOH to a volume of the HB solution. The number of moles of B^- produced by Reaction 8 will equal the number of moles of OH^- in the 10 mL of NaOH, and will also equal the number of moles of HB that will be used up in the reaction with OH^-.

The volume of 0.10 M HB you select must contain the number of moles of HB present in the final buffer *plus* the number of moles used up in producing the B^- that is in the buffer. Knowing the *total* number of moles of HB you need to make the buffer, calculate the volume of the 0.10 M HB that is required. Mix that volume with 10 mL of the 0.10 M NaOH and measure the pH.

DISPOSAL OF REACTION PRODUCTS. With adequate dilution, the reaction products may be poured down the drain.

Name ______________________ Section ______________

Experiment 25

Observations and Calculations: pH: Buffers and Their Properties

A. Determination of pH by the Use of Acid-Base Indicators

Indicator	Color with 0.1 M Solution of HCl	NaH_2PO_4	$HC_2H_3O_2$	$ZnSO_4$
Methyl violet	______	______	______	______
Thymol blue	______	______	______	______
Methyl yellow	______	______	______	______
Congo red	______	______	______	______
Bromcresol green	______	______	______	______
pH range	______	______	______	______

Circle the observation(s) for each solution that was most useful in estimating the pH range.

B. Measurement of the pH of Some Typical Solutions

Record the pH and the color observed with bromcresol green for each of the 0.1 M solutions that were tested.

	NaCl	Na_2CO_3	$NaC_2H_3O_2$	$NaHSO_4$
pH	______	______	______	______
Color	______	______	______	______

For any two solutions having a pH less than 6 or greater than 8, write a net ionic equation to explain qualitatively why the solution has that pH.

Solution ______ Equation ______________________

Solution ______ Equation ______________________

Explain why the color observed with bromcresol green for each of the four solutions is reasonable, given the pH.

C. Some Properties of Buffers

Buffer system selected ______________ HB is ______________ (name the acid)

1. pH of buffer ______ $[H^+]$ ______ M K_a (by Eq. 4a) ______
2. pH of diluted buffer ______ $[H^+]$ ______ M K_a ______

   pH after addition of 5 of drops NaOH ______

   pH after addition of 5 drops of HCl ______

(c

3. pH of buffer in which $\frac{[HB]}{[B^-]} = 0.10$ ________ K_a ________

pH after addition of excess NaOH ________

4. pH of distilled water ________

pH after addition of 5 drops HCl ________

pH after addition of 10 drops NaOH ________

5. pH of buffer solution to be prepared ________

Average value of K_a (as calculated in Parts 1, 2, and 3) ________

$\frac{[HB]}{[B^-]}$ in buffer (from Eq. 4a) ________

$\frac{\text{Volume 0.10 M HB}}{\text{Volume 0.10 M NaB}}$ needed in buffer ________

Volume 0.10 M HB used ________ mL Volume 0.10 M NaB used ________ mL

pH of prepared buffer ________

D. Preparing a Buffer from an Unknown Acid Solution Optional

pH of buffer to be designed and prepared ________

pH of half-neutralized solution ([HB] = [B⁻]) ________

$[H^+]$ in that solution ________ M K_a of unknown acid ________

$$\frac{[HB]}{[B^-]} \text{ needed in buffer} = \_\_\_\_\_\_\_\_ = \frac{\text{no. moles HB in buffer}}{\text{no. moles } B^- \text{ in buffer}} \quad (9)$$

Volume of 0.10 M NaOH to be added to the acid solution 10.0 mL

No. moles OH^- in that volume ________ moles

No. moles B^- produced and present in final buffer ________ moles

No. moles HB that react with the added NaOH ________ moles

No. moles HB that must be present in final buffer (Eq. 9) ________ moles

Total number of moles of HB needed to make up the buffer ________ moles

Volume of 0.10 M HB required ________ mL

pH of prepared buffer ________

Unknown no. ________

Name ______________________ Section ______________

Experiment 25

Advance Study Assignment: pH Measurements and the Properties of Buffers

1. A solution of a weak acid was tested with the indicators used in this experiment. The colors observed were as follows:

Methyl violet	violet	Congo red	violet
Thymol blue	yellow	Bromcresol green	yellow
Methyl yellow	orange		

What is the approximate pH of the solution?

____

2. The pH of a 0.10 M HCN solution is 5.2.

a. What is $[H^+]$ in that solution?

______________ M

b. What is $[CN^-]$? What is [HCN]? (Where do the H^+ and CN^- ions come from?)

______________ M

c. What is the value of K_a for HCN? (Use Eq. 4.)

____

3. Formic acid, HFor, has a K_a value equal to about 1.8×10^{-4}. A student is asked to prepare a buffer having a pH of 3.60 from a 0.10 M HFor and a 0.10 M NaFor solution. How many milliliters of the NaFor solution should she add to 20 mL of the 0.10 M HFor to make the buffer?

______________ mL

4. When 5 drops of 0.10 M NaOH were added to 20 mL of the buffer in problem 3, the pH went from 3.60 to 3.71. Write a net ionic equation to explain why the pH didn't go up to about 10, as it would have if that amount of NaOH were added to distilled water or to 20 mL 0.00025 M HCl, which also would have a pH of 3.60.