Chapter 14

Acid-Base Equilibria

"How inappropriate to call this planet Earth, when clearly it is Ocean."

Arthur C. Clarke
Introduction

Life on earth flourishes in a water environment in which the acidity is maintained within a very narrow range by dynamic acid-base reactions. A variety of interrelated reactions bind and release hydrogen ions and, in the process, keep the pH not too far from seven. The pH of natural fluids is a useful index of the status of equilibrium reactions in which water participates. The reaction of dissolved carbon dioxide with water is one of the most important processes that release hydrogen ions:

\[
\begin{align*}
\text{CO}_2(\text{g}) & \quad \rightleftharpoons \quad \text{CO}_2(\text{aq}) \\
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \quad \rightleftharpoons \quad \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \quad \rightleftharpoons \quad \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \quad \rightleftharpoons \quad \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

Pure water in contact with air having an average CO₂ content has a pH that stays about 5.65. In man, the hydrogen ion concentration in blood is maintained very close to \(4 \times 10^{-8}\) M (pH 7.4), which is a requirement for the optimal performance of many enzyme systems. The ability of natural systems to maintain hydrogen ion concentrations at precise low levels is a direct consequence of the "feedback" properties of acid-base equilibria. These equilibria are dynamic, reversible, and fast. Any challenge to the natural system by abnormal or unusual changes is immediately detected and effectively neutralized.

The effect of an outside influence on a system at equilibrium may be predicted by means of Le Chatelier’s principle, which states that if an equilibrium is upset, the system responds in a direction that will reestablish equilibrium. It is important to emphasize that the principle holds even in very complicated natural systems in which there are many connected chemical and biological equilibria. Equilibria are connected if a component of one reaction (either reactant or product) also takes part in another reaction. A good example is the carbon dioxide–water system introduced earlier. An increase in the atmospheric carbon dioxide concentration (\(\text{CO}_2(\text{g})\)) will lead to an increase in dissolved carbon dioxide (\(\text{CO}_2(\text{aq})\)), which will increase the carbonic acid (\(\text{H}_2\text{CO}_3\)) concentration and will eventually lead to increased acidity (\(\text{H}^+\) concentration). Similarly, any reaction that results in the removal of carbonate (\(\text{CO}_3^{2-}\)) or bicarbonate (\(\text{HCO}_3^-\)) will have a ripple effect in the system and lead to increased acidity and an increased dissolution of gaseous carbon dioxide.

Homeostasis (i.e., maintenance), which occurs as a result of Le Chatelier’s principle, is often called buffering action. In chemistry, acid-base systems with these maintenance properties are called buffer systems.

Earth is the water planet. Water is the key to all maintenance of life. It is the liquid that mediates all terrestrial exchanges of hydrogen ions between acids and bases. Water, therefore, provides the reference point for all measures of acidity and alkalinity. In this series of laboratory experiments, you have the opportunity to investigate most of the important aspects of acid-base equilibria, including Le Chatelier’s principle, strengths of acids and bases, and buffering action.
Background Chemistry

Many theories have been developed to interpret the nature of acids and bases. One of the simplest and most useful is the Brønsted-Lowry theory. In this theory an acid is defined as a proton (H⁺) donor and a base is defined as a proton acceptor. Let us consider the nature of water as a solvent. In liquid water, the water molecules collide billions of times per second, and a few of these collisions are powerful enough to break covalent bonds. A reaction occurs that may be written as

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

in which the products are hydronium ions (H₃O⁺) and hydroxide ions (OH⁻). The double arrow \( \rightleftharpoons \) is used to show that the reaction is dynamic and reversible. Water molecules are continuously breaking up, and hydronium ions and hydroxide ions are continuously combining to produce water molecules. The rate of the forward reaction

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

is equal to the rate of the reverse reaction

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \leftarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

and, therefore, the concentration of the reactants and products does not change with time. The water system is said to be at equilibrium.

It is interesting to note that in the above equilibrium reaction, water is acting both as an acid (proton donor) and as a base (proton acceptor). In pure water, the self-dissociation produces (at 25°C) equal concentrations of H₃O⁺ and OH⁻, which are 10⁻⁷ M. The law of mass action can be applied to any reaction at equilibrium, and when applied to the self-dissociation of water, gives

\[ K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \]

where \( K_c \) is called the equilibrium constant for the reaction. Now the molar concentration of H₂O in water is 55.6 M and can be regarded as constant. We can simplify the above expression to

\[ K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \]

where \( K_w \) is called the ion-product constant of water. Since at 25°C,

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} M \]
Then
\[ K_w = 10^{-7} \times 10^{-7} = 10^{-14} \]

Of course, all equilibrium constants are temperature dependent. The value for \( K_w \) at 25 °C, i.e., \( 1.00 \times 10^{-14} \), is used throughout this laboratory module. It is convenient to use logarithmic scales for the expression of \([H^+]\) and often for equilibrium constants:

\[ \text{pH} = -\log_{10} [H^+] \]

\[ \text{pK} = -\log_{10} K \]

and generally,

\[ \text{pX} = -\log_{10} X \]

Thus, the pH of pure water at 25 °C is 7.00, and the pK\(_w\) for water at 25 °C is 14.00.

We can now consider what happens when an acid, e.g., acetic acid (CH\(_3\)COOH), is added to water. Since CH\(_3\)COOH is an acid, protons are donated by CH\(_3\)COOH and are accepted by the solvent water, which acts as a base:

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]

The equilibrium constant for this reaction is called an acid dissociation constant \( K_a \), and applying the law of mass action,

\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \]

The value of \( K_a \) is \( 1.75 \times 10^{-5} \) at 25 °C. This very small value means that the equilibrium lies very much to the left. Very few molecules of CH\(_3\)COOH dissociate to give CH\(_3\)COO\(^-\) (acetate ion) and H\(_3\)O\(^+\). Acids that have \( K_a \) values smaller than \( 10^{-2} \) are said to be weak acids. Acids with \( K_a \) values greater than \( 10^{-2} \) (usually >> \( 10^{-2} \)) are said to be strong acids. Hydrochloric acid is an example of a strong acid in aqueous solution:

\[ \text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{Cl}^- + \text{H}_3\text{O}^+ \]

where the acid dissociation constant is so large (\( \sim 10^{-4} \)) that the equilibrium lies almost completely to the right, and the reaction is normally written as

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ \]

The addition of acids to water, whether weak or strong, will always result in an increase in \([\text{H}_3\text{O}^+]\) and, therefore, a decrease in pH (since \( \text{pH} = -\log_{10} [\text{H}^+] \)). The pH of acidic solutions is always less than 7.00.
Bases in aqueous solution can also be characterized as weak or strong depending on the value of the base dissociation constant $K_b$. The addition of the base ammonia (NH$_3$) to water results in

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

where the solvent water acts as an acid and

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.75 \times 10^{-5} \text{ (at 25°C)}$$

Ammonia is a weak base and is not dissociated to any great extent in aqueous solution. Sodium hydroxide (NaOH) is an example of a strong base that is completely dissociated in aqueous solution. The pH of basic solutions is always greater than 7.00.

All the reactions discussed so far and all the reactions you will investigate in this module involve water as the solvent. All the equilibrium constants are, therefore, valid only for aqueous solutions and are dependent on the proton-donating and proton-accepting ability of the water molecule. It is very convenient to employ a simpler way of writing acid-base equilibria in aqueous solution than that used thus far. It may be assumed that all ions in an aqueous solution are hydrated, including the H$_3$O$^+$ ion. Thus, self-dissociation of water may be written as

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

and the dissociation of a weak acid HA may be written as

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

Unfortunately, the dissociation of weak bases must still be written with H$_2$O as a reactant in order to maintain the species balance, e.g.,

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

All the acids discussed thus far have been capable of donating one proton and are called monoprotic acids. There are many acids that can donate two or more protons, e.g., H$_3$PO$_4$ is an example of a triprotic acid:

$$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- \quad K_1$$

$$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \quad K_2$$

$$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} \quad K_3$$
These polyprotic acids donate protons in a stepwise manner. The first acid dissociation constant is usually larger than the second acid dissociation constant, and so on. In the H₃PO₄ dissociation shown above, K₁ > K₂ > K₃.

Acid-base equilibria are often investigated by carrying out titration reactions. An acid-base titration is the process of incremental addition of a solution of acid (or base) to a solution of base (or acid) such that the extent of the neutralization reaction can be monitored. A titration is really a very simple way of obtaining a tremendous amount of useful information about an acid-base system.

One of the most important criteria for the use of titration methods in the study of equilibria is that equilibrium be achieved rapidly. Proton transfer reactions, especially in water, are usually very fast, with half-lives of less than milliseconds. The rapid rate of chemical reactions involving protons is in part due to the rapid rate at which protons travel through an aqueous solution. It has been proposed that H⁺ moves through an aqueous solution by a "jump" or "proton-hopping" mechanism (see Figure 14.1).

![Proton-Hopping Mechanism in Water](image)

Figure 14.1 Proton-Hopping Mechanism in Water

Once the acid-base system has achieved equilibrium, then a wide variety of quantitative monitoring techniques can easily be used to probe the state of the system. The master variable in acid-base systems is [H⁺] (or pH), and the most common method of analysis is to examine the change of concentration of other species (at equilibrium) as a function of changes in [H⁺].

In this module you will experimentally investigate a wide variety of acid-base reactions and compare your results with computer simulations carried out on the main frame computer system at Colorado State University (a Cyber 205). Graphical presentation of the data in the form of titration curves reveals a rich source of useful information about acids and bases and their reactions.
Pre-Laboratory Quiz

1. What is the pH of human blood?

2. Write down the set of 4 coupled equilibria that results from the dissolution of gaseous $\text{CO}_2$ in pure water.


4. Give the self-dissociation reaction of water.

5. What is the value of the ion product of water (at 25 °C)?
6. Give a definition of a weak base.

7. What is a titration?

8. Give the chemical formula and name for one triprotic acid.

9. How do protons travel very rapidly through water?

10. Give a definition of a strong acid.
Laboratory Experiments

Flowchart of the Experiments

Section A. Conductimetry and the Strength of Acids and Bases

Section B. Acid-Base Equilibria and Indicator Dyes

Section C. Determination of the $K_a$ Values of Weak Acid Indicators

Section D. pH Measurement with Indicator Color Probes

Section E. The Study of Acid-Base Equilibria by Graphical Interpretation of Titration Data

Part 1. Titration of a Strong Acid with a Strong Base
Part 2. Titration of a Weak Acid with a Strong Base
Part 3. The Measurement of the $K_a$ of a Weak Acid
Part 4. The Henderson-Hasselbalch Equation
Part 5. Titration Curves and Buffer Solutions
Part 6. The Dilution of Buffers
Part 7. The Selection of Weak Acids to Make Buffer Solutions
Part 8. The Titration of Weak Bases with Strong Acids

Section F. The Titration of Polyprotic Acids

Section G. Calculations on Diprotic and Triprotic Acids

Requires two three-hour class periods to complete
Throughout this module you will be investigating acid-base equilibria by analyzing the progress of acid-base reactions in volumetric titrations. The quality of the results from these experiments will depend on the care with which you carry out solution transfers, dilutions, and drop additions. Large-drop microburets (described in Chapter 3, Section C) are satisfactory for most of the titrations. Microburets may be calibrated (when necessary) by means of an analytical balance or volumetrically.

**CAUTION:** Most acids and bases are corrosive. If you get any of these solutions on your skin, wash well with cold water and inform your instructor.

### Section A. Conductimetry and the Strength of Acids and Bases

**Goals:**
1. To be able to interpret the conductivity experiments demonstrated by your instructor.
2. To be able to identify strong and weak acids and bases by means of $K_a$, $K_b$, $pK_a$, and $pK_b$ values.

**Discussion:**
Your instructor will demonstrate several conductivity experiments for you. Record your observations of these experiments in your notebook. A discussion of two of the experiments follows.

1. The ability of a solution to conduct electricity depends on the concentration of ions in the solution. A 0.1 M HCl solution is a good conductor because the HCl molecules are completely dissociated into ions:

   $$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$

   which may be conveniently abbreviated

   $$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$$

   because water is the solvent in aqueous solutions. The dissociation occurs extremely rapidly to instantaneously give a solution that is 0.1 M H$^+$ and 0.1 M Cl$^-$. Acids that dissociate completely are called strong acids, and the $K_a$ value is very large (> $10^4$ for HCl).

2. The 0.1 M CH$_3$COOH (acetic acid) solution is a poor conductor because the solution contains mostly undissociated CH$_3$COOH molecules. Acetic acid dissociates rapidly, but only to a small extent:

   $$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$$

   This reaction may be abbreviated

   $$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$$

   The $K_a$ of CH$_3$COOH is small (1.8 x $10^{-5}$); thus, the solution contains only small concentrations of H$^+$ and CH$_3$COO$^-$ (acetate ion). Acids that do not appreciably
dissociate in aqueous solution are called weak acids. Weak acids have $K_a$ values that are smaller than about $10^{-2}$.

Your instructor will also demonstrate conductance experiments with NaOH (strong base) and NH$_3$ (weak base) solutions and carry out an acid-base reaction between NH$_3$ and CH$_3$COOH. Try to come up with your own interpretation of what is occurring in these experiments. Use the following guidelines:

- Try to interpret the results from the conductance experiments in the form of chemical equilibria reactions.
- Predict what would happen in a conductivity experiment if an H$_2$SO$_4$ solution was titrated with the strong base Ba(OH)$_2$.

HINT: First, write a balanced chemical equation and think about the products that are formed.

- Use your calculator to find the $pK_a$ and $pK_b$ values for all the acids and bases used in this section.

### Section B. Acid-Base Equilibria and Indicator Dyes

**Goal:**
To investigate several aspects of acid-base equilibria by means of a colored dye called bromocresol green.

**Discussion:**
Bromocresol green is one of a class of organic compounds that can exist in different colored forms depending on whether the compound is protonated or unprotonated. (The terms protonated and unprotonated refer to the acid form and the conjugate base form of the indicator.) You have already done experiments on a naturally occurring dye (red cabbage extract) in an earlier module. The chemical structure of most of these organic indicators is rather complex; e.g., bromocresol green has the formula C$_{21}$H$_{14}$O$_5$Br$_4$S (molar mass: 698 g mol$^{-1}$). However, these structures can be symbolized in a simple and convenient way by writing the protonated, acid form of the dye as HIn. The dissociation of the acid indicator can thus be written

$$\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$$

for which

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

The protonated form HIn usually has a different color than the unprotonated form In$^-$. 

**Experimental Steps:**
1. Clean a 1 x 12 well strip.
2. Locate a microburet of 0.03% bromocresol green indicator solution. Deliver 1 drop to each of 6 wells.
3. Use a clean large-drop microburet to quantitatively dilute 1 drop of 0.05 M HCl to 0.01 M HCl.

NOTE: Use good wash and transfer techniques!

4. Add 1 drop of 0.01 M HCl to the first well. Stir.

- What observation would lead you to conclude that the time for mixing to occur is much longer than the time required for the acid-base reaction?
- You have just added a strong acid (HCl) — i.e., a solution of H⁺ and Cl⁻ ions (each of which is 0.01 M concentration) — to the dye system that was originally at equilibrium. On the basis of Le Chatelier’s principle, explain the color change.
- What is the approximate pH of the mixed solution?

5. Add 1 drop of 0.01 M NaOH to the indicator in the third well.

- Describe what happens and explain the change according to Le Chatelier’s principle.

6. Add 3 drops of pH 4.0 solution (from Reagent Central) to wells 1, 2, and 3. Stir.

NOTE: The pH 4.0 solution is a buffer solution (you will be exploring buffers in a later section) that reacts with strong acids and strong bases to produce a final solution that has a pH of approximately 4, i.e., [H⁺] = 10⁻⁴ M.

- Explain the color changes you observed in Step 6.
- Design and execute a simple experiment to show that the indicator equilibrium reaction is reversible.
- Record the results in your notebook.

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**Section C. Determination of the Kₐ Values of Weak Acid Indicators**

**Goal:**
To carry out a determination of the acid dissociation equilibrium constant of several colored, weak acid indicators.

**Discussion:**
One of the simplest ways to measure Kₐ values of weak acid indicators is to place the weak electrolyte in a series of solutions of exactly known pH values and allow any acid-base reactions to come to equilibrium. Once equilibrium is achieved — and of course, with acid-base reactions this happens rapidly — the appropriate color changes reveal the relative concentration of HIn and In⁻ in the various solutions.

**Experimental Steps:**
1. Clean a 96-well tray (preferably with flat-bottomed wells).
2. Locate the 12 reagent bottles containing solutions of known pH 1.0 through 12.0. Deliver 2 drops of pH 1.0 to the first well in row A, 2 drops of pH 2.0 to the second well, 2 drops of pH 3.0 to the third well, and so on. Repeat the procedure in rows B, C, and D. (You now have 4 rows of 12 solutions going from pH 1.0 on the left to pH 12.0 on the right.)
3. Use a microburet to deliver 1 drop of methyl orange to each well of row A.
4. Similarly, deliver 1 drop of bromocresol green to the wells of row B, 1 drop of bromothymol blue to the wells of row C, and 1 drop of phenolphthalein to row D. Stir the solutions with a microstirrer.

- Record the solution colors in a table in your laboratory notebook.

In the above experiment, each weak acid indicator is "locked" in a certain equilibrium position that is dependent on the [H⁺] of the solution. The [H⁺] varies between $10^{-1}$ M (pH 1.0) and $10^{-12}$ M (pH 12.0) in each row. The $K_a$ for an indicator is a constant for a particular indicator (at constant temperature):

$$
HIn \rightleftharpoons H^+ + In^- 
$$

$$
K_a = \frac{[H^+][In^-]}{[HIn]}
$$

Rearranging the $K_a$ expression gives

$$
\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]}
$$

which shows that at different [H⁺]'s, the [In⁻]/[HIn] ratio must vary. Since HIn and In⁻ are different colors, then at some [H⁺] the [In⁻]/[HIn] ratio will be 1.0, i.e.,

$$
[In^-] \approx [HIn]
$$

and the color of the solution will be intermediate between the color of HIn and the color of In⁻. Experimentally, this means a color change from the color of HIn to that of In⁻ in going from left to right in a row. Now, when [HIn] ≈ [In⁻], then

$$
\frac{K_a}{[H^+]} = 1.0
$$

and therefore $K_a \approx [H^+]$ at that place in the row.

6. Determine the $K_a$ and p$K_a$ values of the 4 weak acid indicators and report them in your notebook.

- Why are these values only approximate?
- How could they be measured more accurately using the same type of method?

It is interesting to note that the human eye-brain system, with normal color vision, can easily discriminate a 100-fold change in the [In⁻]/[HIn] ratio. An indicator solution will appear to have the "pure" color of HIn at

$$
\frac{[HIn]}{[In^-]} = \frac{10}{1}
$$
Thus,

\[
\frac{K_a}{[H^+]} = \frac{10}{1}
\]

Similarly, the solution will be perceived to have the "pure" color of In⁻ at

\[
\frac{[HIn]}{[In^-]} = \frac{1}{10}
\]

Thus,

\[
\frac{K_a}{[H^+]} = \frac{1}{10}
\]

Thus, the pH transition range of an indicator from one "pure" color to another is

\[
pH \text{ transition range} = pK_a \pm 1.0
\]

Table 14.1 lists some common acid-base indicators, along with pH transition ranges and colors in acidic and basic solutions. Using the table, calculate the pH transition range for the 4 weak acid indicators that you have investigated in this section.

### Section D. pH Measurement with Indicator Color Probes

**Goal:**
To use a solution of a combination of indicators (a universal indicator) as a color probe for sensing [H⁺] and, therefore, pH.

**Discussion:**
The author and Peter Markow have tested over 5000 combinations of acid-base indicators and have selected a universal indicator that may be used to obtain an easily seen color change, over small intervals, from pH 1.0 to pH 12.0. You will be preparing a set of solutions of different pH and color in order to be able to use the set as a colorimetric pH meter for measuring the pH of various sample solutions.

**Experimental Steps:**
1. Clean a 1 x 12 well strip.
2. Use a microburet to deliver 1 drop of the Thompson-Markow universal indicator solution to each well.
3. Add 3 drops of pH 1.0 solution to the first well, 3 drops of pH 2.0 solution to the second well, and so on. Stir.
   - Describe the color of each pH value in your lab book.

**NOTE:** You now have 12 solutions of known pH, each of which has a different color. This set of solutions can now be used to measure the pH of any unknown solution by a simple color comparison.

4. Measure the pH of 5 of the colorless solutions located in the 24-well tray, e.g., 0.05 M CH₃COOH, etc.

**NOTE:** To measure the pH, drop 3 drops of the unknown solution into a well of another 1 x 12 well strip. Add 1 drop of universal indicator and stir.
<table>
<thead>
<tr>
<th>Name</th>
<th>pH Transition Range</th>
<th>Acid Color</th>
<th>Basic Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malachite green</td>
<td>0.0 – 2.0</td>
<td>yellow</td>
<td>green</td>
</tr>
<tr>
<td>Cresol red</td>
<td>0.2 – 1.8</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Metacresol purple</td>
<td>1.2 – 2.8</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>1.2 – 2.8</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Orange IV</td>
<td>1.3 – 3.2</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Methyl yellow</td>
<td>2.9 – 4.0</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Bromophenol blue</td>
<td>3.0 – 4.6</td>
<td>yellow</td>
<td>purple</td>
</tr>
<tr>
<td>Congo red</td>
<td>3.0 – 5.0</td>
<td>blue</td>
<td>red</td>
</tr>
<tr>
<td>Methyl Orange</td>
<td>red</td>
<td></td>
<td>yellow</td>
</tr>
<tr>
<td>Bromocresol green</td>
<td>yellow</td>
<td></td>
<td>blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.4 – 6.2</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>Chlorophenol red</td>
<td>4.8 – 6.4</td>
<td>yellow</td>
<td>purple</td>
</tr>
<tr>
<td>Litmus</td>
<td>4.5 – 8.3</td>
<td>red</td>
<td>blue</td>
</tr>
<tr>
<td>Paranitro phenol</td>
<td>5.0 – 7.0</td>
<td>colorless</td>
<td>yellow</td>
</tr>
<tr>
<td>Bromocresol purple</td>
<td>5.2 – 6.8</td>
<td>yellow</td>
<td>purple</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>yellow</td>
<td></td>
<td>blue</td>
</tr>
<tr>
<td>Neutral red</td>
<td>6.8 – 8.0</td>
<td>bluish red</td>
<td>yellow</td>
</tr>
<tr>
<td>Phenol red</td>
<td>6.4 – 8.2</td>
<td>yellow</td>
<td>red</td>
</tr>
<tr>
<td>Cresol red</td>
<td>7.0 – 8.8</td>
<td>yellow</td>
<td>purple</td>
</tr>
<tr>
<td>Metacresol purple</td>
<td>7.4 – 9.0</td>
<td>yellow</td>
<td>purple</td>
</tr>
<tr>
<td>Curcumin</td>
<td>7.8 – 9.2</td>
<td>yellow</td>
<td>brown</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>8.0 – 9.6</td>
<td>yellow</td>
<td>blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>colorless</td>
<td></td>
<td>pink</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>9.3 – 10.5</td>
<td>colorless</td>
<td>blue</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>10.0 – 12.1</td>
<td>yellow</td>
<td>brown-red</td>
</tr>
<tr>
<td>Curcumin</td>
<td>10.2 – 11.8</td>
<td>red</td>
<td>orange</td>
</tr>
<tr>
<td>Malachite green</td>
<td>11.5 – 14.0</td>
<td>blue</td>
<td>colorless</td>
</tr>
<tr>
<td>Clayton yellow</td>
<td>12.2 – 13.2</td>
<td>yellow</td>
<td>amber</td>
</tr>
<tr>
<td>Red cabbage extract</td>
<td>2.5 – 4.0</td>
<td>red</td>
<td>pale violet</td>
</tr>
<tr>
<td>Red cabbage extract</td>
<td>6.0 – 8.5</td>
<td>pale violet</td>
<td>blue</td>
</tr>
<tr>
<td>Red cabbage extract</td>
<td>9.0 – 10.5</td>
<td>blue</td>
<td>green</td>
</tr>
<tr>
<td>Red cabbage extract</td>
<td>10.5 – 14.0</td>
<td>green</td>
<td>yellow</td>
</tr>
</tbody>
</table>

Table 14.1 Some Common Acid-Base Indicators
5. Place the pH meter strip and the second strip together and view against a white background. Slide the strips relative to each other and decide on a match.

NOTE: If the color of the unknown lies between 2 wells of the pH meter strip, then try to interpolate the pH value.

- Report the pH values in your notebook.

6. Keep the pH meter strip for the next series of experiments. Evaporation of the solutions may be stopped by sealing the strip with a piece of transparent sticky tape.

NOTE: The accuracy of pH measurement by this method depends on your ability to discriminate color hue differences. If you have difficulty with color discrimination, consult your instructor.

Section E. The Study of Acid-Base Equilibria by Graphical Interpretation of Titration Data

Goal: To investigate various quantitative aspects of acid-base chemistry by interpreting experimental titration curves and by comparing the data with computer-simulated titrations.

Discussion: Titration curve data provide a simple, powerful basis for both experimental and theoretical analysis of reaction stoichiometry (the measurement of concentration of acid, base, and salt solutions); the determination of equilibrium constants of acids and bases; the determination of molar mass; the buffer concept; the nature of polyprotic acid systems; and the use of Henderson-Hasselbalch expressions.

Section E is subdivided into Parts 1 through 8. Each part is an investigation of a particular type of titration and the information that can be derived from graphical presentations of titration data. Recall from the Background Chemistry section of this chapter that an acid-base titration is the process of incremental addition of a solution of acid (or base) to a solution of base (or acid) such that the extent of the neutralization reaction can be monitored. Each point in the titration represents the state of the acid-base system after equilibrium has been reached. The reason is that acid-base reactions are very fast, and equilibrium is usually achieved in less than a millisecond — provided that the reaction mixture is stirred! The change in [H+] that occurs during the titration may be measured by color comparison with the colorimetric pH meter.

As you work through each of the experimental sections in this chapter, you will need to refer to Figures 14.2 through 14.18. All these figures are located in sequential order at the end of this chapter. Feel free to remove them from the book.

Section E. Part 1. Titration of a Strong Acid with a Strong Base

Experimental Steps:

1. Clean a 96-well tray (flat-bottomed wells).
2. Deliver 1 drop of universal indicator to each well of row A.
NOTE: Use a clean large-drop microburet for all titrations. First, use good transfer technique to rinse and half-fill the microburet with 0.05 M HCl.

3. Quantitatively deliver (using standard technique) 1 drop of 0.05 M HCl to each well of row A.

4. Wash, rinse, and half-fill the same microburet with 0.01 M NaOH.

5. Carry out a serial titration of the 0.05 M HCl with 0.01 M NaOH — i.e., add 1 drop NaOH to the first well, 2 drops NaOH to the second well, and so on. Stir.

6. Use the pH meter strip (from the last section) to measure the pH values for the solution in each well.
   • Record the pH values.
   • On the graph paper provided in Figure 14.2, plot a graph of pH versus drops of added 0.01 M NaOH — the axes are already drawn for you. Draw a smooth curve through the data points using a sharp pencil.

NOTE: You might want to look at Figure 14.3 to get an idea of the form of the curve. Figure 14.3 is a computer-simulated titration curve for the titration that you have just carried out experimentally. This type of graph is called a titration curve. The simulated curve was computer generated by solving the exact mathematical equations for the acid-base equilibria involved in this titration. The pKw of water was given a value of 14.00. The dilution of the solutions by the added indicator was taken into account in computing the pH values in the titration. If you wish to know more about the computer program, consult your instructor.
   • Compare your graph with Figure 14.3.
   • What chemical reaction is taking place in the titration you just performed?
   • What is the net ionic equation for the reaction?

Since all drops from the same microburet are the same volume, the addition of 1 drop of 0.01 M NaOH to 1 drop of 0.05 M HCl will neutralize 1/5th of the HCl. This occurs because of the stoichiometry of the reaction. All the HCl will have been neutralized by the addition of 5 drops of base. This point in the titration is called the equivalence point. The computer data show that the equivalence point occurs at exactly pH 7.00 and 5.00 drops of 0.01 M NaOH.

7. Look at your experimental titration curve.

NOTE: The equivalence point is not easy to locate on experimental curves. One way is to draw a vertical line at the 5 drop point. You can see that the difficulty arises because of the very large pH rise (i.e., approximately 8 pH units, a change in [H+] of 100,000,000!) that occurs close to the equivalence point. The very large pH rise near the equivalence point is not always seen in a strong acid–strong base titration.

8. Look at Figure 14.4.
Seven titration curves are shown for strong acid (HCl) with strong base (NaOH). For each curve the concentration of acid and base are the same, e.g., the curve labelled 1 M is the curve for the titration of 5 drops of 1 M HCl with 1 M NaOH.

- Why is the pH rise for the titration of $10^{-5}$ M HCl with $10^{-5}$ M NaOH very small?
- On Figure 14.5 (which is a copy of Figure 14.4), draw in the pH transition ranges for the following single indicators: methyl orange, bromocresol green, bromothymol blue, and phenolphthalein. Use the $pK_a$ values that you calculated from the experimental data obtained in the earlier part of the laboratory.

  NOTE: Remember that the range is $pK_a \pm 1$!

- What indicator would be suitable for a titration of 0.001 M HNO$_3$ with 0.001 M KOH solution? Give reasons for your selection.

9. Figure 14.6 shows 4 titration curves of monoprotic strong acids titrated with 0.10 M NaOH.

- As a homework assignment, calculate the molarity of each acid, given

  Curve A = 25.00 mL of acid of unknown concentration titrated with 0.10 M NaOH
  Curve B = 5.00 mL of acid of unknown concentration titrated with 0.10 M NaOH
  Curve C = 10.00 mL of acid of unknown concentration titrated with 0.10 M NaOH
  Curve D = 25.00 mL of acid of unknown concentration titrated with 0.10 M NaOH

### Section E. Part 2. Titration of a Weak Acid with a Strong Base

**Experimental Steps:**

1. Deliver 1 drop of universal indicator to each well in row B of the 96-well tray.
2. Use good wash, rinse, and transfer technique to deliver 1 drop of 0.05 M CH$_3$COOH to each well of row B.
3. Carry out a serial titration of the acetic acid with 0.01 M NaOH. Stir.
4. Match colors with the pH meter strip and measure the solution pH values.
5. Plot the titration curve on the same graph paper (Figure 14.2) as the previous titration.

  - Draw a smooth titration curve. The computer-simulated curve is shown in Figure 14.7.

  - What are the chemical reaction and net ionic reaction for the neutralization reaction that takes place during the titration?

  NOTE: Data selected from the computer simulation show that the equivalence point pH is 8.31 and that it occurs after the addition of exactly 5 drops of 0.01 M NaOH.

6. Compare this pH value with that obtained at the equivalence point in the strong acid–strong base titration.

The solution at the equivalence point in the acetic acid titration is a sodium acetate solution. Sodium acetate (CH$_3$COONa) is a salt that is completely dissociated in aqueous solution into acetate ions CH$_3$COO$^-$ and sodium ions Na$^+$:

$$\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+$$
The acetate ion is a weak base (i.e., it can accept a proton):

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]

Thus, the solution at the equivalence point is slightly basic (pH 8.31) because of the hydroxide ions \( \text{OH}^- \) produced in the last reaction.

**Section E. Part 3. The Measurement of the \( K_a \) of a Weak Acid from the Titration Curve**

**Experimental Steps:**

1. Look at Figure 14.7. The part of the curve before the equivalence point gives the pH of partially neutralized acetic acid solutions.
   - What is the limiting reagent?

   The solutions contain unreacted acetic acid and acetate ions from the neutralization reaction

\[ \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \]
\[ \text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ \]
\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

The \( K_a \) expression for acetic acid and \( K_w \) for water are

\[ K_a = 1.75 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \]

\[ K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-] \]

At a point in the titration halfway from the start to the equivalence point (at 2.5 drops NaOH), 1/2 of the CH₃COOH has been neutralized. Thus, if we neglect the [H⁺] from water, then

\[ [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] \]

Substituting this into the \( K_a \) expression,

\[ K_a = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \frac{[\text{H}^+]}{} \]

\[ K_a = [\text{H}^+] \]

Or \( pK_a = \text{pH at the midpoint!} \)

- To find the \( pK_a \) of CH₃COOH from Figure 14.7, draw a vertical line from 2.5 drops to intersect the curve. From the intersection draw a horizontal line to the pH axis, and \( \text{pH} = pK_a \).

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What is the $K_a$ of CH$_3$COOH?

This $K_a$ value is typical of the $K_a$ values for many organic carboxylic acids that have the structure

$$R \text{– } O^\cdot \text{COOH}$$

The hydrogen atom that dissociates is the H atom attached to the oxygen atom of the carboxylate group.

### Section E. Part 4. The Henderson-Hasselbalch Equation

**Discussion:**

Again, consult Figure 14.7. A very useful relationship that links the pH of solutions in titrations of weak acids with $pK_a$ is the *Henderson-Hasselbalch equation*,

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

for a weak acid HA.

If the $pK_a$ of the weak acid is known — e.g., the value obtained for CH$_3$COOH in Part 3 — then for

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Taking $\log_{10}$ of the $K_a$ expression

$$\log_{10} K_a = \log_{10} [\text{H}^+] + \log_{10} [\text{CH}_3\text{COO}^-] - \log_{10} [\text{CH}_3\text{COOH}]$$

and changing the sign throughout results in

$$-\log_{10} K_a = -\log_{10} [\text{H}^+] - \log_{10} [\text{CH}_3\text{COO}^-] + \log_{10} [\text{CH}_3\text{COOH}]$$

Since $pK_a = -\log_{10} K_a$ and $pH = -\log_{10} [\text{H}^+]$

then

$$pH = pK_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
The last term in the above equation is simply the logarithm of the ratio of $[\text{CH}_3\text{COO}^-]$, formed in the neutralization, to the unreacted $[\text{CH}_3\text{COOH}]$. You may show that this is correct by consulting Figure 14.7 and filling in the following table.

<table>
<thead>
<tr>
<th>Drops of 0.01 M NaOH Added</th>
<th>$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$</th>
<th>pH from Curve</th>
<th>pH Calculated from H-H Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NOTE: Use the $pK_a$ value for CH$_3$COOH that you obtained in Part 3.

**Section E. Part 5. Titration Curves and Buffer Solutions**

**Discussion:**

Look at Figure 14.7, particularly the part of the curve before the equivalence point.

Note that the pH change that occurs on the addition of strong base NaOH is quite small. Partially neutralized solutions of weak acids or weak bases (see later) that resist change in pH upon the addition of small amounts of strong acid or strong base are called *buffer solutions*. The part of the titration curve where buffering occurs is called the *buffer region*. This buffering action occurs because the solutions contain relatively large concentrations of weak acid CH$_3$COOH and its salt, CH$_3$COONa (produced in the neutralization reaction). The addition of OH$^-$ from the added strong base NaOH results in

$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$

and the OH$^-$ is converted in water. The pH of the solution will change very little. The addition of H$^+$ from a strong acid to a buffer solution of this type results in

$$\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$$

and produces the weak acid CH$_3$COOH. The pH of the solution will change, but not by very much. In general, acidic buffer solutions are prepared by titrating appropriate weak acids with strong bases until the desired pH is obtained.

The slope of the titration curve in Figure 14.7 is a quantitative measure of the buffering ability, or *buffer capacity*, of the solution. Titration curves with small values of slope — i.e., "flat" regions — mean that those solutions have good buffer capacity. The steep part of the titration curve — i.e., close to the equivalence point — means that these solutions have small or no buffer capacity.
Section E. Part 6. The Dilution of Buffers

Experimental Steps: 1. Look at Figure 14.8. The 5 titration curves are for
   (a) 1.0 M CH₃COOH with 1.0 M NaOH
   (b) 0.1 M CH₃COOH with 0.1 M NaOH
   (c) 0.01 M CH₃COOH with 0.01 M NaOH
   (d) 0.001 M CH₃COOH with 0.001 M NaOH
   (e) 0.0001 M CH₃COOH with 0.0001 M NaOH

   • Draw a vertical line at 2 drops of added NaOH to intersect all 5 curves.
   • What is the value of the \( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \) ratio?
   • What are the pH values of the 5 solutions?

NOTE: These data show that buffer solutions can be diluted and still maintain approximately the same pH value. However, the buffer will collapse with excessive dilution.

Section E. Part 7. The Selection of Weak Acids to Make Buffer Solutions of Desired pH

Experimental Steps: 1. Look at Figures 14.9 and 14.10 which show titration curves for a series of weak acids with different \( K_a \) values.

NOTE: All the curves are for 0.1 M weak acid solutions titrated with 0.1 M strong base. The \( K_a \) values range from very large (strong acid) to \( 10^{-10} \) (very weak acid) as shown on the figures. The buffer regions with good buffer capacity are in the range \( pK_a \pm 1 \).

   • Draw 2 vertical lines on Figure 14.9 to show the regions of good buffer capacity.

NOTE: One interesting feature of the titration curves in Figures 14.9 and 14.10 is that all the curves give a small-slope, good buffer region after the equivalence point. All the solutions contain the salt of the weak acid and excess of strong base NaOH. Solutions that contain strong bases (or strong acids — e.g., see titration curves on Figure 14.4) are also regarded as buffers. The buffering action arises as a consequence of the high concentration of water in aqueous solutions (~ 55.6 M H₂O) and the nature of the pH scale. These buffers are called pseudobuffers.

Section E. Part 8. The Titration of Weak Bases with Strong Acids

Experimental Steps: 1. Deliver 1 drop of universal indicator into each well of row C of the 96-well tray. Retain the serial titrations in rows A and B for comparison.
2. Carry out a serial titration of the weak base 0.05 M NH₃ with 0.01 M HCl. The diluted HCl can be made by careful quantitative dilution of 0.05 M HCl. Stir.

3. Measure the pH values of the solutions.
   - Plot the titration curve on Figure 14.2.

4. Compare with the computer-simulated curve (Figure 14.11).
   NOTE: Data from the computer calculation give an equivalence point pH of 5.70 at 5.0 drops of added 0.01 M HCl.

5. Look at Figure 14.11.
   - Determine the $K_b$ and $pK_b$ of ammonia and the $K_a$ and $pK_a$ of the ammonium ion.
   - What is the chemical reaction in this titration?

6. Look at Figure 14.12. The titration curves are for the following titrations:
   (a) 1.0 M NH₃ titrated with 1.0 M HCl
   (b) 0.1 M NH₃ titrated with 0.1 M HCl
   (c) 0.01 M NH₃ titrated with 0.01 M HCl
   (d) 0.001 M NH₃ titrated with 0.001 M HCl
   (e) 0.0001 M NH₃ titrated with 0.0001 M HCl
   - Draw in lines indicating buffer regions.
   - What is the effect of dilution on the buffer solutions?

   NOTE: Figures 14.13 and 14.14 show the effect of $K_b$ of the weak base on titration curves. All the titration curves are for 0.1 M base with 0.1 M monoprotic strong acid.

7. Select an indicator that would work well for a titration of 0.1 M weak base with a $K_b$ of 1.0 x $10^{-6}$ with an 0.1 M HCl solution.
   - Are titrations of bases with $K_b$ values of less than $10^{-8}$ feasible in aqueous solutions? Give reasons for your answer.
   - Suppose you wish to make a buffer solution of pH 8.2 for a clinical physiological experiment. Describe how you would do this.

   HINT: Look at Figure 14.13.

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### Section F. The Titration of Polyprotic Acids

**Goal:** To apply the principles of graphical interpretation of titration data to investigate polyprotic acid equilibria.

**Experimental Steps:**
1. Deliver 1 drop of universal indicator to each well of row D of the 96-well tray.
2. Use a large-drop microburet to deliver 1 drop of 0.04 M H₃PO₄ (phosphoric acid) to each well in row D.

3. Carry out a serial titration of the phosphoric acid with 0.01 M NaOH. Stir.
   - Determine the solution pH values and plot the titration curve on the same graph as the computer-simulated titration curve (Figure 14.15).

4. Look at Figure 14.15.
   There appear to be only 2 equivalence points, even though phosphoric acid H₃PO₄ is a triprotic acid! The pH at the 2 equivalence points can be found from the computer data. The first equivalence point pH is 4.83 and occurs after 4.0 drops of NaOH have been added. The second equivalence point pH is 9.36 after a total of 8.0 added drops of NaOH.

5. On the computer-simulated titration curve in Figure 14.15, label the start of the titration as point A, the first equivalence point C, and the second equivalence point D.
   At point A, no NaOH has been added, and the solution contains phosphoric acid (H₃PO₄) and dihydrogen phosphate ions H₂PO₄⁻ from
   $$H₃PO₄ \rightleftharpoons H^{+} + H₂PO₄⁻$$
   The first dissociation constant $K_1$ of H₃PO₄ has a value of $7.02 \times 10^{-3}$:
   $$K_1 = \frac{[H^{+}][H₂PO₄⁻]}{[H₃PO₄]} = 7.02 \times 10^{-3}$$
   which shows that H₃PO₄ is a borderline weak/strong acid. Thus, the first dissociation is significant, and the pH of the solution is quite low (~2). Now as NaOH is added in the titration, some of the H₃PO₄ is neutralized according to
   $$H₃PO₄ + NaOH \rightarrow NaH₂PO₄ + H₂O$$
   - Which ionic species are present in solution at any point between A and C (excluding indicator ions)?
   At point C, all the H₃PO₄ has been titrated, and the solution contains only NaH₂PO₄ (completely dissociated, of course, because it is a salt).
   - What indicator would be most suitable for the location of the first equivalence point?
   As the titration proceeds beyond C, the weak acid H₂PO₄⁻ is neutralized:
   $$NaH₂PO₄ + NaOH \rightarrow Na₂HPO₄ + H₂O$$
   and NaOH is the limiting reagent.
• Which two salts form the buffer system in the buffer region between points C and D?

At the second equivalence point D, the predominant species is H₂PO₄⁻ (and the spectator ion Na⁺), which is the very weak acid.

• What is the value of the acid dissociation constant $K_a$ of H₂PO₄⁻?

HINT: Think about the titration between points C and D.

After point D further titration produces no third equivalence point. The reason is that the neutralization of HPO₄²⁻ by NaOH, i.e.,

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

produces the phosphate ion PO₄³⁻, which is as strong a base as NaOH. Another way of looking at it is that HPO₄²⁻ is such a weak acid ($K_a = 4.68 \times 10^{-13}$) that it cannot be titrated in aqueous solution.

6. Look at Figure 14.16. The 3 curves are for titrations of

(a) 1 M H₃PO₄ with 1 M NaOH
(b) 0.1 M H₃PO₄ with 0.1 M NaOH
(c) 0.01 M H₃PO₄ with 0.01 M NaOH

• Why are the titration curves for the different reagent concentrations so similar?

• How could you prepare a buffer solution with a pH of 2.70 and with very good buffer capacity?

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Section G. Calculations on Diprotic and Triprotic Acids

Goal:

To apply the principles that you have learned in this module to diprotic and triprotic acid systems. You may do this as a homework assignment for extra credit.

Experimental Steps:

1. Look at Figure 14.17. The curve is for the titration of 10 mL of an unknown concentration, diprotic acid H₂A, titrated with 0.10 M NaOH.

• Make a list of all the information (qualitative and quantitative) that can be derived from this titration curve.

2. Look at Figure 14.18. The curve is for the titration of 10 mL of an unknown concentration, triprotic acid H₃X, titrated with 0.1 M NaOH.

• Again, list all the information that can be derived from these data.
EXPERIMENTAL TITRATION CURVE

Figure 14.2  1 Drop of 0.05 M HCl Titrated With 0.01 M NaOH

Drops of Added 0.01 M NaOH
COMPUTER-SIMULATED TITRATION CURVE

Figure 14.3 1 Drop of 0.05 M HCl Titrated With 0.01 M NaOH

Drops of Added 0.01 M NaOH
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF STRONG ACID WITH STRONG BASE

Figure 14.4 Effect of Concentration of Reactants

Drops of Added NaOH
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF STRONG ACID WITH STRONG BASE

Figure 14.5  pH Transition Ranges For Some Indicators

Drops of Added NaOH
COMPUTER-SIMULATED TITRATION CURVES

Figure 14.6 Strong Acids Titrated With Strong Base
COMPUTER-SIMULATED TITRATION CURVE

Figure 14.7 1 Drop of 0.05 M CH₃COOH With 0.01 M NaOH
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF WEAK ACIDS WITH STRONG BASE

Figure 14.8 Effect of the Concentration of Reagents

Drops of Added NaOH
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF VARIOUS 0.10 M WEAK ACIDS WITH STRONG BASE

Figure 14.9 Effect of $K_a$

pH

Drops of Added 0.10 M NaOH
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF VARIOUS 0.10 M WEAK ACIDS WITH STRONG BASE

Figure 14.10 Effect of $K_a$
COMPUTER-SIMULATED TITRATION CURVE

Figure 14.11 1 Drop of 0.05 M NH₃ Titrated With 0.01 M HCl
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF NH₃ WITH STRONG ACID (HCl)

Figure 14.12 Effect of the Concentration of Reagents
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF VARIOUS 0.10 M WEAK BASES WITH STRONG ACID

Figure 14.13  Effect of $K_a$

Drops of Added 0.10 M HCl
COMPUTER-SIMULATED TITRATION CURVES FOR 5 DROPS OF VARIOUS 0.10 M WEAK BASES WITH STRONG ACID

Figure 14.14 Effect of $K_b$
COMPUTER-SIMULATED TITRATION CURVE

Figure 14.15  1 Drop of 0.04 M H₃PO₄ With 0.01 M NaOH
COMPUTER-SIMULATED TITRATION CURVES FOR 4 DROPS OF $10^{-2}$ M, $10^{-1}$ M, AND 1 M $H_3PO_4$ WITH STRONG BASE

Figure 14.16 Effect of Concentration of Reagents
COMPUTER-SIMULATED TITRATION CURVE OF 10 mL OF AN UNKNOWN CONCENTRATION OF DIPROTIC ACID WITH 0.10 M NaOH

Figure 14.17

10 mL of unknown acid titrated with 0.1 M NaOH

mL of Added 0.01 M NaOH
COMPUTER-SIMULATED TITRATION CURVE OF 10 mL OF AN UNKNOWN
CONCENTRATION OF TRIPROTIC ACID WITH 0.10 M NaOH

Figure 14.18

10.00 mL of unknown acid titrated with 0.1000 M NaOH

mL of Added 0.10 M NaOH