

## Chemistry of Acids and Bases

The chemistry of acids and bases is an area of fundamental importance in chemistry. In this experiment you will study acid-base equilibria by determining the pH of a number of acids and bases and their mixtures and by performing a pH titration. In particular, the aims of this experiment are:

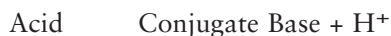
1. To demonstrate that only a very small concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are generated in solutions of weak acids and bases, respectively.
2. To demonstrate the acid-base properties of salts of weak acids and bases.
3. To prove the buffering action of a solution of a weak acid and its salt or of a weak base and its salt.
4. To demonstrate the pH changes occurring in the course of the titration of a weak polyprotic acid with a strong base and how to determine the values for the acid.
5. To demonstrate the connection between the pH of a solution and the color of an acid-base indicator.

This experiment is based on experiments done in general chemistry at the University of Auckland in Auckland, New Zealand. We thank Dr. Sheila Woodgate for sharing this information.

### Introduction to Acids and Bases

#### 1. Acidic and Basic Substances

Acids are molecules or ions that act as proton ( $\text{H}^+$ ) donors. As illustrated in *Figure 1*, the acid can be a neutral molecule, a cation, or an anion. The species that results from the loss of the  $\text{H}^+$  ion by the acid is called its conjugate base. Thus, the conjugate base will always be one unit more negative in its charge than the acid.



Bases are the opposite of acids: bases are proton acceptors. This means that the conjugate acid of a base will be more positively charged than the base.

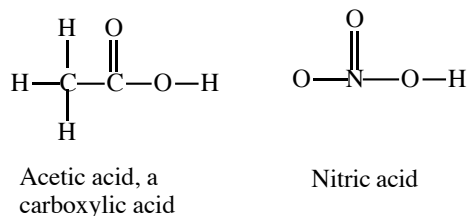
A complete discussion of acid-base chemistry is given in Chapters 17 and 18 of *Chemistry & Chemical Reactivity*.

**NOTE: If you download this experiment from the Net, the double arrows font used for an equilibrium process does not print.**

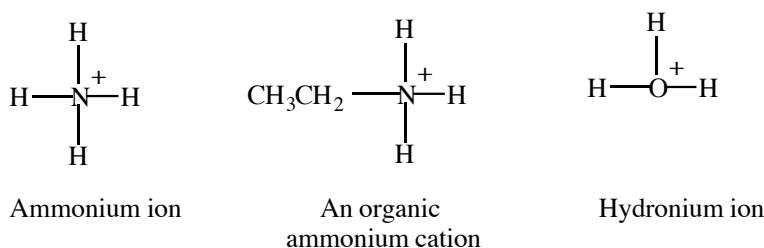
	Neutral Acid		Cationic Acid		Anionic Acid
<b>ACID</b>	$\text{CH}_3\text{CO}_2\text{H}$	$\text{H}_2\text{O}$	$\text{NH}_4^+$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{PO}_4^-$
	acetic acid	water	ammonium ion	hydronium ion	dihydrogen phosphate ion
	$+\text{H}^+ \rightleftharpoons -\text{H}^+$	$+\text{H}^+ \rightleftharpoons -\text{H}^+$	$+\text{H}^+ \rightleftharpoons -\text{H}^+$	$+\text{H}^+ \rightleftharpoons -\text{H}^+$	$+\text{H}^+ \rightleftharpoons -\text{H}^+$
<b>BASE</b>	$\text{CH}_3\text{CO}_2^-$	$\text{OH}^-$	$\text{NH}_3$	$\text{H}_2\text{O}$	$\text{HPO}_4^{2-}$
	acetate ion	hydroxide ion	ammonia	water	hydrogen phosphate ion
	Anionic Base		Neutral Base		Dianion Base

**Figure 1** Some representative acids and bases.

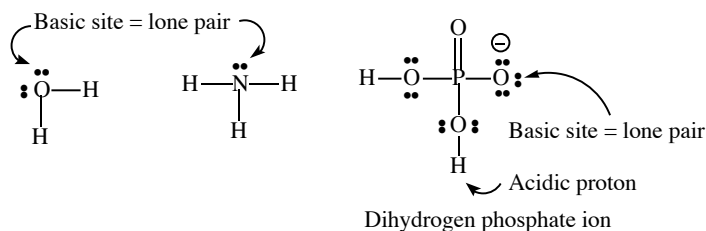
If we expand the view of acids in *Figure 1*, you will notice that the H atom lost as an  $H^+$  ion is often attached to an electronegative atom such as oxygen or a halogen. We can also notice that, in  $-OH$  acids, the  $-OH$  group is often attached to an atom that is also double-bonded to another atom such as O. These observations are true for acids such as acetic acid and nitric acid.



In cationic acids, the acidic hydrogen atom is often bonded to a positively charged nitrogen or oxygen. Indeed, a very common class of cationic acids is represented by ones of the type  $R_3NH^+$ , where R is an organic group and/or an H atom.



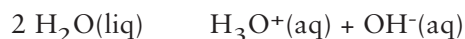
Bases are proton acceptors and so must have one or more lone pairs on the acceptor atom.



Finally, notice that the dihydrogen phosphate ion, for example, can be both an acid and a base. Such substances are called *amphiprotic*. We shall examine its chemistry in Part 4 of this experiment.

## 2. Water as an Acid or Base—Concept of pH

Water can function as an acid or base (*Figure 1*). In pure water an *autoionization* occurs, water molecules interacting to produce equal concentrations of hydronium and hydroxide ions.



Thus, both hydronium and hydroxide ions are present in pure water, though the concentrations are too low to be detected except by the most sensitive electrical conductivity measurements.

Autoionization of water is described on pages 787-788 of *Chemistry & Chemical Reactivity*.

Acids increase the concentration of  $\text{H}_3\text{O}^+$  ions in aqueous solution, and bases increase the  $\text{OH}^-$  concentration. These concentrations are important because they provide an indication of the level of acidity of the solution and reflect the strength of the acid or base.

The concentration of hydronium ion in solution is given by the solution pH, where pH is defined by

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{or} \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

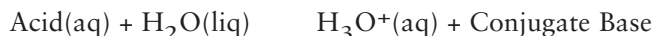
Thus, if the pH of a solution is 4.56, for example, the  $[\text{H}_3\text{O}^+]$  is  $2.8 \times 10^{-5}$  M.

The equilibrium involving water and its ions can be measured using a pH meter equipped with a glass electrode (*Figure 2*). This electrode has a sensitive glass membrane that can exchange protons with the solution. Transfer of charge in the form of protons onto the glass gives rise to a very small electric potential difference, which can be measured by the instrument. The potential is displayed in pH units that vary with the hydronium ion concentration.

The pH scale is described on pages 803-805 of *Chemistry & Chemical Reactivity*.

### 3. Aqueous Solutions of Acids and Bases

Aqueous solutions of acids have a higher concentration of  $\text{H}_3\text{O}^+$  than pure water owing to the reaction



This must mean that the pH of an aqueous solution of an acid is lower than that of pure water.

The pH of the aqueous solutions of two different acids can be used as a measure of the relative strengths of the acids.

- For strong acids the reaction of the acid with water lies completely toward products, the  $\text{H}_3\text{O}^+$  ion and appropriate conjugate base.
- For weak acids the reaction with water is incomplete. (Typical weak acids are <5% ionized.) Thus, the pH of an aqueous solution of a weak acid will be less than that of pure water but greater than if the acid were completely ionized.



A modern digital pH meter.

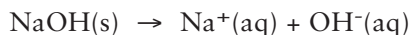


Close-up of a pH probe

**Figure 2** A pH meter with a glass electrode of the type used in General Chemistry. A glass electrode and its functioning is explained in the sidebar on Screen 17.4 of the *Saunders Interactive General Chemistry CD-ROM*.

In general, for equal concentrations of two different acids, the pH of the stronger acid solution will be lower.

Basic substances give rise to solutions having an excess of hydroxide ion, either by dissolving (e.g., NaOH)



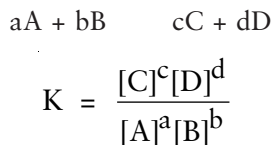
or by reacting with water (e.g.,  $\text{NH}_3$ ).



Because the presence of excess  $\text{OH}^{\text{-}}$  ion in solution means that the  $\text{H}_3\text{O}^{\text{+}}$  concentration must be lower than in pure water, *aqueous solutions of bases will have a pH higher than that of pure water. As the base strength increases, the pH increases.*

#### 4. Equilibrium Constants: $K_a$ and $K_w$

The concentrations of reactants and products for any equilibrium process are related by its equilibrium constant  $K$ . In general, the value of  $K$  is the quotient of the product of the concentrations of the products divided by the product of the concentrations of the reactants. Each concentration is raised to the power of the compound's stoichiometric coefficient in the balanced equation. Thus, for the reaction



The concentrations are given in mol/L.

In the case of a weak acid, we have



$$K_a = \frac{[\text{H}_3\text{O}^{\text{+}}][\text{Conjugate base}]}{[\text{Acid}]}$$

Notice that the concentration of water does not appear in the equilibrium constant expression. Also notice that we have added a subscript  $a$  to the symbol  $K$  to make it clear that this equilibrium constant is for the ionization of a weak acid.

The equilibrium constant  $K_a$  is very useful because it

- allows us to compare directly the relative strengths of acids,
- and enables us to calculate the concentrations of conjugate base and hydronium ion for a given acid concentration.

A useful way to express values of acid ionization constants is as  $\text{p}K_a$ . Just as we can say that  $\text{pH} = -\log [\text{H}_3\text{O}^{\text{+}}]$ , we say that  $\text{p}K_a = -\log K_a$ . In the case of pH, you know that higher values of pH mean a lower concentration of hydronium ion. Similarly, higher values of  $\text{p}K_a$  reflect lower values of  $K_a$ , that is, weaker acids.

Acid ionization constants for weak acids,  $K_w$ , and related topics are discussed in *Chemistry & Chemical Reactivity, Chapter 17. See pages 798-819 in particular.*

	ACID	Acid Ionization Constant, $K_a$	$pK_a$	
<i>Decreasing acid strength</i> ↓	$H_3PO_4$	$7.5 \times 10^{-3}$	3.13	<i>Increasing <math>pK_a</math> value</i> ↓
	□	□		
	$CH_3CO_2H$	$1.8 \times 10^{-5}$	4.75	
	$NH_4^+$	$5.6 \times 10^{-10}$	9.25	

Water can self-ionize to produce both hydronium and hydroxide ions. Its equilibrium constant—designated  $K_w$  for “water ionization constant”—is  $1.01 \times 10^{-14}$  at 25 °C.

$$K_w = 1.01 \times 10^{-14} = [H_3O^+][OH^-]$$

This equation is useful because one can use a measured pH to calculate  $[H_3O^+]$  and then calculate  $[OH^-]$  from the  $K_w$  expression.

## 5. Buffer Solutions

An objective of this experiment is to help you understand buffer solutions. A buffer, which is normally “built” from a weak acid and its conjugate base, resists changes in pH on dilution or on adding another acid or base. Because a buffer contains both a weak acid and its conjugate base, we often write the equilibrium constant expression for the weak acid in the form

$$[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conjugate base}]} K_a$$

This clearly makes the point that the hydronium ion concentration in a buffer solution—and thus its pH—is related to the ratio of weak acid and conjugate base concentrations and to the value of  $K_a$ .

## 6. Titrations

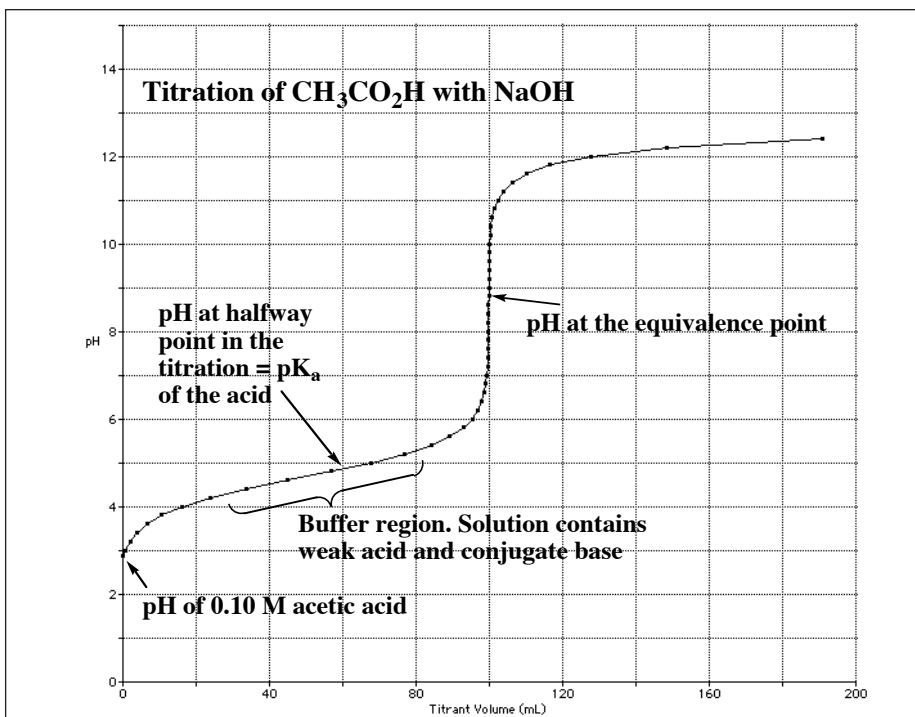
Chemists often use the technique of “titration” to follow quantitatively a reaction of an acid with a base. You performed a titration in General Chemistry I to learn the molar mass of an unknown acid. In this experiment we want to titrate a weak acid with a strong base with the following objectives:

- To observe the changes in pH as the acid is consumed by the base.
- To observe the shape of a typical titration curve—a plot of pH versus volume of base added.
- To determine the  $pK_a$  of the acid (when the acid titrated is a weak acid).
- To observe how the color change of an indicator is related to pH.

The titration curve for the reaction of 100 mL of 0.100 M acetic acid (a weak acid) with 0.100 M NaOH (a strong base) is given in *Figure 3* [and is seen as *Figure 18.6* on page 862 in *Chemistry & Chemical Reactivity*]. There are three important points on this curve.

Buffers are discussed in *Chemistry & Chemical Reactivity*, Section 18.3, pages 851-858.

Titrations are discussed in *Chemistry & Chemical Reactivity*, Section 18.4, pages 858-867. See Section 18.5 (pages 867-868) for a discussion of acid-base indicators.



**Figure 3** Titration curve for the titration of 100 mL of 0.10 M acetic acid (a weak acid) with 0.10 M NaOH (a strong base). See also page 862 of *Chemistry & Chemical Reactivity*.

1. *At the beginning of the titration:*

No NaOH has been added, so we have 100 mL of 0.100 M acetic acid. Calculating the hydronium ion concentration gives  $[\text{H}_3\text{O}^+] = 1.3 \times 10^{-3}$  M.

2. *The halfway point:*

At this point 50 mL of 0.10 M NaOH has been added to the original 100 mL of 0.10 M acetic acid. Therefore, half of the acid has been consumed and converted to conjugate base, and half the acid remains. This is a buffer solution with the ratio of [acid] to [conjugate base] equal to 1. Thus means, then, that  $[\text{H}_3\text{O}^+] = K_a$  or  $\text{pH} = \text{p}K_a$ . This is clearly important as it is a simple way to determine the  $\text{p}K_a$  for a weak acid!

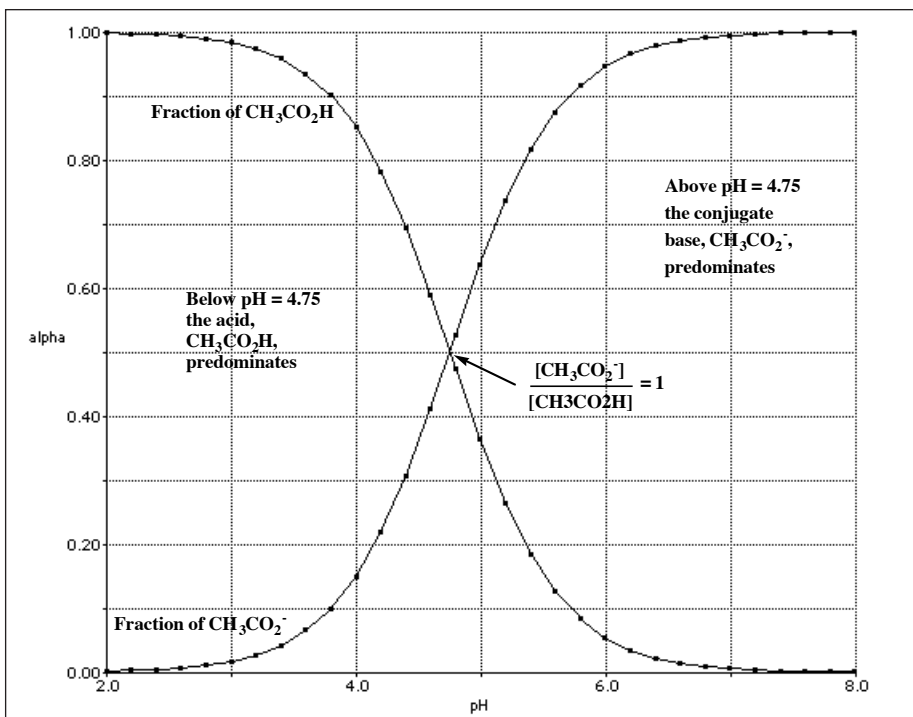
3. *Equivalence point:*

Here the acid has been completely consumed and converted into its conjugate base. Therefore, the pH is greater than 7. The pH can be calculated knowing the conjugate base concentration. See Example 18.2 on page 846 of *Chemistry & Chemical Reactivity*.

At the halfway point in the titration of a weak acid with a strong base, the pH is equal to the  $\text{p}K_a$  of the acid. See pages 861-863 of *Chemistry & Chemical Reactivity*.

Another useful way to look at acid-base reactions is to examine a plot of the relative concentrations of weak acid and conjugate base as a function of pH. In *Figure 4* you see such a plot for acetic acid.

- As the pH increases (say as the acid is titrated with NaOH), the fraction of acid declines and that of the conjugate base,  $\text{CH}_3\text{CO}_2^-$ , increases. The halfway point.
- The point at which the curves cross (and this is where  $[\text{conjugate base}]/[\text{acid}] = 1$ ) is at a pH of 4.74. This is the halfway point in a titration of acetic acid with NaOH.



**Figure 4.** A composition diagram for acetic acid. As the pH increases (the solution becomes more basic) the fraction of acetic acid in solution decreases, and the fraction of the conjugate base (the acetate ion) increases. (The line descending from the left is the fraction of  $\text{CH}_3\text{CO}_2\text{H}$  in the solution. The line ascending from the left is the fraction of  $\text{CH}_3\text{CO}_2^-$  in the solution.) At a pH of 4.75, the concentrations of the acid and conjugate base are equal, and  $\text{pH} = \text{pK}_a$  of the acid. This is the halfway point in a titration of the acid with a strong base.

- As the pH increases (more NaOH is added in the titration), the fraction of acid declines and that of the conjugate base increases.
- The fraction of acid remaining has almost reached zero (and the fraction of conjugate base is approaching 1) at a pH greater than 7. Thus, the pH at the equivalence point must be greater than 7.

In this experiment, you will perform *either* of two possible titrations:

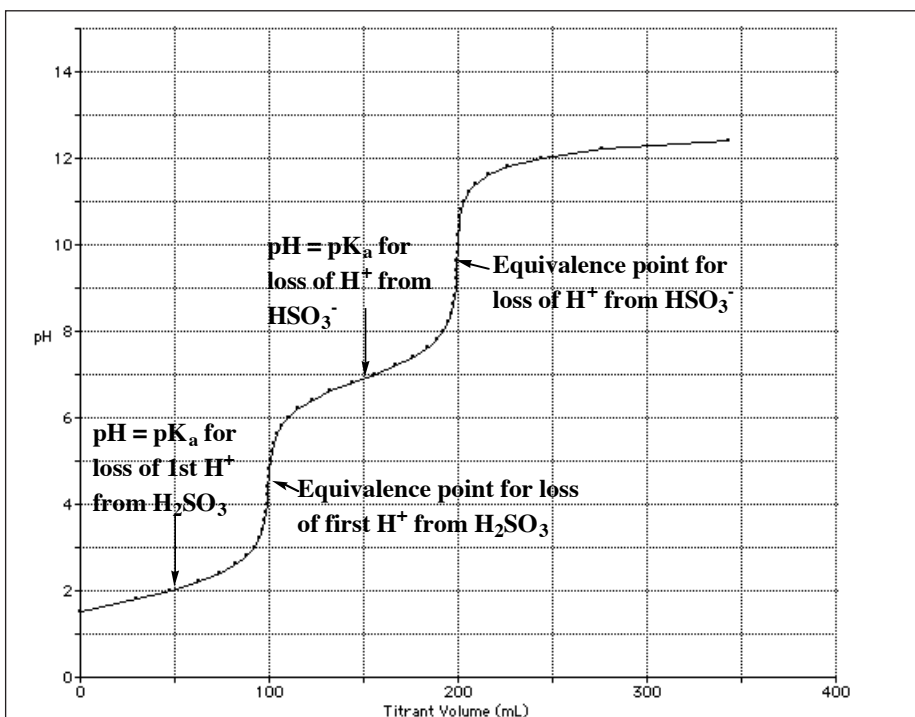
- Titration of a strong acid (HCl) with a strong base (NaOH).
- Titration of a weak acid (phosphoric acid,  $\text{H}_3\text{PO}_4$ ) with the strong base NaOH. In principle, three protons can be titrated.



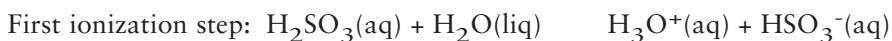
You will see how it turns out in the experiment, but curves for an acid with two protons — sulfurous acid,  $\text{H}_2\text{SO}_3$  — are illustrated in *Figure 5* and *6* as an example.



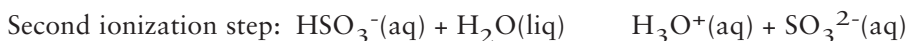
## Titration and Composition Curves for Sulfurous Acid, $\text{H}_2\text{SO}_3$



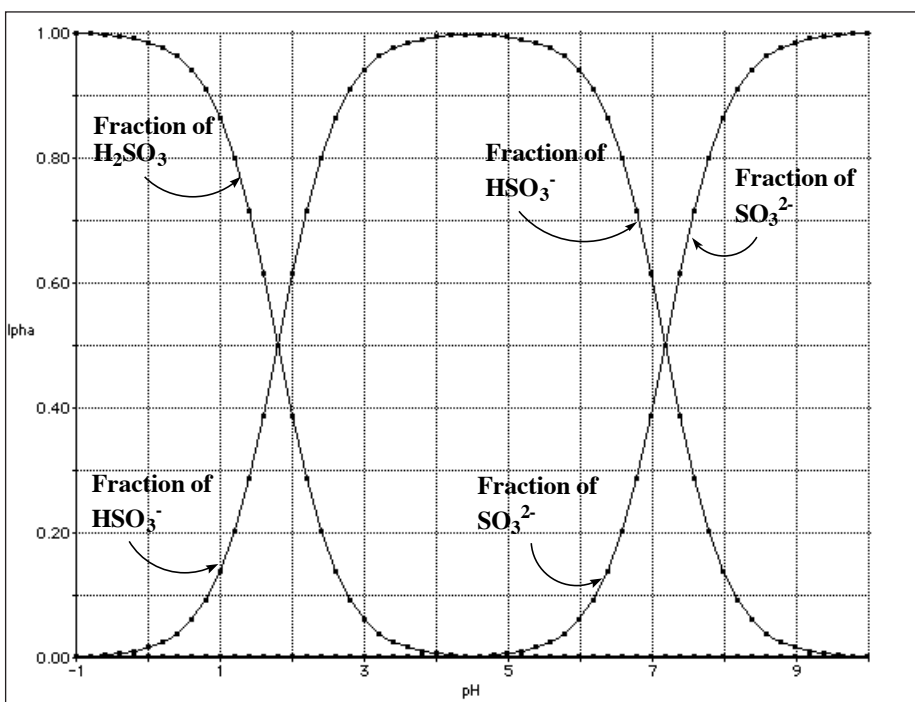
**Figure 5** Titration of 100 mL of 0.10 M  $\text{H}_2\text{SO}_3$  with 0.10 M NaOH. Because  $\text{H}_2\text{SO}_3$  has two titratable  $\text{H}^+$  ions, there are two equivalence points observed. The  $\text{pK}_a$  value for each step can be obtained from the pH at the halfway point.



$\text{pK}_1$  from pH halfway to first equivalence point = 2.0



$\text{pK}_2$  from pH halfway to second equivalence point = 6.9



**Figure 6** Composition diagram for  $\text{H}_2\text{SO}_3$  as a function of pH. At a pH of -1, the predominant species in solution is  $\text{H}_2\text{SO}_3$ . As the pH increases  $\text{HSO}_3^-$  is formed and at a pH of about 2.5, the ratio of  $\text{H}_2\text{SO}_3$  to  $\text{HSO}_3^-$  is 1. At a pH of about 4.5, there is no more  $\text{H}_2\text{SO}_3$  in solution; the acid is now predominantly  $\text{HSO}_3^-$ . As the pH increases still more, the  $\text{HSO}_3^-$  anion disappears and the second  $\text{H}^+$  is removed. At about pH = 9, the solution now contain only  $\text{SO}_3^{2-}$  ion.



# Chemistry of Acids and Bases

## EXPERIMENTAL MEASUREMENTS

### Part 1. Determination of $K_w$

Collect about 10 mL of 0.010 M NaOH in a small beaker. Measure the pH and record the value on *page 12*. Perform the calculations indicated.

This experiment must be performed with a partner. However, each student must do his or her own calculations.

### Part 2. Determination of $K_a$ for the Ammonium Ion, $\text{NH}_4^+$

a) Label 5 test tubes A-E and collect about 15 mL of each of the solutions listed in the table below:

Test Tube	Contents
A	0.10 M ammonium chloride
B	1.0 M ammonium chloride
C	Solution prepared by diluting 100 mL of buffer solution D to 1 L
D	0.50 M $\text{NH}_4\text{Cl}$ in 0.50 M $\text{NH}_3$
E	0.10 M $\text{NH}_3$

b) Measure the pH very carefully of solutions A-E. Record your results in the Table on *page 13* (and again in the Table on *page 15* in the column labeled "Initial pH.")

- Before beginning, and in between measurements, rinse the glass electrode thoroughly with deionized water and then remove any excess water with a clean tissue.
- It is necessary to stir the electrode in the solutions until the meter reading stabilizes.
- You will get better results if you measure the pHs of the solutions in the order listed in the table.

**Retain solutions A-E for the next part of the experiment**

### Part 3. The Ammonium Ion/Ammonia Buffer System

*The directions that follow apply to each of the solutions A-E listed above.*

- Divide solution A equally between two test tubes. Using a pipet, add 1 mL of 0.050 M HCl to one test tube and 1 mL of 0.050 M NaOH to the other test tube.
- Mix well and then measure the pH of each of the solutions after having added the HCl or NaOH.
- Record your results in the Table on *page 15* in the columns immediately to the left and right of the column labeled "Initial pH."

## Part 4. Titration Curves

In this part of the experiment you will perform either of two possible titrations:

a) Titrate a strong acid (HCl) with a strong base (NaOH).

OR

b) Titrate the weak acid  $\text{H}_3\text{PO}_4$  (phosphoric acid) with a strong base, NaOH.

Your objectives are:

- to observe the shape of the titration curve;
- to determine the value of  $K_a$  (and  $\text{p}K_a$ ) for the weak acid (for option *b* only);
- and to observe the relationship between the end point of the titration (the point at which the indicator turns color) and the equivalence point (the point at which the number of moles of  $\text{OH}^-$  supplied by the base is exactly equal to the number of moles of  $\text{H}^+$  supplied by the acid).

### Experimental Directions for the Titration

Working with your partner, follow the directions below.

#### *Student A*

Rinse a clean 100 mL graduated cylinder with a little 0.10 M NaOH solution and then collect about 65 mL of this solution. Rinse your clean buret with about 10 mL of the NaOH solution. Discard the rinse solution before refilling your buret with NaOH solution to above the 0.00 mL mark. Run the solution down to 0.00 mL.

#### *Student B*

You will use two indicators in this titration, and you need to know their color in both acid and base forms. To do this, add about 10 mL of deionized water to four small test tubes, labeled A, B, C, and D.

- To A, add 2 drops 2 M HCl and 2 drops bromcresol green
- To B, add 2 drops 2 M HCl and 2 drops phenolphthalein
- To C, add 2 drops 2 M NaOH and 2 drops bromcresol green
- To D, add 2 drops 2 M NaOH and 2 drops phenolphthalein

Record the observations in the Table on *page 17*.

*Either Student A or B, Depending on Option Chosen*

#### *Option (a): Titrate HCl with NaOH*

Collect 30-35 mL of 0.10 M HCl in a clean, dry 100 mL beaker. Using a 25 mL pipet, which has been rinsed with the acid solution, transfer 25.00 mL of the 0.10 M HCl to a clean 100 mL beaker. Finally, add both bromcresol green (3 drops) and phenolphthalein (3 drops) to this beaker.

#### *Option (b): Titrate $\text{H}_3\text{PO}_4$ with NaOH*

Collect 15 mL of 0.10 M phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in a clean, dry 100 mL beaker. Using a 10 mL pipet, which has been rinsed with the acid solution, transfer 10.00 mL of the 0.10 M  $\text{H}_3\text{PO}_4$  to a clean 100 mL beaker, and add about 15 mL of deionized water. Finally, add both bromcresol green (3 drops) and phenolphthalein (3 drops) to this beaker.

No matter which option is chosen, wash the pH electrode thoroughly with water and place it in the beaker containing the HCl or phosphoric acid solution and indicators. Adjust the buret so its tip is about 1.5 cm above the surface of the acid solution.

*Student A:*

Operate the buret. Add increments of the NaOH solution. Read the actual volume to 2 decimal places, and then carefully stir the solution in the beaker with the pH electrode.

*Student B:*

Record on one copy of the report form the volume of NaOH solution, the pH of the solution (after stirring), and the color of the solution. Plot the results on the graph paper provided.

Your "pH versus volume of NaOH" results should be plotted with the NaOH volume on the x axis and the pH on the vertical or y axis. See Figures 3 and 5.

