pH Measurements- Buffers and their properties

Introduction

One of the more important properties of an aqueous solution is its concentration of hydrogen ion. The H⁺ or H₃O⁺ 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:

\[ \text{pH} = -\log[H^+] \] (1)

where the logarithm is taken to the base 10. If [H⁺] is 1 x 10⁻⁴ moles per liter, the pH of the solution is, by the equation, 4. If the [H⁺] is 5 x 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:

\[ [H^+] \times [OH^-] = Kw = 1 \times 10^{-14} \text{ at } 25^\circ C \] (2)

In distilled water [H⁺] equals [OH⁻], so, by Equation (2), [H⁺] must be 1 x 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 [OH⁻] of 1 x 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, HC2H3O2, and ammonia, NH3, are classic examples of a weak acid and a weak base.

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

\[
\text{HB(aq)} \rightleftharpoons \text{H}^+(aq) + \text{B}^-(aq) \tag{3}
\]

At equilibrium,

\[
\frac{[H^+][B^-]}{[HB]} = K_a \tag{4}
\]

\(K_a\) is a constant characteristic of the acid HB. In solutions containing HB, the product of concentrations in the equation will remain constant at equilibrium independent of the manner in which the solution was made. A similar relation can be written for solutions of a weak base.

The value of the ionization constant \(K_a\) for a weak acid can be found experimentally in several ways. We need to find the concentrations of each of the species in Equation 4 by one means or another. In this experiment we will determine \(K_a\) for a weak acid in connection with our study of the properties of those solutions we call buffers.

Salts that can be formed by the reaction of strong acids and bases – such as NaCl, KBr, or NaNO3 – ionize completely but do not react with water when in solution. They form neutral solutions with a pH of about 7. When dissolved in water, salts of weak acids or weak bases furnish ions that tend to react to some extent with water, producing molecules of the weak acid or base and liberating some OH\(^-\) or H\(^+\) ion to the solution.

If HB is a weak acid, the B- ion produced when NaB is dissolved in water will react with water to some extent, according to the equation.

\[
\text{B}^-(aq) + \text{H}_2\text{O} \rightleftharpoons \text{HB(aq)} + \text{OH}^-(aq) \tag{5}
\]
Solutions of sodium acetate, NaC$_2$H$_3$O$_2$, the salt formed by reaction of sodium hydroxide with acetic acid, will be slightly basic because of the reaction of C$_2$H$_3$O$_2^-$ ion with water to produce HC$_2$H$_3$O$_2$ and OH$^-$. Because of the analogous reaction of the NH$_4^+$ ion with water to form H$_3$O$^+$ ion, solutions of ammonium chloride, NH$_4$Cl, will be slightly acidic.

Salts of most transition metal ions are acidic. A solution of CuSO$_4$ or FeCl$_3$, will typically have a pH equal to 5 or lower. The salts are completely ionized in solution. The acidity comes from the fact that the cation is hydrated (e.g., Cu(H$_2$O)$_4$)$^{2+}$ or Fe(H$_2$O)$_6$)$^{3+}$. The large + charge on the metal cation attracts electrons from the O—H bonds in water, weakening them and producing some H+ ions in solution; with CuSO$_4$ solutions the reaction would be:

\[
\text{Cu(H}_2\text{O)}_4^{2+}(\text{aq}) \rightleftharpoons \text{Cu(H}_2\text{O)}_3\text{OH}^+(\text{aq}) + \text{H}^+(\text{aq})
\]  

Buffers

Some solutions, called buffers, are remarkably resistant to pH changes. Water is not a buffer, since its pH is very sensitive to addition of any acidic or basic species. Even bubbling your breath through a straw into distilled water can change its pH by at least 1 unit, just due to the small amount of CO$_2$ in exhaled air. With a good buffer solution, you could blow your exhaled air into it for half an hour and not change the pH appreciably. All living systems contain buffer solutions, since stability of pH is essential for the occurrence of many of the biochemical reactions that go on to maintain the living organism.

There is nothing mysterious about what one needs to make a buffer. All that is required is a solution containing a weak acid and its conjugate base. An example of such a solution is one containing the weak acid HB, and the B$^-$ ion, its conjugate base, obtained by dissolving the salt NaB in water.

The pH of such a buffer is established by the relative concentrations of HB and B$^-$ in the solution. In such a solution [H$^+$] can be calculated by manipulating Equation 4:

\[
[H^+] = K_a \times \frac{[HB]}{[B^-]}
\]  

If, for example, we mix, 500 mL of 0.10 M HB with 500 mL 0.10 M NaB, we will have a typical buffer, containing an acid and its conjugate base. The [H$^+$] in this solution is easily found. Since we have equal amounts of HB and B$^-$ present, their concentrations are equal, and by Equation (4a), [H$^+$] equals $K_a$. 

You might wonder why [HB] and [B\(^-\)] do not change when 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 \(1 \times 10^{-5}\)M, and so, in our example, where we have 1 L of solution, we will have \(1 \times 10^{-5}\) moles of H\(^+\). This means that \(1 \times 10^{-5}\) 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 relation 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 \(1.0 \times 10^{-5}\), 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 \(3.2 \times 10^{-5}\)M. Then, by Equation (4a):

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

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 HC\(_1\), a strong acid, to our buffer, the following reaction will occur:

\[
H^+(aq) + B^-(aq) \rightarrow HB(aq) + H_2O \quad (7)
\]

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

\[
OH^-(aq) + HB(aq) \rightarrow B^-(aq) + H_2O \quad (8)
\]
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 of the pH will be small since the ration 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 x 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 Ka 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.
Procedure
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 ½ inch depth in tube). To each tube add a drop or two of one of the indicators in Table 21.1, 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 21.1, 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 NaH₂PO₄ 0.1 M H₂C₂H₂O₂ 0.1 M ZnSO₄
Record the colors you observe and the pH range for each solution.

Table 21.1

<table>
<thead>
<tr>
<th>Indicator</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>vio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thymol blue</td>
<td>red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl yellow</td>
<td>red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Congo red</td>
<td>violet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>orange-red</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromeresol green</td>
<td>yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>blue</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Measurement for 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.

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  Na₂CO₃  NaC₂H₃O₂  NaHSO₄
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 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

\[
\begin{align*}
&\text{HC}_2\text{H}_3\text{O}_2^- \quad \text{NH}_4^+ \quad \text{NH}_3 \quad \text{HCO}_3^- \quad \text{CO}_3^{2-} \\
\text{acetic acid-acetate ion} & \quad \text{ammonium ion-ammonia} & \quad \text{hydrogen carbonate-carbonate}
\end{align*}
\]

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\textsubscript{2}H\textsubscript{3}O\textsubscript{2}, 0.10 M NH\textsubscript{4}C1 or 0.10 M NaHCO\textsubscript{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 Ka 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 and measure the pH again after adding 5 drops of 0.10 M NaOH. 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 Ka. 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 HC1 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

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 Ka for your unknown acid.

3. Given the pH of the buffer you need to design, and the value of Ka you just found, calculate the value of [HB][B⁻] that is needed in the buffer.

Noting that [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 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.
Data Sheet: pH and Buffers

A. Determination of pH Using Acid-Base Indicators

<table>
<thead>
<tr>
<th>Indicator</th>
<th>HCl</th>
<th>Color with 0.1 M Solution of NaH₂PO₄</th>
<th>HC₂H₃O₂</th>
<th>ZnSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thymol blue</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Congo red</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brom cresol green</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH range</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 brom cresol green for each of the 0.1 M solutions that were tested.

<table>
<thead>
<tr>
<th>pH</th>
<th>NaCl</th>
<th>Na₂CO₃</th>
<th>NaC₂H₃O₂</th>
<th>NaH₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 brom cresol 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 \( K_a \) (Eq. 4a) ______

2. pH of diluted buffer ______ [H+] ______ M \( K_a \) ______
   pH after addition of 5 drops of NaOH ______
   pH after addition of 5 drops of HCl ______

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) ______

Volume 0.10 M HB needed in buffer ______
Volume 0.10 M NaB ______

Volume 0.10 M HB used ______ mL Volume 0.10 M NaB used ______ mL

pH of prepared buffer ______

Sample calculation
D. Preparing a Buffer from an Unknown Acid Solution

pH of buffer to be designed and prepared  

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

[H⁺] in that solution M  

Ka of unknown acid  

\[ \frac{[HB]}{[B^-]} \] needed in buffer =  

\[ \frac{\text{no. moles HB in buffer}}{\text{no. moles B⁻ in buffer}} \]  

(9)

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

No. moles OH⁻ in that volume  

No. moles B⁻ produced and present in final buffer  

No. moles HB that react with the added NaOH  

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

Total number of moles HB needed to make up the buffer  

Volume of 0.10 M HB required  

pH of prepared buffer  

Unknown No.  

Sample calculation
Advanced Study Assignment: pH and 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   Bromocresol 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?)
   c. What is the value of Ka for HCN? (Eq.4.) _________

3. When 5 drops of 0.10 M NaOH were added to 20 mL of the formic acid/sodium formate (HCO$_2$H/NaCO$_2$H) buffer, the pH went from 3.60 to 3.71. Complete the following ionic equation and use it 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 HC1, which also would have a pH of 3.60.

   Ionic equation:   HCO$_2$H   +   OH$^-$ →
                   Acid       Base       Conj. Base     Conj. Acid