

UNIT 2



Acid-Base Equilibria

Unit Outcomes

At the end of this unit, you will be able to:

- understand the Arrhenius, Brønsted-Lowry and Lewis concepts of acids and bases;
- understand the dissociation of water, weak monoprotic and polyprotic acids, and bases;
- know how to solve equilibrium problems involving concentration of reactants and products, K_a , K_b , pH and pOH;
- understand the common-ion effect, buffer solutions, hydrolysis of salts, acid-base indicators and acid-base titrations;
- explain how buffering actions affect our daily lives, using some examples;
- determine the equivalents of acids and base, respectively, that are required to neutralize specific amounts of base and acid;
- predict, in qualitative terms, whether a solution of a specific salt will be acidic, basic or neutral;
- know how to solve problems involving concentration and pH of acid-base titration; and
- describe scientific enquiry skills along this unit: classifying, communicating, asking questions, applying concepts and making generalizations.

MAIN CONTENTS

- 2.1 Acid-Base Concepts
- 2.2 Ionic Equilibrium of Weak Acids and Weak Bases
- 2.3 Common-ion Effect and Buffer Solution
- 2.4 Hydrolysis of Salts
- 2.5 Acid-base Indicators and Titrations
 - *Unit Summary*
 - *Review Exercises*

Experimental Activity

While working with your groups collect a lemon, orange and a piece of soap.

Procedure:

1. Prepare lemon and orange juices and put them in two different test tubes.
2. Put a piece of blue litmus paper in each test tubes. What did you observe? What do you conclude from this test?
3. Take a piece of soap and dissolve it in 10 mL of water. Add a piece of red litmus paper or 2-3 drops of phenolphthalein solution.

What do you observe and what do you conclude from this test?

Acids and bases are important in numerous chemical processes that occur around us. Their importance vary greatly, for example, from industrial processes to biological ones and from reactions in the laboratory to those in our environment. Proteins, enzymes, food products, medicines, blood, genetic material, and other components of living matter contain both acids and bases.

In this unit you will learn three definitions of acids and bases that will allow you to understand ever-increasing numbers of reactions in different phases of life. While dealing with the acids and the basis, you will also be able to apply the principles of chemical equilibrium to this essential group of substances.

After presenting the classical (**Arrhenius**) acid-base definition, we will examine the acid dissociation to see why acids vary in strength. The pH scale is introduced as a means of comparing the acidity or basicity of aqueous solutions. Then, we will notice that the short coming of the Arrhenius theory are overcome by the theory proposed independently by **J.N. Brønsted** in Denmark and **T.M. Lowry** in Great Britain.



Weak acids and weak bases are important weak electrolytes. They are found in many chemical and biological processes of interest. Amino acids, for example, are both weak acids and weak bases. In this unit, we will learn some ways of expressing concentrations of hydronium ions and of hydroxide ions in solutions of weak acids and weak bases. Then you will examine equilibria involving these weak electrolytes. You will also see that the indicators, used in titration, such as phenolphthalein, are weak acids or weak bases. Finally you will learn how to use these properties to select an appropriate indicator for a titration.

2.1 ACID-BASE CONCEPTS

At the end of this subunit, you will be able to:

- define acid by the Arrhenius concept;
- explain why proton exists bounded to water molecules, as H_3O^+ , in all acid-base reactions;
- give examples of Arrhenius acids;
- define base using the Arrhenius concept;
- give examples of Arrhenius bases;
- define acid using the Brønsted-Lowry concept;
- give examples of Brønsted-Lowry acids;
- define base using the Brønsted-Lowry concept;
- give examples of Brønsted-Lowry bases;
- explain what conjugate acids and conjugate bases are;
- identify the acid-base conjugate pairs from a given reaction;
- write an equation for self-ionization of water and ammonia;
- explain what is meant by amphiprotic species;
- give examples of reactions of amphiprotic species;
- define an acid by using Lewis concept;
- give examples of Lewis acids;
- define a base using the Lewis concept;
- give examples of Lewis bases.

Activity 2.1



In grade 10 Chemistry, you have learnt the acid-base concepts. Recall this and discuss the following questions in group. After discussion write a report and present to the class:

1. Explain the concept of acid-base using examples.
2. Which of the concepts is more general?

Biography



Svante August Arrhenius

Svante August Arrhenius (1859-1927), was a Swedish chemist helped lay the foundations of modern chemistry. Born near Uppsala, Sweden, he was educated at the University of Uppsala and received his Ph.D. in 1884. While still a student, he studied the conductive properties of electrolytic (charge-conducting) solutions. In his doctoral thesis, he formulated the theory of electrolytic dissociation.

This theory holds that, in electrolytic solutions, the dissolved chemical compounds in the solution are dissociated into ions, even when there is no current flowing through the solution. Arrhenius also postulated that the degree of dissociation increases as the solution becomes more dilute. This hypothesis later turned out to be significantly true only for weak electrolytes. His theory was initially thought to be completely wrong, and his thesis was given the lowest possible passing grade. Later, however, Arrhenius' theory of electrolytic dissociation became generally accepted, and eventually became one of the cornerstones of modern physical chemistry and electrochemistry.

2.1.1 The Arrhenius Concept of Acids and Bases

Activity 2.2



Form groups and discuss the following questions and write a report of your discussion.

1. Explain Arrhenius acids and bases concepts using suitable examples?
2. Does hydrogen ion exist freely in water?

What are the drawbacks of the Arrhenius' concepts of acids and bases?

The Arrhenius definition of acids and bases has the following limitations.

- * It defines acids and bases in terms of what happens when compounds dissolve in water. However, similar chemistry occurs in many reactions that take place in solvents other than water, and this definition does not work for such reactions.
- * It does not explain why some compounds in which hydrogen has an oxidation number of + 1 (such as HCl) dissolve in water to give acidic solutions, whereas others (such as NH_3) do so.

- * Only the compounds that contain the OH^- ion can be classified as Arrhenius bases. The Arrhenius definition does not explain why compounds such as Na_2CO_3 have basic properties.

Exercise 2.1

Based on their dissociations in water solution, classify each of the following compounds as Arrhenius acid, Arrhenius base, or as a compound that cannot be classified as an Arrhenius acid or Arrhenius base.

- a $\text{H}_3\text{PO}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 b $\text{NaCl}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 c $\text{Ca}(\text{OH})_2 + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
 d $\text{NH}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

2.1.2 Brønsted-Lowry Concept of Acids and Bases

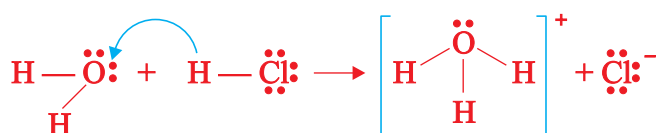
Activity 2.3



From what you have learnt in Grade 10 Chemistry discuss the following questions.

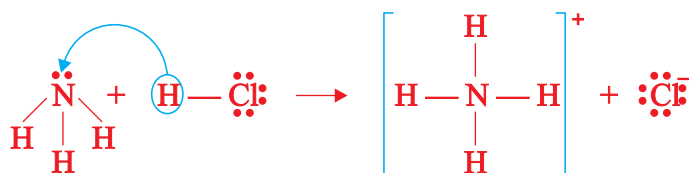
1. What are acids and bases according to Brønsted-Lowry concept?
2. How does it differ from Arrhenius definition? What are the similarities?
3. Give two Brønsted-Lowry bases that are not Arrhenius bases.
4. Are there any Brønsted acids that do not behave as Arrhenius acids?

Consider the ionization of hydrochloric acid in water:

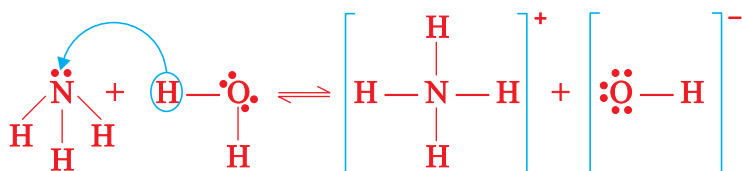


Which one is a Brønsted-Lowry acid and which one is a Brønsted-Lowry base?

The Brønsted-Lowry concept is not limited to reactions in aqueous solution. For example, HCl is an acid in liquid ammonia, $\text{NH}_3(\text{l})$, just as it is in water.



The Brønsted-Lowry concept successfully explains how ammonia acts as a base in water, which the Arrhenius definition fails to do. In the ionization of ammonia, NH_3 , water is the acid. The ionization of ammonia in water is a reversible reaction. This reversible acid-base reaction can be written as:



Once an acid has given up a proton, the remaining part can be a proton acceptor and is, now called a **conjugate base**. On the other hand, when a base accepts a proton, the species formed is called **conjugate acid**.

Every acid has a conjugate base, and every base has a conjugate acid. Thus, for any conjugate acid-base pair:

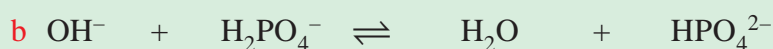
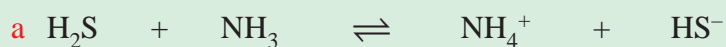
- The conjugate base has one less H and one more minus charge than the acid.
- The conjugate acid has one more H and one less minus charge than the base.

Table 2.1 The conjugate pairs in some Acid-Base Reactions.

Acid	+	Base	\rightleftharpoons	Conjugate base	+	Conjugate acid
HF	+	H_2O	\rightleftharpoons	F^-	+	H_3O^+
HCOOH	+	CN^-	\rightleftharpoons	HCOO^-	+	HCN
NH_4^+	+	CO_3^{2-}	\rightleftharpoons	NH_3	+	HCO_3^-
H_2PO_4^-	+	OH^-	\rightleftharpoons	HPO_4^{2-}	+	H_2O
H_2SO_4	+	N_2H_5^+	\rightleftharpoons	HSO_4^-	+	$\text{N}_2\text{H}_6^{2+}$
HPO_4^{2-}	+	SO_3^{2-}	\rightleftharpoons	PO_4^{3-}	+	HSO_3^-

Example 2.1

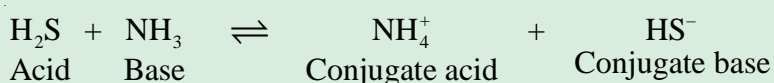
Identify the Brønsted-Lowry acids and bases and their respective conjugates in each of the following reactions.



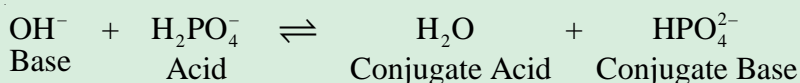
Solution:

To identify Brønsted-Lowry acids and bases, we look for the proton donors and proton-acceptors in each reaction.

a H_2S is converted to HS^- by donating a proton. So, H_2S is an acid, and HS^- is its conjugate base. NH_3 accepts the proton lost by the H_2S . As a result, NH_3 is a base, and NH_4^+ is its conjugate acid.



b OH^- accepts a proton from H_2PO_4^- . Therefore, OH^- is a base and H_2O is its conjugate acid. H_2PO_4^- donates a proton to OH^- . Thus, H_2PO_4^- is an acid, and HPO_4^{2-} is its conjugate base.

**Exercise 2.2**

Identify the Brønsted-Lowry acids, bases, conjugate acids and conjugate bases in each of the following reactions.

- a** $\text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{NH}_4^+ + \text{CO}_3^{2-}$
- b** $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$
- c** $\text{H}_2\text{O} + \text{SO}_3^{2-} \rightleftharpoons \text{OH}^- + \text{HSO}_3^-$
- d** $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$

Strengths of Conjugate Acid-Base Pairs

The stronger the acid, the weaker is its conjugate base. Similarly, the stronger the base, the weaker is its conjugate acid. For example, HCl is a strong acid, and its conjugate base Cl^- , is a weak base. Acetic acid, CH_3COOH , is a weak acid, and its conjugate base, CH_3COO^- , is a strong base. The following chart shows the strength of conjugate acid-base pairs .



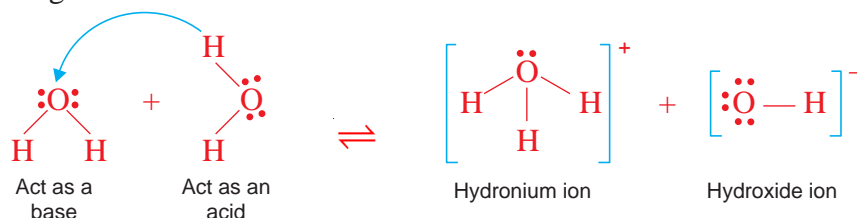
	Strong	Acid $\left\{ \begin{array}{l} \text{HCl} \\ \text{H}_2\text{SO}_4 \\ \text{HNO}_3 \\ \text{H}_3\text{O}^+ \end{array} \right.$	Base $\left\{ \begin{array}{l} \text{Cl}^- \\ \text{HSO}_4^- \\ \text{NO}_3^- \\ \text{H}_2\text{O} \end{array} \right.$	Negligible
	Weak	$\left\{ \begin{array}{l} \text{HSO}_4^- \\ \text{H}_2\text{SO}_3 \\ \text{H}_3\text{PO}_4 \\ \text{HF} \\ \text{CH}_3\text{COOH} \\ \text{H}_2\text{CO}_3 \\ \text{H}_2\text{S} \\ \text{HSO}_3^- \\ \text{H}_2\text{PO}_4^- \\ \text{HCN} \\ \text{NH}_4^+ \\ \text{HCO}_3^- \end{array} \right.$	$\left\{ \begin{array}{l} \text{SO}_4^{2-} \\ \text{HSO}_3^- \\ \text{H}_2\text{PO}_4^- \\ \text{F}^- \\ \text{CH}_3\text{COO}^- \\ \text{HCO}_3^- \\ \text{HS}^- \\ \text{SO}_3^{2-} \\ \text{HPO}_4^{2-} \\ \text{CN}^- \\ \text{NH}_3 \\ \text{CO}_3^{2-} \end{array} \right.$	Weak
	Negligible	$\left\{ \begin{array}{l} \text{HPO}_4^{2-} \\ \text{H}_2\text{O} \\ \text{HS}^- \\ \text{OH}^- \end{array} \right.$	$\left\{ \begin{array}{l} \text{PO}_4^{3-} \\ \text{OH}^- \\ \text{S}^{2-} \\ \text{O}^{2-} \end{array} \right.$	Strong
				

Chart 1.1 Strengths of Conjugate Acid-Base Pairs.

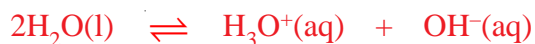
Auto-ionisation of Substances

Name the ions present in water. How are they formed?

The auto-ionisation (self-ionization) of a substance involves the transfer of a proton from one molecule of the substance to another molecule of the same substance. For example, water undergoes auto-ionisation as shown below:



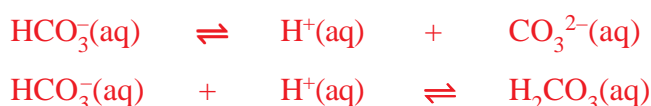
This can be represented by the following equation:



Note that, in this reaction, some water molecules behave as acids, donating protons, while the other water molecules behave as bases, accepting protons.

Amphiprotic Species

Many molecules and ions gain or lose a proton, under appropriate conditions. Such species are said to be **amphiprotic**. For example,



In other words, amphiprotic species are species that can act as both an acid and a base. *Can you suggest more examples of amphiprotic species?*

Exercise 2.3

- Define each of the following terms and give examples for each.
 - autoionization
 - amphiprotic species
- Identify the amphiprotic species in each of the following reactions.
 - $$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{H}_2\text{PO}_4^-(\text{aq})$$

$$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$$
 - $$\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$$

$$\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
- Which of the two is the stronger base? Give your reason.
 - HPO_4^{2-} or PO_4^{3-}
 - HS^- or S^{2-}
 - CO_3^{2-} or HCO_3^-
- What is the weakness of the Brønsted-Lowry acids and bases theory?
- Write the self-ionization of water and ammonia.

2.1.3 Lewis Concept of Acids and Bases

Activity 2.4

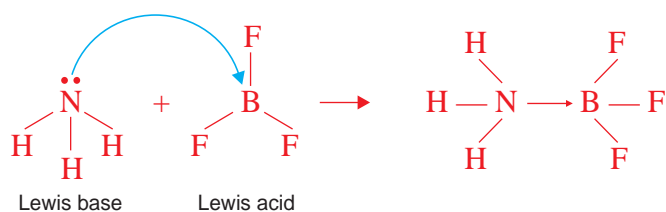


Form groups and discuss the following and report the result of your discussion to your teacher.

- Explain Lewis concept of acids and bases.
- How do Lewis acids and bases differ from Brønsted-Lowry acids and bases?

- Are all Brønsted-Lowry acids and bases also acids and bases according to Lewis concept?
- Is there any limitation to the Brønsted-Lowry definition of acids and bases? Explain if any.

The Lewis acid-base concept includes many reactions that do not involve proton-transfer reactions. Consider, for example, the reaction between boron trifluoride (BF_3) and ammonia to form a compound, $\text{BF}_3 \leftarrow \text{:NH}_3$.



The boron atom in boron trifluoride, BF_3 , has only six electrons in its valence shell and needs two electrons to satisfy the octet rule. Consequently, BF_3 (*Lewis acid*) accepts a pair of electrons from NH_3 (*Lewis base*).

This example suggests that in a Lewis acid-base reaction, we should look for:

- a species that has an available empty orbital to accommodate an electron pair such as the B atom in BF_3 , and
- a species that has lone-pair electrons such as NH_3 .

The Lewis definition allows us to consider typical Brønsted-Lowry bases, such as OH^- , NH_3 , and H_2O , as Lewis bases. They all have electron pairs available to donate for electron-deficient species.

Note that any molecule or negatively charged species having an excess of electrons can be considered as a Lewis base, and any electron-deficient molecule or positively charged species can be considered as a Lewis acid.

Exercise 2.4

Identify Lewis acids and Lewis bases in each of the following reactions.

- $\text{SiCl}_4 + 2\text{Cl}^- \rightarrow [\text{SiCl}_6]^{2-}$
- $\text{PF}_5 + \text{F}^- \rightarrow [\text{PF}_6]^-$
- $\text{Cu}^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$
- $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$
- $\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4$



2.2 IONIC EQUILIBRIA OF WEAK ACIDS AND BASES

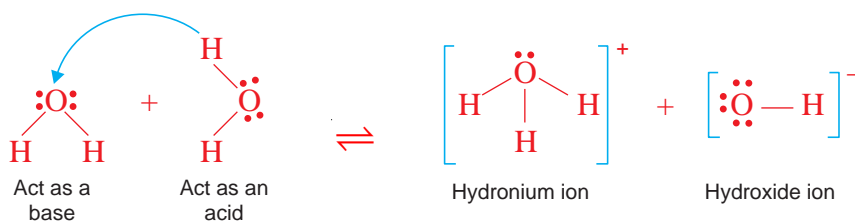
At the end of this subunit, you will be able to:

- describe the ionization of water;
- derive the expression of ion product for water, K_w ;
- explain the effect of temperature on K_w ;
- explain why water is a weak electrolyte;
- use K_w to calculate $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ in aqueous solution;
- define pH;
- define pOH;
- explain the relationship between pH and pOH;
- calculate pH from $[\text{H}^+]$ and $[\text{H}^+]$ from pH;
- calculate pOH from $[\text{OH}^-]$ and $[\text{OH}^-]$ from pOH;
- write an expression for the percent ionization of weak acids or weak bases;
- calculate the percent dissociation of weak acids and bases;
- write the expression for the acid-dissociation constant, K_a ;
- calculate K_a for an acid from the concentration of a given solution and its pH;
- calculate $[\text{H}^+]$ and pH of an acidic solution from given values of K_a and the initial concentration of the solution;
- write the expression for the base-dissociation constant, K_b ;
- calculate K_b for a base from the concentration of a basic solution and its pOH; and
- calculate the $[\text{OH}^-]$ and pOH of a basic solution from a given value of K_b and the initial concentration of the solution.

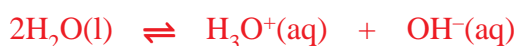
2.2.1 Ionization of Water

How do you calculate the concentration of H_3O^+ ions if the concentrations of OH^- ions and K_w , at 25°C are given?

Recall that water is amphoteric. So, to a slight extent, water molecules can transfer protons among themselves. In the self-ionization of water, the proton lost by one water molecule is gained by the other.



The self-ionization of water can be represented by the following equation:



Since this reaction is reversible, we can apply the law of mass action to write the equilibrium constant expression.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \text{where, } K_c \text{ is the equilibrium constant, in terms of concentration.}$$

Because only very small fractions of water molecules are ionized, the concentration of water, $[\text{H}_2\text{O}]$, remains unchanged. This equilibrium expression can be simplified by including the constant $[\text{H}_2\text{O}]^2$ term with the value of K_c to obtain a new equilibrium constant, the ion-product for water, K_w .

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

Note that K_w is the product of the molar concentrations of H_3O^+ and OH^- ions at a particular temperature.

Since we use $\text{H}^+(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

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

In pure water at 25°C , the concentrations of H^+ and OH^- ions are equal and found to be $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$ and $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ at 25°C ,

$$K_w = [\text{H}^+][\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

As you have learned in your studies of chemical equilibrium in Grade 11, the value of K_c , in this case K_w , changes as temperature changes. In any aqueous solution at 25°C , no matter what it contains, the product of $[\text{H}^+]$ and $[\text{OH}^-]$ must always equal 1.0×10^{-14} . There are three possible situations.

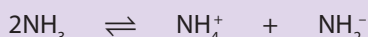
- A neutral solution, where $[\text{H}^+] = [\text{OH}^-]$.
- An acidic solution, where $[\text{H}^+] > [\text{OH}^-]$.
- A basic solution, where $[\text{OH}^-] > [\text{H}^+]$.

Activity 2.5



Form groups and discuss the following. Write a report on the discussion and present to the class.

Many substances undergo auto-ionization in analogous to water. For example, the auto-ionization of liquid ammonia is:



- Write a K_c expression for auto-ionization of ammonia that is analogous to the K_w expression for water.
- Name the strongest acids and strongest bases that can exist in liquid ammonia?
- For water, a solution with $[\text{OH}^-] < [\text{H}_3\text{O}^+]$ is acidic. What are the analogous relationships in liquid ammonia?

Exercise 2.5

- Calculate $[\text{H}^+]$ or $[\text{OH}^-]$, as required, for each of the following solutions at 25°C , and state whether the solution is neutral, acidic, or basic.
 - $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$
 - $[\text{OH}^-] = 1.0 \times 10^{-8} \text{ M}$
 - $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$
- Calculate the concentration of OH^- in a solution in which
 - $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-5} \text{ M}$
 - $[\text{H}_3\text{O}^+] = [\text{OH}^-]$
 - $[\text{H}_3\text{O}^+] = 10^2 \times [\text{OH}^-]$
- Calculate $[\text{H}_3\text{O}^+]$ in a solution that is at 25°C and has $[\text{OH}^-] = 6.7 \times 10^{-2} \text{ M}$. Is the solution neutral, acidic, or basic?
- At 40°C , the value of K_w is 2.92×10^{-14} . Calculate the $[\text{H}^+]$ and $[\text{OH}^-]$ of pure water at 40°C .
- Why water is a weak electrolyte?

The pH scale

The concentration of H^+ in aqueous solution is usually very small and inconvenient to express and to draw as graphs. **Sören Sörensen**, in 1909, developed the pH scale to solve this problem. The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L):

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

Note that the negative logarithm gives us positive numbers for pH. *What is the pH value of a neutral, basic and acidic solution?*

A pH-meter (Figure 2.1) is used to measure the pH of a solution.



Figure 2.1 pH-meter.

Activity 2.6



In your group, measure the pH of the following substances, using a pH-meter. Copy and fill in the following table. Compare your results with those of other groups. Find the pH values of the substances in reference books and other sources and compare your results with the values you observed.

Substance	pH	Acidic, Basic or Neutral
Beer		
Milk of Magnesia		
Tomato juice		
Lemon juice		
Human saliva		
Drinking water		

pH decreases as the concentration of H^+ ions increases; in other words, the more acidic the solution, the lower its pH; the more basic the solution, the higher its pH.

The pH notation has been extended to other exponential quantities. For example, hydroxide concentrations can be expressed in terms of pOH, where $pOH = -\log [OH^-]$. Similarly, pK_w can be expressed as $-\log K_w$.

Activity 2.7



Derive the relationship, $pH + pOH = pK_w = 14$ at $25^\circ C$.

Example 2.2

Calculate the pH of a basic solution, in which $[OH^-] = 2.0 \times 10^{-3}$ at $25^\circ C$.

Solution:

From the given $[OH^-]$, we can determine $[H^+]$, using the relation

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ M}$$

$$pH = -\log (5.0 \times 10^{-12}) = 11.30$$

Example 2.3

Calculate:

- the pH and pOH of a juice solution in which $[H_3O^+]$ is 5.0×10^{-3} M
- the $[H_3O^+]$ and $[OH^-]$ of human blood at $pH = 7.40$

Solution:

a Given:

$$[H_3O^+] = 5.0 \times 10^{-3} \text{ M}$$

$$\begin{aligned} pH &= -\log[H_3O^+] = -\log (5.0 \times 10^{-3}) \\ &= 3 - \log 5.0 = 2.3 \end{aligned}$$

$$pH + pOH = 14$$

$$pOH = 14 - pH = 14 - 2.3 = 11.7$$

Required:

$$pH = ? \text{ and } pOH = ?$$

$$\text{b } \text{pH} = 7.40, \quad [\text{H}_3\text{O}^+] = ? \qquad [\text{OH}^-] = ?$$

$$-\log [\text{H}_3\text{O}^+] = 7.40$$

$$\log [\text{H}_3\text{O}^+] = -7.40$$

$$[\text{H}_3\text{O}^+] = 10^{-7.40}$$

$$= 4.0 \times 10^{-8} \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-8}} = 2.5 \times 10^{-7} \text{ M}$$

Exercise 2.6

1. A solution formed by dissolving an antacid tablet has a pH of 9.18 at 25°C. Calculate $[\text{H}^+]$, $[\text{OH}^-]$ and pOH.
2. A solution is prepared by diluting concentrated HNO_3 to 2.0 M, 0.30 M and 0.0063 M HNO_3 at 25°C. Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH and pOH of the three solutions.

2.2.2 Measures of the Strengths of Acids and Bases in Aqueous Solution

The strength of acids and bases can be described in many ways. Some of the ways are the concentration of hydrogen and hydroxide ions, **pH** and **pOH**, percent dissociation, K_a and K_b .

1. Concentration of hydrogen and hydroxide ions

Acid strength refers to the ability of an acid to release protons. A strong acid gives up protons more easily than a weak acid. For two acids of equal concentrations, the strongest acid produces the greater quantity of hydrogen ions. Base strength refers to the ability of a base to accept protons. A strong base accepts more protons readily than a weak base. A solution of a stronger base will contain a larger concentration of hydroxide ions than a solution of a weaker base if both solutions are of equal concentration.

Activity 2.8



In unit two of Grade 10 Chemistry, you learned about the strength of acids and bases. By referring to this text book and other chemistry books, list strong acids, strong bases, weak acids and weak bases. Then discuss what you have written with the rest of the class.

2. pH and pOH

If the pOH of a solution at 25°C is 12, is it acidic, neutral or basic?

It is possible to predict the strength of acids from their pH values. The smaller the pH value, the stronger the acid. The concentration of hydroxide ions in a solution can be expressed in terms of the pOH of the solution. Hence, the strength of bases can also be determined from their pOH values. The smaller the pOH value, the stronger the base.

3. Percent Ionization

How do you determine the percent ionization of an acid or a base?

The extent to which an acid or base ionizes is called **percent ionization**. Mathematically,

$$\text{Percent ionization} = \frac{\text{Ionized acid or base concentration at equilibrium}}{\text{Initial concentration of ionized acid or base}} \times 100$$

The strength of an acid depends on the percentage of the acid molecules that dissociate in water solution. If a higher percentage of the original acid molecules dissociate, then the acid is a strong acid. Strong acids and strong bases ionize nearly completely in water. However, weak acids and weak bases dissociate partially in water, and their percent of ionization is small.

4. Dissociation (Ionization) Constants

Acid Dissociation Constant, K_a

What is the relationship between strength of acids with their acid-dissociation constant values?

The acid-dissociation constant is a quantitative measure of the strength of the acid in a given solvent. For the dissociation of the acid, HA;



the dissociation-constant expression can be written as:

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]}$$

Since the concentration of water is nearly constant, we can write;

$$K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The product of the two constants, K and $[\text{H}_2\text{O}]$, is itself a constant. It is designated as K_a , which is the acid-dissociation constant or the acid-ionization constant. Hence for a weak acid, HA:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The K_a value for a strong acid is very large, because $[\text{HA}]$ in the denominator is very small since the acid dissociates essentially completely. Similarly, the K_a value for a weak acid is relatively small, since $[\text{H}_3\text{O}^+]$ and $[\text{A}^-]$ are very small, and $[\text{HA}]$ in the denominator is large. The ionization-constants of some weak monoprotic acids are tabulated in Table 2.2.

Table 2.2 Ionization constant of some weak monoprotic acids at 25°C.

Name of the Acid	Formula	K_a
Acetic acid	CH_3COOH	1.8×10^{-5}
Ascorbic acid	$\text{C}_6\text{H}_8\text{O}_6$	8.0×10^{-5}
Benzoic Acid	$\text{C}_6\text{H}_5\text{COOH}$	6.5×10^{-5}
Formic acid	HCOOH	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hypobromous acid	HOBr	2.5×10^{-9}
Hypochlorous acid	HOCl	3.0×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}

How do you calculate the pH of weak acids?

Generally, we can calculate the hydrogen-ion concentration or pH of an acid solution at equilibrium, given the initial concentration of the acid and its K_a value. Alternatively, if we know the pH of a weak acid solution and its initial concentration, we can determine its K_a .

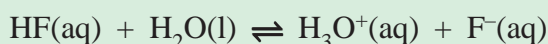
The following may help you to solve weak-acid dissociation problems.

1. identify the major species that can affect the pH of the solution. In most cases we can ignore the dissociation of water. Why?
2. write balanced equations for the reactions producing H_3O^+ .
3. list the initial concentration of the species participating in the equilibrium.
4. define the change needed to achieve equilibrium. That is, define x .
5. write the equilibrium concentration, in terms of x .
6. write the acid dissociation constant, K_a , in terms of equilibrium concentration.

7. first solve for x by the approximation method. If the approximation is not valid, use the quadratic equation.
8. having solved for x , calculate the equilibrium concentrations of all species and/or the pH of the solution.

Example 2.4

Calculate the pH of a 0.50 M HF solution at 25°C. The ionization of HF is given by



Solution:

The species that can affect the pH of the solution are HF, and the conjugate base F^- . Let x be the equilibrium concentration of H_3O^+ and F^- ions in molarity (M). Thus,



Initial, M	0.50	0.00	0.00
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(0.50 - x)$	x	x

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

Substituting the concentration of HF, H^+ and F^- , in terms of x , gives:

$$K_a = \frac{(x)(x)}{0.50 - x} = 6.8 \times 10^{-4}$$

Rearranging this expression provides:

$$x^2 + 6.8 \times 10^{-4}x - 3.4 \times 10^{-4} = 0$$

This is a quadratic equation that can be solved, using the quadratic formula, or you can use the approximation method for x . Because HF is a weak acid, and weak acids ionize only to a slight extent, x must be small compared to 0.50. Therefore, you can make this approximation:

$$0.50 - x \approx 0.50$$

Now, the ionization constant expression becomes

$$\frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} = 6.8 \times 10^{-4}$$

Rearranging this equation gives:

$$x^2 = (0.5)(6.8 \times 10^{-4}) = 3.4 \times 10^{-4}$$

$$x = \sqrt{3.4 \times 10^{-4}} = 1.8 \times 10^{-2} \text{ M}$$

Thus, we have solved for x without using the quadratic equation. At equilibrium, we have

$$[\text{HF}] = (0.50 - 0.018) \text{ M} = 0.48 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.018 \text{ M}$$

$$[\text{F}^-] = 0.018 \text{ M}$$

and the pH of the solution is

$$\text{pH} = -\log(0.018) = 1.74$$

How good is this approximation? Because K_a values for weak acids are generally known to an accuracy of only $\pm 5\%$, it is reasonable to require x to be less than 5% of 0.50, the number from which it is subtracted. In other words, the approximation is valid if the percent ionization is equal to or less than 5%.

$$\frac{0.018}{0.50} \times 100\% = 3.6\% \quad \text{Is the approximation valid?}$$

Exercise 2.7

For a 0.036 M HNO_2 solution.

- Write a chemical equation that shows the ionization of nitrous acid in water.
- Calculate the equilibrium concentration of hydrogen ions and nitrous acid at 25°C , using the approximation method. Then check whether the approximation is valid or not.
- If the approximation is invalid, use the quadratic formula to calculate the concentration of hydrogen ions.
- Calculate the pH of the solution.

Base dissociation constant, K_b

In the same way as for acids, the dissociation of a base in water can be written as



which gives the equilibrium expression of the form:

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

where K_b is the base dissociation constant. K_b values for strong bases are large, while K_b values for weak bases are small. Table 2.3 shows the K_b values of some common weak bases at 25°C.

Table 2.3 Values of K_b for some Common Weak Bases at 25°C.

Base	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	4.0×10^{-10}
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	4.7×10^{-4}
Hydrazine	N_2H_4	1.7×10^{-6}
Hydroxylamine	NH_2OH	1.1×10^{-6}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	1.7×10^{-9}

In solving problems involving weak bases, you should follow the same guidelines as you followed for weak acids. The main difference is that we calculate $[\text{OH}^-]$ first, instead of $[\text{H}^+]$.

Exercise 2.8

For a 0.040 M ammonia solution:

- Write a chemical equation that shows the ionization of ammonia in water.
- Calculate the equilibrium concentration of ammonia, ammonium ions and hydroxide ions, using the approximation method. Check whether the approximation is valid or not.
- If the approximation is invalid, use the quadratic formula to calculate the concentration of ammonia, ammonium ions and hydroxide ions.
- Calculate the pOH and pH of the solution.

2.3 COMMON ION EFFECT AND BUFFER SOLUTION

At the end of this subunit, you will be able to:

- define the common-ion effect;
- explain the importance of the common-ion effect;
- define buffer solution;
- give some common examples of buffer systems;
- explain the action of buffer solutions and its importance in chemical processes;
- calculate the pH of a given buffer solution; and
- demonstrate the buffer action of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$.

2.3.1 The Common ion Effect

Activity 2.9



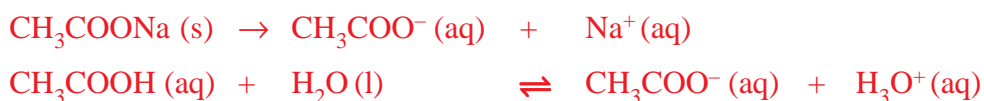
In Grade 11 Chemistry, you learned **Le Chatelier's** principle. Make a group and discuss the following and present your report to the class.

Industrially, ammonia is produced by the Haber process.

- Write a chemical equation for the production of ammonia in the process.
- Assume that the reaction is at equilibrium. What is the effect of
 - adding more ammonia to the equilibrium system?
 - removing ammonia from the equilibrium system?
 - adding more hydrogen gas to the equilibrium system?
 - decreasing the concentration of both hydrogen and nitrogen gases from the equilibrium system?
 - increasing temperature?
 - decreasing pressure?
 - adding finely divided iron as a catalyst?

The common-ion effect is caused by the addition of a compound having an ion in common with the dissolved substance that shift the equilibrium.

The presence of the common ion suppresses the ionization of a weak acid or a weak base. For example, if sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions.



Sodium acetate, CH_3COONa , is a strong electrolyte, so it dissociates completely in solution, but acetic acid, CH_3COOH , is a weak acid and ionizes partially. According to **Le Chatelier's** principle, the addition of CH_3COO^- ions from CH_3COONa to a solution of CH_3COOH will suppress the ionization of CH_3COOH and decrease the concentration of hydrogen ions.

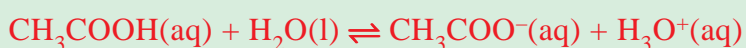
Therefore, a solution containing both CH_3COOH and CH_3COONa will be less acidic than a solution containing only CH_3COOH of the same concentration. The shift in equilibrium of the acetic acid ionization is caused by the acetate ions from the sodium acetate. CH_3COO^- is the common ion because it is supplied by both CH_3COOH and CH_3COONa .

Example 2.5

Determine the $[\text{H}_3\text{O}^+]$ and $[\text{CH}_3\text{COO}^-]$ in a solution that is 0.10 M in both CH_3COOH and HCl .

Solution:

0.10 M HCl ionizes completely to form 0.10 M H_3O^+ and 0.10 M Cl^- ions. The Cl^- ion is a spectator ion, and it has no influence on the concentrations of CH_3COO^- and H_3O^+ .



Initial, M	0.10	0.00	0.10
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(0.10 - x)$	x	$0.10 + x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.10 + x)(x)}{0.10 - x}$$

$$1.8 \times 10^{-5} = \frac{x(1.00 + x)}{1.00 - x}$$

If x is very small, you can approximate $(1.00 - x)$ and $(1.00 + x)$ to 1.00.

$$1.8 \times 10^{-5} = \frac{x(\cancel{1.00})}{(\cancel{1.00})}$$

$$x = [\text{H}_3\text{O}^+] = 10^{-5} \text{ M}$$

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

$$= -\log (18 \times 10^{-5}) = 4.74$$

Exercise 2.9

- Calculate the pH of a solution containing 0.20 M CH_3COOH and 0.30 M CH_3COONa .
- What would be the pH of a 0.20 M CH_3COOH solution if no salt were present?

2.3.2 Buffer Solutions

How does a buffer solution resist a pH change?

A buffer solution is a solution that resists changes in pH from the addition of a limited amount of an acid or a base. Table 2.4 shows how the pH of unbuffered and buffered solutions change when a small amount of acid or base is added.

Table 2.4 Comparison of buffered and unbuffered solutions.

	Initial pH of 1.0 L sample	pH after addition of 0.010 mol NaOH	pH after addition of 0.010 mol HCl
Unbuffered solution: 1.28×10^{-5} M HCl	4.8	12.0	2.0
Buffered solution: 0.099 M CH_3COOH 0.097 M CH_3COONa	4.8	4.8	4.7

Buffers contain either a weak acid and its conjugate base or a weak base and its conjugate acid.

A buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that are added to it. Similarly, it must contain a relatively large concentration of base to react with any H^+ ions. To understand the action of buffer, consider a buffer that contains approximately equal molar amounts of a weak acid, HA, and its conjugate base, A^- . When a strong acid is added to the buffer, it supplies hydrogen ions that react with the base A^- .



On the other hand, when a strong base is added to the buffer, it supplies hydroxide ions that react with the acid, HA.



Thus, a buffer solution resists changes in pH through its ability to combine with the H^+ and OH^- ions.

Buffers are very important to chemical and biological systems. The pH in the human body varies greatly from one fluid to another. For example; the pH of blood is about 7.4, whereas the gastric juice in our stomach has a pH of about 1.5. The pH values, which are crucial for proper enzyme function and the balance of osmotic pressure, are maintained by buffers in most cases.

Activity 2.10



By reading references or using other sources, write a report on the buffer system in human blood. Discuss the report with the rest of the class.

Example 2.6

1. Calculate the pH of a buffer system containing 1.0 M CH_3COOH and 1.0 M CH_3COONa .
2. What is the pH of the buffer system in (1) after the addition of 0.10 mol of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when HCl is added.

Solution:

1. In this case, you are asked to calculate the pH of the buffer system of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ before adding HCl. Hence, you can apply the same method you have used to calculate a solution containing common ions:

	$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
Initial, M	1.0 0 1.0
Change, M	$-x$ $+x$ $+x$
Equilibrium, M	$(1.0 - x)$ x $(1.0 + x)$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(1.0 + x)}{1.0 - x} = 1.8 \times 10^{-5}$$

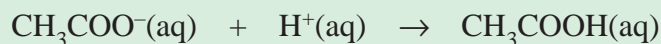
Assuming $1.0 + x \approx 1.0$ and $1.0 - x \approx 1.0$, we obtain

$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)} = \frac{x(1.0)}{1.0}$$

$$x = [\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

2. The H^+ ions provided by the strong acid, HCl, react completely with the conjugate base of the buffer, which is CH_3COO^- .



The moles of H^+ ions added = 0.10 mol.

The moles of acetate ions before HCl is added = $1.0 \text{ M} \times 1 \text{ L} = 1.0 \text{ mol}$.

0.10 mol H^+ consumes 0.10 mol CH_3COO^- .

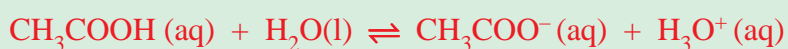
Therefore, the number of moles of CH_3COO^- that remains unreacted = $1.0 \text{ mol} - 0.10 \text{ mol} = 0.9 \text{ mol}$.

Moles of CH_3COOH formed = 0.10 mol

Total moles of $\text{CH}_3\text{COOH} = 0.10 \text{ mol} + 1.0 \text{ mol} = 1.1 \text{ mol}$

$$[\text{CH}_3\text{COO}^-] = \frac{0.9 \text{ mol}}{1 \text{ L}} = 0.9 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = \frac{1.1 \text{ mol}}{1 \text{ L}} = 1.1 \text{ M}$$



Initial, M	1.1	0.90	0.00
Change, M	-x	+x	+x
Equilibrium, M	(1.1 - x)	(0.90 + x)	x

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(0.90 + x)(x)}{1.1 - x} = 1.8 \times 10^{-5}$$

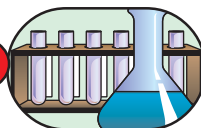
Since x is very small compared to 1.1 and 0.9, $0.90 + x \approx 0.90$ and $1.1 - x \approx 1.1$, you obtain:

$$1.8 \times 10^{-5} = \frac{(0.90 + x)x}{1.1 - x} \approx \frac{(0.90)x}{1.1}$$

$$x = [\text{H}_3\text{O}^+] = 2.2 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log (2.2 \times 10^{-5}) = 4.66$$

Experiment 2.1



The Buffer Action of Solutions

Objective: To investigate the buffer action of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$.

Apparatus: 20 mL test tubes, droppers, beakers and pH meter.

Chemicals: CH_3COOH , CH_3COONa , distilled water, 0.01 M HCl, universal indicator, 0.010 M NaOH.

**Procedure:**

1. Mix 5 mL of 0.10 M CH_3COONa with 5 mL of 0.10 M CH_3COOH in a 200 mL test tube. In a second test tube add 100 mL of distilled (or *de-ionized*) water. Add 5 drops of universal indicator to each sample and estimate pH.
2. Add 5 mL of 0.010 M HCl to each test tube, estimate pH, and record each pH change. If universal indicator is not available, add 2 drops of methyl orange indicator to each and record the volume (*drops*) of 0.10 M HCl to reach its end-point.
3. Again prepare a solution in step 1. Test the buffering capacity of each with 5 mL of 0.010 M NaOH. If universal indicator is not available, add 2 drops of alizarin yellow R and record the volume (*drops*) of 0.010 M NaOH to reach its end-point.

Results and discussion:

- a What did you observe from procedure 1?
- b What did you observe from procedure 2?
- c Give your conclusion on each step.

Exercise 2.10

Calculate the pH:

- a of a buffer solution containing 0.1 M acetic acid and a 0.1 M solution of sodium acetate.
- b when 1.0 mL of 0.10 M HCl is added to 100 mL of the buffer in (a);
- c when 1.0 mL of 0.10 M NaOH is added to 100 mL of the buffer in (a);
- d of an unbuffered solution containing 1.8×10^{-5} HCl;
- e change of the an unbuffered solution in (d) after adding
 - i) 1.0 mL of 0.1 M NaOH to 100 mL of the solution,
 - ii) 1.0 mL of 0.10 M HCl to 100 mL of the solution.

2.4 HYDROLYSIS OF SALTS

At the end of this subunit, you will be able to:

- define hydrolysis;
- explain why a salt of weak acid and strong base gives a basic solution;
- explain why a salt of strong acid and weak base gives an acidic solution; and
- explain why salts of weak acids and weak bases give acidic, basic or neutral solutions.

What does salt hydrolysis mean?

The word ‘hydrolysis’ is derived from the Greek words hydro, meaning ‘water’, and lyses, meaning ‘to split apart’. Solutions of salts contain two types of ions, namely cations and anions. The term salt hydrolysis describes the reaction of an anion or a cation of a salt, or both, with water. Depending on the strengths of the parent acids and bases, the cation of a salt can serve as an acid, base or neutral.

2.4.1 Hydrolysis of Salts of Strong Acids and Strong Bases

The anions derived from strong acids are weak conjugate bases and do not undergo hydrolysis. The strong bases are the ionic hydroxides of Group IA and IIA metals. The cations of these metals also do not hydrolyze. For example, sodium chloride, NaCl, is a salt of a strong acid, HCl, and a strong base, NaOH. Since chloride ions, Cl^- , and sodium ions, Na^+ , do not hydrolyze, the solution of the salt will be *neutral*. Can you give more examples?

2.4.2 Hydrolysis of Salts of Weak Acids and Strong Bases

Solutions of these salts are basic because the anion of the weak acid is a moderately strong base and can be hydrolyzed as follows.

**Activity 2.11**

Consider Na_2CO_3 and discuss the following :

- What are the ‘parents’ (*acid* and *base*) of this salt?
- Which ions of the salt can be hydrolyzed?
- What will be the nature of Na_2CO_3 solution? Will it be acidic, basic or neutral?

2.4.3 Hydrolysis of Salts of Strong Acids and Weak Bases

A cation (*the conjugate acid of a weak base*) hydrolyzes as an acid. As in the first case, anions of a strong acid are weak conjugate bases and do not hydrolyze.

Consider the hydrolysis of NH_4Cl . Ammonium ion, NH_4^+ , is acidic and reacts with water to produce ammonia and hydronium ions.



What will be the pH of the solution of this salt? Is it acidic, basic or neutral?

2.4.4 Hydrolysis of Salts of Weak Acids and Weak Bases

The solution of these salts contain both a strong acid (the cation of the weak base) and a strong base (the anion of the weak acid). Whether the solution of such a salt is acidic, basic or neutral depends on the relative strengths of the acidic cation and the basic anion. If the acid is stronger than the base, the solution is acidic and if the base is stronger than the acid, the solution is basic. If they are of equal strengths, the solution is neutral.

How do you determine the strength of the acid and the base?

Activity 2.12



In the following table you are given K_a and K_b values of some cations and anions, respectively.

Anion	K_b	Cation	K_a
F^-	1.4×10^{-11}	NH_4^+	5.6×10^{-10}
CNS^-	2.0×10^{-5}		
CH_3COO^-	5.6×10^{-10}		

Using the above table, determine whether the solutions of NH_4F , NH_4CNS and CH_3COONH_4 are acidic, basic or neutral. Discuss your results with your classmates.

2.5 ACID-BASE INDICATORS AND TITRATIONS

At the end of this subunit, you will be able to:

- define acid-base indicators;
- write some examples of acid-base indicators;
- suggest a suitable indicator for a given acid-base titration;
- explain the equivalents of acids and bases;
- calculate the normality of a given acidic or basic solution;
- define acid-base titration;
- define end point;
- define equivalence point;
- distinguish between end point and equivalent point; and
- discuss titration curves.

2.5.1 Acid–Base Indicators

How do acid-base indicators change colour?

Acid-base indicators are weak organic acids or weak organic bases that indicate whether a solution is acidic, basic or neutral.

Let us consider a weak organic acid that is denoted by **HIn**. In order to be effective indicators, **HIn**, and its conjugate base, **In⁻**, must have different colours. In solution, the acid ionizes as follows:



If the indicator is in sufficiently acidic medium, the equilibrium, according to **Le Chatelier's** principle, shifts to the left and the predominant colour of the indicator is that of nonionized form (HIn). On the other hand, in a basic medium, the equilibrium shifts to the right and the colour of the solution will be that of the ionized form (In⁻).

Since the indicator molecule is a weak acid, the ratio of **HIn** and **In⁻** is governed by the [H₃O⁺] of the test solution.



$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

Rearranging this equation gives

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{\text{In}}}$$

To illustrate how an indicator works, consider an indicator that has a yellow colour in acid form (HIn) and a red colour in basic form (In⁻). K_{In} is 1.0×10^{-6} . Thus, we have

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}_3\text{O}^+]}{1.0 \times 10^{-6}}$$

The colour we observe in a solution of this indicator depends on the ratio of [HIn] to [In⁻]. In a solution of **pH** = 4.0, [H₃O⁺] is 1×10^{-4} , so

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-6}} = \frac{100}{1}$$

This means that the concentration on **HIn** is 100 times that of **In⁻**, and so the solution appears yellow.

A solution having a pH of 5, $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-5}$

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{1.0 \times 10^{-5}}{1.0 \times 10^{-6}} = \frac{10}{1}, \text{ still appears yellow.}$$

$$\text{At pH of 6.0, } [\text{H}_3\text{O}^+] \text{ is } 1 \times 10^{-6}, \text{ and } \frac{[\text{HIn}]}{[\text{In}^-]} = \frac{1.0 \times 10^{-6}}{1.0 \times 10^{-6}} = \frac{1}{1}$$

Equal concentrations of **HIn** and **In⁻** give the solution an orange colour.

$$\text{At pH} = 7.0, [\text{H}_3\text{O}^+] \text{ is } 1 \times 10^{-7}, \text{ and } \frac{[\text{HIn}]}{[\text{In}^-]} = \frac{1.0 \times 10^{-7}}{1.0 \times 10^{-6}} = \frac{1}{10}$$

Here the concentration of **In⁻** is 10 times that of **HIn**, and so the solution appears red.

Indicators are used in the laboratory for estimating the **pH** of a solution and to reveal the equivalence point of a titration. Equivalence point is the point at which stoichiometrically equivalent quantities of an acid and a base have been brought together.

Some common indicators and their colors in acids and in bases are shown in **Table 2.5**.

Table 2.5 Some common indicators.

Indicator	Acid Colour	Base Colour	pH range of Colour change
Methyl violet	Yellow	Violet	0.0 – 1.6
Methyl orange	Red	Yellow	3.2 – 4.4
Bromcresol green	Yellow	Blue	3.8 – 5.4
Methyl red	Red	Yellow	4.8 – 6.0
Litmus	Red	Blue	5.0 – 8.0
Bromthymol blue	Yellow	Blue	6.0 – 7.6
Thymol blue	Yellow	Blue	8.0 – 9.6
Phenolphthalein	Colorless	Pink	8.2 – 10.0
Thymolphthalein	Colorless	Blue	9.4 – 0.6
Alizarin yellow R	Yellow	Red	10.1 – 12.0

The colour change of phenolphthalein in acidic and basic solutions is shown in **Figure 2.2**.



Figure 2.2 The colour changes of phenolphthalein in basic (a) and acidic (b) solutions.

2.5.2 Equivalents of Acids and Bases

Activity 2.13



Discuss the following questions in group and write a short report.

1. What is an equivalent of an acid and a base?
2. How does the equivalent mass of an acid and a base obtained?
3. What is the difference between normality and molarity? Discuss this in terms of acid-base reaction and in terms of oxidation-reduction reactions.

According to the definition of normality, the number of equivalents is the normality multiplied by the volume of solution, in litres. If we add enough acid to neutralize a given volume of base, the following equation holds:

$$N_1V_1 = N_2V_2$$

Where N_1 and V_1 refer to the normality, and volume of the acid solution, respectively, and N_2 and V_2 refer to the normality and volume of the base solution, respectively.

Example 2.7

What volume of 2.0 N NaOH is required to neutralize 25.0 mL of 2.70 N H_2SO_4 ?

Solution:

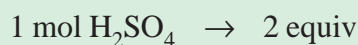
$$N_1V_1 = N_2V_2$$

$$V_2 = \frac{N_1V_1}{N_2} = \frac{(2.70 \text{ N } \text{H}_2\text{SO}_4)(25.0 \text{ mL})}{2.00 \text{ N } \text{NaOH}} = 33.8 \text{ mL}$$

Example 2.8

What is the number of equivalents in 4.00 mol H_2SO_4 , assuming that the H_2SO_4 will react with a base to replace both hydrogen atoms?

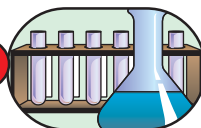
Solution:



$$\frac{4.00 \text{ mol } \text{H}_2\text{SO}_4 \times 2 \text{ equiv}}{1.00 \text{ mol } \text{H}_2\text{SO}_4} = 8.00 \text{ equiv}$$

Exercise 2.11

1. What volume of 0.1 N HNO_3 is required to neutralize 50.0 mL of a 0.15 N solution of $\text{Ba}(\text{OH})_2$?
2. A solution of H_2SO_4 is made by dissolving 196 g of the acid in enough water to produce a 500.0 mL solution. Determine the normality of the solution.

2.5.3 Acid-Base Titrations**Experiment 2.2****Acid-base Titration**

Objective: To find the normality of a given hydrochloric acid solution by titrating against 0.1 N standard sodium hydroxide solution.

Apparatus: 10 mL pipette, burette, 150 mL Erlenmeyer flask, beaker, funnel, burette clamp and metal stand.

Procedure:

1. Clean the burette with distilled water and rinse it with the 0.1 N sodium hydroxide solution; and fix the burette on the burette clamp in vertical position (Figure 2.3).
2. Using a funnel, introduce 0.1 N sodium hydroxide solution into the burette. Allow some of the solution to flow out and make sure that there are no air bubbles in the solution (why?). Record level of the solution, corresponding to the bottom of the meniscus, to the nearest 0.1 mL. Measure exactly 10 mL of hydrochloric acid solution (given) with the help of a 10 mL pipette and add it into a clean 150 mL Erlenmeyer flask and add two or three drops of phenolphthalein indicator.

Caution: When you suck hydrochloric acid or any reagent solution, into a pipette, have the maximum caution not to suck it into your mouth.

Titration: First hold the neck of the Erlenmeyer flask with one hand and the stop-cock with the other. As you add the sodium hydroxide solution from the burette, swirl the content of the flask gently and continuously. Add sodium hydroxide solution until the first faint pink colour comes which disappears on swirling. Add more sodium hydroxide drop wise until the pink colour persists for a few seconds. Find the difference between the initial level and the end point level of the burette.

Observations and analysis:

1. Colour change at the end point is from _____ to _____.
2. What is the volume of sodium hydroxide added at the end point?
3. What is the normality of hydrochloric acid at the end point?
4. What is the similarity and difference between equivalence point and end point level after reaching the end point.

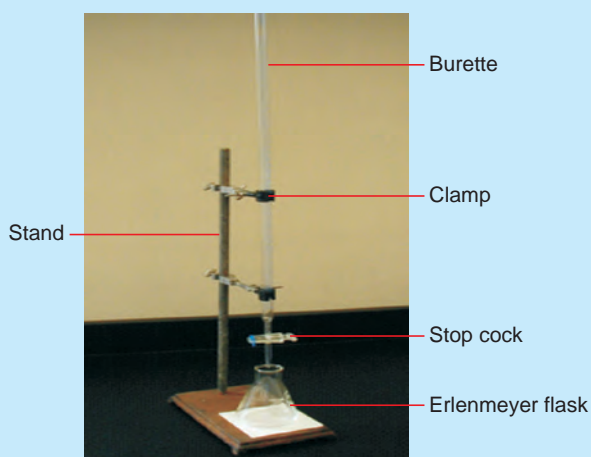


Figure 2.3 Titration Setup.



A titration is a technique in which a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the *known solution*) is added from a burette to a known quantity of the analyte (the *unknown solution*) until the neutralization reaction is complete. The point at which the acid has completely reacted with or been neutralized by the base, or vice versa, is called the equivalence point of the titration.

Knowing the volume of titrant added allows the determination of the concentration of the unknown. Often, an indicator is used to signal the end of the reaction, the end point. The end point of titration is the pH at which the indicator changes colour. A graph of pH as a function of the added titrant is called a **titration curve**. Figure 2.4 shows the technique of titration.

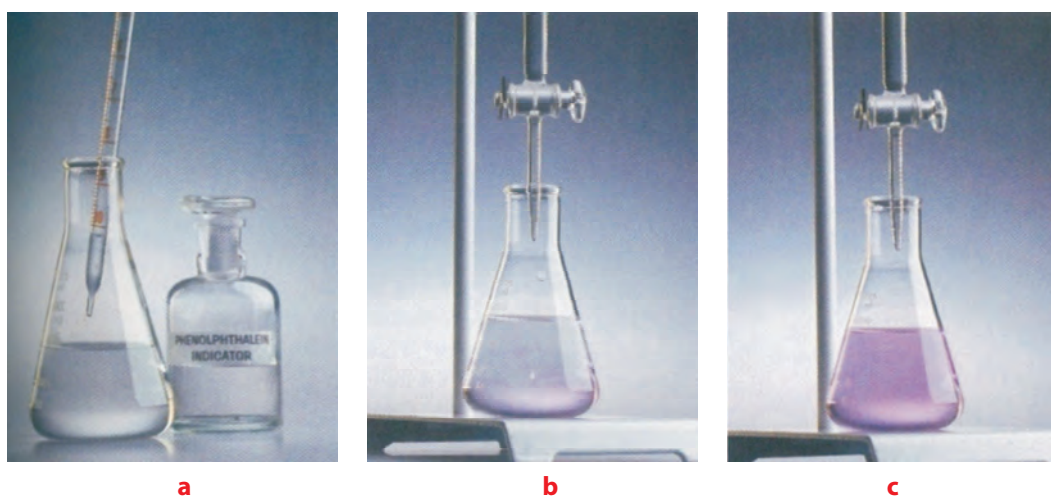


Figure 2.4 The Techniques of Titration.

- a** A precisely measured volume $\text{HCl}(\text{aq})$ is discharged from a pipette into a quantity of water in small flask. Then a few drops of phenolphthalein indicator solution are added. The solution is colourless. What does this indicate?
- b** $\text{NaOH}(\text{aq})$ is slowly added from a burette into the flask. Until all of the HCl has been neutralized, the HCl is in excess and the NaOH is the limiting reactant. The solution remains colourless, indicating that it is still acidic.
- c** At the point when the acid has just been completely neutralized, which is the equivalence point, HCl and NaOH are in stoichiometric proportions. An additional drop of $\text{NaOH}(\text{aq})$ beyond this point makes the solution slightly basic, and the indicator turns to a light pink colour. The titration is stopped, and the volume of solution delivered from the burette is recorded.

To perform a successful titration, we must use an indicator that changes color at the equivalence point.

Strong Acid-Strong Base Titrations

What is the pH of a solution of strong acid-strong base titration at the equivalence point? What are the indicators used in this type of titration?

Take 20 mL of 0.5 M HCl (a strong acid), in a small flask and slowly add 0.5 M NaOH (a strong base) to it. To establish data for a titration curve, we can calculate the pH of the accumulated solution at different points in the titration. Then we can plot these pH values *versus* the volume of NaOH(aq) added. From the titration curve, we can establish the pH at the equivalence point and identify appropriate indicators for the titration. The pH at different points in the titration of 20 mL of 0.5 M HCl with 0.5 M NaOH can be calculated as follows:

a *Before the addition of any NaOH*

Because HCl is a strong acid, it ionizes completely. Therefore, the initial solution has $[\text{H}_3\text{O}^+] = 0.5 \text{ M}$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.5) = 0.3$$

b *After the addition of 5 mL of 0.5 M NaOH*

The total number of moles of H_3O^+ to be titrated is:

$$0.02 \text{ L} \times 0.5 \text{ mol/L} = 0.01 \text{ mol}$$

The number of moles of OH^- in 5 mL of 0.5 M NaOH is:

$$0.005 \text{ L} \times 0.5 \text{ mol/L} = 0.0025 \text{ mol}$$

Since 0.0025 moles of NaOH neutralizes 0.0025 moles of HCl, the number of moles of H_3O^+ ion unneutralized is $0.01 \text{ mol} - 0.0025 \text{ mol} = 0.0075 \text{ mol}$.

The total volume is $20 \text{ mL} + 5 \text{ mL} = 25 \text{ mL} = 0.025 \text{ L}$.

Concentration of H_3O^+ unneutralized is:

$$\frac{0.0075 \text{ mol}}{0.025 \text{ L}} = 0.3 \text{ mol/L}$$

$$\text{pH} = -\log 0.3 = 0.52$$

c *pH after the addition of 10.0 mL NaOH*

The moles of H_3O^+ to be titrated is again $0.02 \text{ L} \times 0.5 \text{ M} = 0.01 \text{ mol}$.

The moles of OH^- added is $0.01 \text{ L} \times 0.5 \text{ M} = 0.005 \text{ mol}$

Since 0.005 mol OH^- neutralizes 0.005 mol H_3O^+ , then the amount of H_3O^+ that remains unneutralized is $0.01 \text{ mol} - 0.005 \text{ mol} = 0.005 \text{ mol}$.

The total volume of the solution is $20 \text{ mL} + 10 \text{ mL} = 30 \text{ mL} = 0.03 \text{ L}$.

The concentration of unneutralized H_3O^+ is:

$$\frac{0.005 \text{ mol}}{0.030 \text{ L}} = 0.17 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.17 = 0.77$$

d *pH after the addition of 15.0 mL NaOH*

The number of mole of H_3O^+ here is also 0.01 mol.

The moles of OH^- ion added is $0.5 \text{ M} \times 0.015 \text{ L} = 7.5 \times 10^{-3} \text{ mol}$.

7.5×10^{-3} moles OH^- ions neutralizes $7.5 \times 10^{-3} \text{ mol}$ H_3O^+ ions.

Then, the amount of H_3O^+ ions that remain unneutralized is:

$$0.01 \text{ mol} - 7.5 \times 10^{-3} \text{ mol} = 2.5 \times 10^{-3} \text{ mol}$$

Total volume is $20 \text{ mL} + 15 \text{ mL} = 35 \text{ mL} = 0.035 \text{ L}$

The concentration of H_3O^+ unneutralized is:

$$\frac{2.5 \times 10^{-3} \text{ mol}}{0.035 \text{ L}} = 0.07 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.07 = 1.15$$

e *pH after the addition of 20 mL NaOH*

This is a simple calculation, because it involves a complete-neutralization reaction, and the salt (NaCl) does not undergo hydrolysis. *What do you call this point?*

At this point, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.0 \times 10^{-7}) = 7$$

f *pH after the addition of 25 mL NaOH*

Do any moles of H_3O^+ remain unneutralized here?

The moles of OH^- ions added is $0.5 \text{ M} \times 0.025 \text{ L} = 0.0125 \text{ mol}$. Since all the H_3O^+ ions are neutralized, there is only 0.0125 mol OH^- .

The total volume here is $20 \text{ mL} + 25 \text{ mL} = 45 \text{ mL} = 0.045 \text{ L}$.

Concentration of OH^- is:

$$\frac{0.0125 \text{ mol}}{0.045 \text{ L}} = 0.28 \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.28 = 0.55$$

$$\text{pH} = 14 - 0.55 = 13.45$$

Can you now calculate the pH after the addition of 30 mL of 0.5 M NaOH?

Now you have the data for a titration curve.

Volume of 0.5 M NaOH added (mL)	0.00	5.00	10.00	15.00	20.00	25.00	30
pH	0.30	0.52	0.77	1.15	7.00	13.45	?

Figure 2.5 shows the titration curve of 20.00 mL of 0.5 M HCl by 0.5 M NaOH.

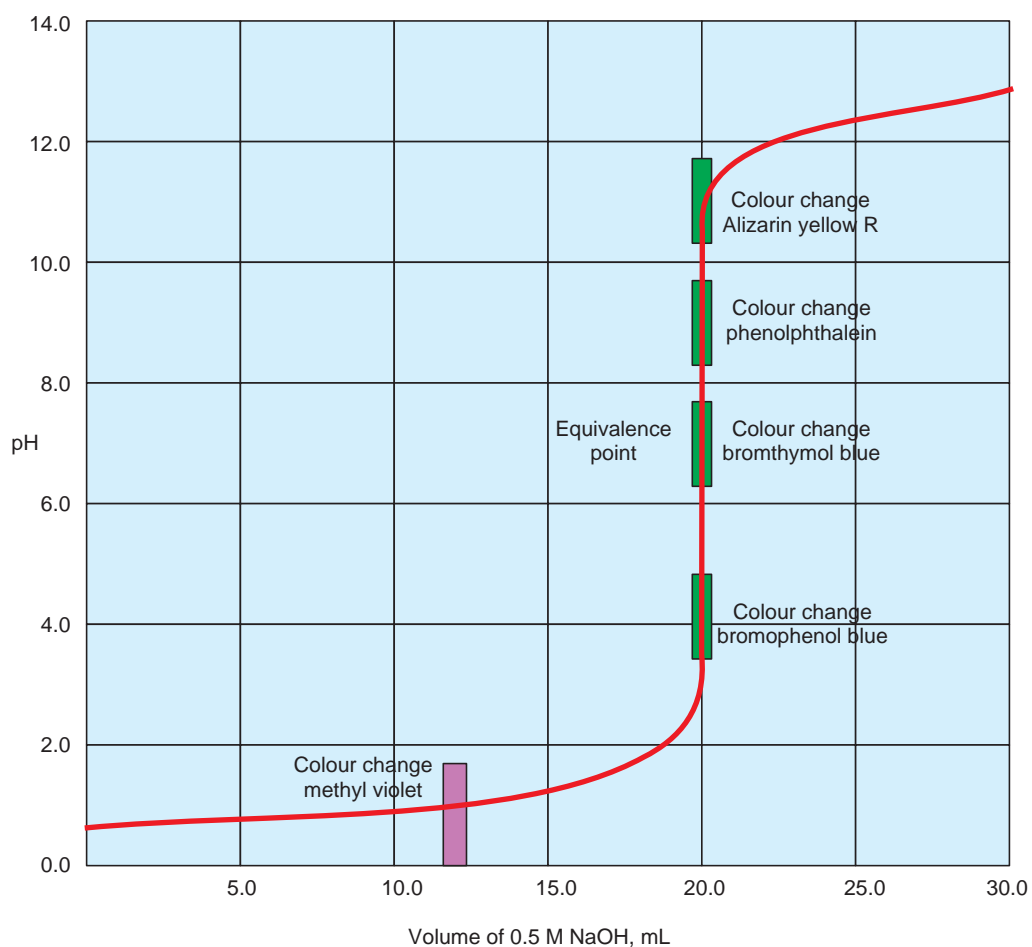


Figure 2.5 Titration curve of 20 mL of 0.5 M HCl by 0.5 M NaOH.



Features of the titration curve for the titration of a strong acid with a strong base.

- * The pH is low at the beginning of the titration.
- * The pH change slowly until just before the equivalence point.
- * Just before the equivalence point, the pH rises sharply.
- * At the equivalence point, the pH is 7.00.
- * Just past the equivalence point, the pH continues its sharp rise.
- * Further beyond the equivalence point, the pH continues to increase, but much less slowly.
- * Any indicator whose colour changes in the pH range from about 4 to 10 can be used in the titration of a strong acid with a strong base. Methyl violet changes colour too soon, and alizarin yellow R too late. So, bromthymol blue and phenolphthalein are preferred for this titration.

Exercise 2.12

Calculate the pH when the following quantities of 0.1 M NaOH solution have been added to 50 mL of 0.1 M HCl solution.

- a 49.00 mL b 49.90 mL c 50.00 mL d 50.10 mL

Weak Acid-Strong Base Titrations

Can you predict the pH range at the equivalence point?

The titration of a weak acid by a strong base is slightly more complicated than the titration of a strong acid by a strong base. The conjugate base of a weak acid will undergo hydrolysis, which will affect the pH of the solution. Thus, we need to consider the stoichiometric reaction between the acid and the base and the equilibrium reaction of the species that remain.

In contrast to the titration of a strong acid with a strong base, the titration of a weak acid with a strong base, has these features:

- * The initial pH is higher because the weak acid is only partially ionized.
- * At the half-neutralization, $\text{pH} = \text{p}K_a$. The solution at this point is a buffer solution in which the concentration of the weak acid and its conjugate base are equal.
- * The pH is greater than 7 at the equivalence point because the anion of the weak acid hydrolyzes.

- * The steep portions of the titration curve just prior to and just beyond the equivalence point is confined to a smaller pH range.
- * The choice of indicator for the titration is more limited. The color change must occur in a basic solution. Generally, the midpoint of the pH range in which the indicator changes colour must be well above pH 7.

As an example, let us consider the titration of 20 mL of 0.5 M acetic acid, CH_3COOH , with 0.5 M NaOH. To establish data for the titration curve, we calculate the pH at different points in the titration, as follows:

a pH before addition of any NaOH

Here we have only 0.5 M acetic acid, and we calculate the equilibrium concentration of H_3O^+ ions to calculate the pH.

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

Initial, M	0.5	0	0
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(0.5 - x)$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.5 - x} = 1.8 \times 10^{-5}$$

We can make the actual assumption, that is $x \ll 0.5$.

$$K_a = \frac{x^2}{0.5 - x} = 1.8 \times 10^{-5}$$

$$x^2 = 0.5 \times 1.8 \times 10^{-5}$$

$$x^2 = 9.0 \times 10^{-6}$$

$$x = \sqrt{9.0 \times 10^{-6}} = 3.0 \times 10^{-3} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.0 \times 10^{-3}) = 2.57$$

b pH after the addition of 5.00 mL NaOH

The original number of moles of CH_3COOH is $0.5 \text{ M} \times 0.020 \text{ L} = 0.01 \text{ mol}$.

The moles of OH^- added is $0.5 \text{ M} \times 0.005 \text{ L} = 0.0025 \text{ mol}$.

All the OH^- ions have reacted, converting 0.0025 mol CH_3COOH to CH_3COO^- . So, at this point we have 0.0025 mol CH_3COO^- and $(0.01 - 0.0025) \text{ mol}$ CH_3COOH or 0.0075 mol CH_3COOH .

The total volume of the solution is $20 \text{ mL} + 5 \text{ mL} = 25 \text{ mL} = 0.025 \text{ L}$.

The concentration of CH_3COO^- and CH_3COOH in 0.025 L solution can be calculated as

$$[\text{CH}_3\text{COOH}] = \frac{0.0075 \text{ mol}}{0.025 \text{ L}} = 0.3 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{0.0025 \text{ mol}}{0.025 \text{ L}} = 0.1 \text{ M}$$



Initial, M	0.3	0.1	0
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$0.3 - x$	$0.1 + x$	x

$$K_a = \frac{(0.1 + x)x}{0.3 - x} = 1.8 \times 10^{-5}$$

Assuming that x is very small when compared to 0.1 and 0.3 , then $0.1 + x = 0.1$, and $0.3 - x = 0.3$, respectively. Thus,

$$1.8 \times 10^{-5} = \frac{0.1x}{0.3}$$

$$x = \frac{0.3 \times 1.8 \times 10^{-5}}{0.1} = 5.4 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.4 \times 10^{-5}) = 4.26$$

- c pH after the addition of 10 mL of 0.5 M NaOH

Number of moles of the original $\text{CH}_3\text{COOH} = 0.01 \text{ mol}$.

Number of moles of OH^- ions added $0.5 \text{ M} \times 0.01 \text{ L} = 0.005 \text{ mol}$.

0.005 mol OH^- ions convert 0.005 mol of CH_3COOH to CH_3COO^- . So, at this point, we have $0.005 \text{ mol CH}_3\text{COO}^-$ and $(0.01 - 0.005) \text{ mol CH}_3\text{COOH}$ or $0.005 \text{ mol CH}_3\text{COOH}$.

The total volume of the solution is $20 \text{ mL} + 10 \text{ mL} = 30 \text{ mL} = 0.03 \text{ L}$.

Concentration of CH_3COOH and CH_3COO^- in 0.03 L solution is

$$[\text{CH}_3\text{COOH}] = \frac{0.005 \text{ mol}}{0.03 \text{ L}} = 0.17 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{0.005 \text{ mol}}{0.03 \text{ L}} = 0.17 \text{ M}$$



Initial, M	0.17	0.17	0
Change, M	-x	+x	+x
Equilibrium, M	(0.17-x)	(0.17+x)	x

$$K_a = \frac{(0.17 + x)x}{0.17 - x} = 1.8 \times 10^{-5}$$

By assuming that x is very small

$$0.17 + x \approx 0.17, 0.17 - x \approx 0.17$$

$$1.8 \times 10^{-5} = \frac{(\cancel{0.17})x}{\cancel{0.17}}$$

$$x = 1.8 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log 1.8 \times 10^{-5} = 4.47$$

d pH, after addition of 20 mL of 0.5 M NaOH

This is the equivalence point. Do you think that the pH at this point equals 7?

Number of moles of OH^- ions added

$$0.5 \text{ M} \times 0.020 \text{ L} = 0.01 \text{ mol}$$

Since 0.01 mol OH^- converts 0.01 mol of CH_3COOH to CH_3COO^- , no more CH_3COOH remains at this point. But now we have 0.01 M CH_3COO^- .



Initial, M	0	0	0
Change, M	-x	+x	+x
Equilibrium, M	(0.01-x)	x	x

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.01 - x}$$

Assuming that x is very small, $0.01 - x \approx 0.01$

$$5.6 \times 10^{-10} = \frac{x^2}{0.01}$$

$$x^2 = 0.01 \times 5.6 \times 10^{-10} = 5.6 \times 10^{-12}$$

$$x = \sqrt{5.6 \times 10^{-12}} = 2.37 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pOH} = -\log 2.37 \times 10^{-6} = 5.63$$

$$\text{pH} = 14 - 5.63 = 8.37$$

- e pH after the addition of 25 mL of 0.5 M NaOH

number of mole of OH^- added $0.5 \text{ M} \times 0.025 \text{ L} = 0.0125 \text{ mol}$

Now the equivalence point is passed, and there is no more CH_3COOH to react with the excess OH^- ion that are added.

The number of moles of OH^- in excess is $(0.0125 - 0.01) \text{ mol}$ or 0.0025 mol .

Total volume of the solution is $20 \text{ mL} + 25 \text{ mL} = 45 \text{ mL} = 0.045 \text{ L}$

The concentration of the excess OH^- ions is

$$\frac{0.0025 \text{ mol}}{0.045 \text{ L}} = 0.055 = [\text{OH}^-]$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.055 = 1.26$$

$$\text{pH} = 14 - 1.26 = 12.74$$

Can you calculate the pH after the addition of 30 mL of 0.5 M NaOH?

From the volume of NaOH added and the pH values calculated, you can tabulate as follows:

Volume of NaOH added (mL)	0.00	5.00	10.00	20.00	25.00	30.00
pH	2.57	4.26	4.47	8.37	12.74	?

Figure 2.6 shows the titration curve for 20.00 mL of 0.5 M CH_3COOH by 0.5 M NaOH.

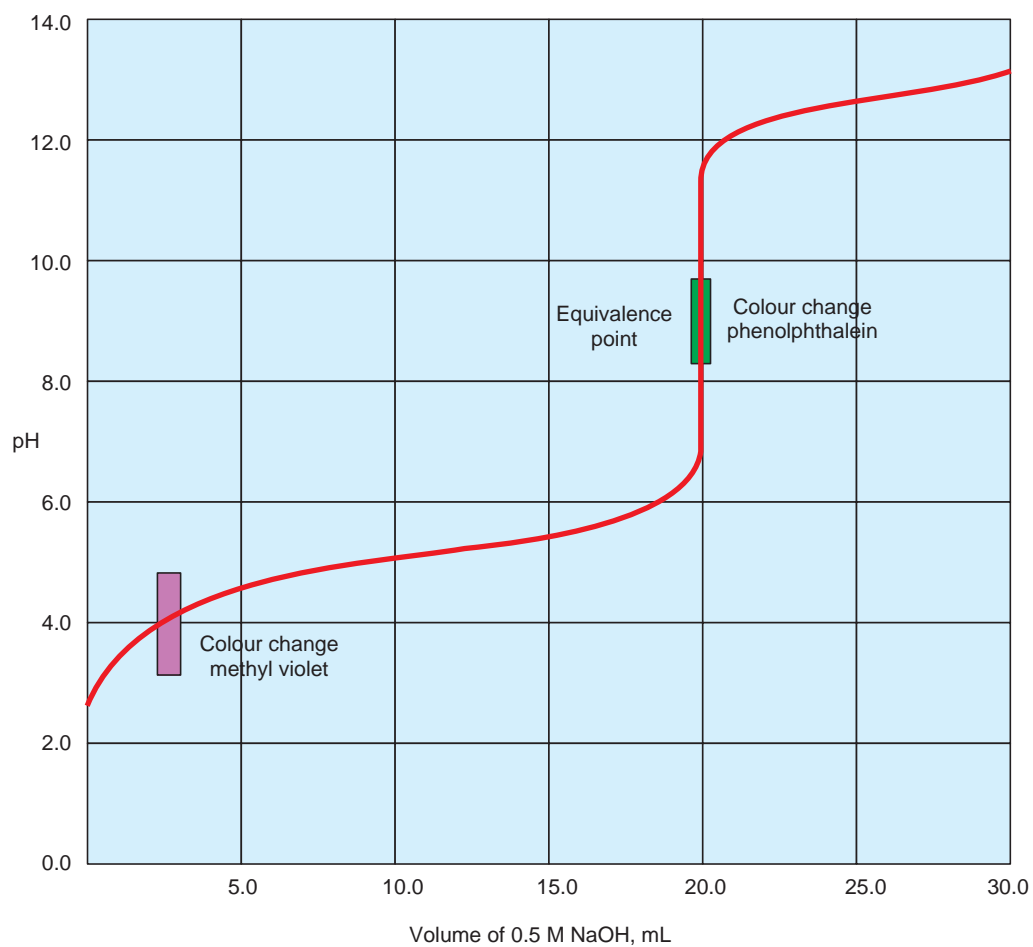


Figure 2.6 Titration curve of 20.00 mL of 0.5 M CH_3COOH by 0.5 M NaOH.

Exercise 2.13

Calculate the pH when the following quantities of 0.1 M NaOH solution have been added to 25.0 mL of 0.1 M acetic acid:

a 10.00 mL

b 25.00 mL

c 35.00 mL

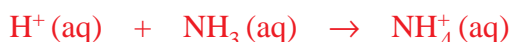
Weak Base-Strong Acid Titrations

How does the titration curve of a weak base with a strong acid differ from the titration curves you have seen so far? What is the pH at equivalence point?

Consider the titration of ammonia, NH_3 , with a strong acid, HCl.



or simply



The pH at the equivalence point is less than 7. Why?

Activity 2.14



A 25.0 mL sample of 0.1 M NH_3 is titrated with 0.1 M HCl.

- Calculate the pH values of the solution after the following volumes of 0.1 M HCl are added. 0.00 mL, 5.00 mL, 10.00 mL, 15.00 mL, 20.00 mL, 22.00 mL, 24.00 mL, 25.00 mL and 26.00 mL.
- Draw a table and put the pH values corresponding to each volume in the table.
- Draw the titration curve.
- Name the appropriate indicator for this titration.

Unit Summary

- The classical (Arrhenius) definition of acids and bases has many limitations but still we cannot ignore it.*
- The Brønsted-Lowry definition is more general, and considers an acid as a proton donor and a base as a proton acceptor. In this definition, every acid has a conjugate base and every base has a conjugate acid. The stronger the acid, the weaker its conjugate base. Similarly, the stronger a base, the weaker its conjugate acid.*
- According to Lewis, a base is any species that donates an electron pair, and an acid is any species that accepts an electron pair.*
- Water spontaneously ionizes to a slight extent (self-ionization or autoionization), forming $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$. The extent of ionization is expressed by the ion-product constant for water, K_w .*

- The strength of acids and bases in aqueous solution depends on several factors such as the percent of dissociation, the dissociation constant, the concentration of hydrogen ions and hydroxide ions, **pH** and **pOH**.
- The extent to which a weak acid ionizes can be expressed by using the equilibrium constant for the ionization reaction.
- Generally, we can calculate the hydrogen-ion concentration or **pH** of an acid solution at equilibrium, given the initial concentration of the acid and its K_a value.
- The common-ion effect tends to suppress the ionization of a weak acid or a weak base. This action can be explained by Le Chatelier's principle.
- A buffer solution is a combination of either a weak acid and its conjugate base or a weak base and its conjugate acid. The solution reacts in such a way that the **pH** of the solution remains nearly constant. Buffer systems play a vital role in maintaining the **pH** of body fluids.
- Acid-base indicators are weak organic acids or bases. They change colour near the equivalence point in an acid-base neutralization reaction.
- The **pH** at the equivalence point of an acid-base titration depends on hydrolysis of the salt formed in the neutralization reaction. For strong acid-strong base titrations, the **pH** at the equivalence point is 7. For weak acid-strong base titrations, the **pH** at equivalence point is greater than 7. For weak base-strong acid titrations, the **pH** at the equivalence point is less than 7.

Check List

Key terms of the unit

- | | |
|--|------------------------------------|
| • Acid-base titration | • Conjugate acid |
| • Acids | • Conjugate base |
| • Amphiprotic species | • Equivalents of acids and bases |
| • Arrhenius acid-base concept | • Hydrolysis of salts |
| • Autoionization | • Lewis concept of acids and bases |
| • Bases | • percent ionization |
| • Brønsted-Lowry concept of acid and bases | • pH scale |
| • Buffer solution | • Solvation |
| • Common ion effect | • Titration curve |

**REVIEW EXERCISE FOR UNIT 2****Part I: Multiple-Choice Questions**

- A Brønsted-Lowry base is defined as a substance that:
 - acts as a proton donor
 - increases $[H^+]$ when placed in water
 - decreases $[H^+]$ when placed in water
 - acts as a proton acceptor
- Given the reaction
$$HC_2O_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + C_2O_4^{2-}(aq)$$
which of the following is a conjugate acid-base pair?
 - $HC_2O_4^-$ and H_2O
 - $HC_2O_4^-$ and H_3O^+
 - H_2O and $C_2O_4^{2-}$
 - $HC_2O_4^-$ and $C_2O_4^{2-}$
- In the reaction
$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$
 $AlCl_3$ acts as a:
 - Salt
 - Lewis base
 - Lewis acid
 - Brønsted base
- Which of the following is the conjugate base of HCO_3^- ?
 - OH^-
 - H_2CO_3
 - CO_3^{2-}
 - HCO_3^+
- What is the pH of an aqueous solution at $25^\circ C$ in which $[OH^-]$ is $0.00250 M$?
 - 2.60
 - 3.60
 - 11.4
 - 12.4
- A substance that is capable of acting as both an acid and a base is:
 - amphiprotic
 - conjugated
 - diprotic
 - binary acid-base
- The magnitude of K_w indicates that:
 - water autoionizes very slowly
 - water autoionizes very quickly
 - water autoionizes only to a very small extent
 - water autoionizes completely

8. When sodium acetate is added to an aqueous solution of acetic acid its pH:
- a increases
 - b decreases
 - c remains constant
 - d may increase or decrease
9. pK_a values of three acids A, B and C, are 4.5, 3.5 and 6.5, respectively. Which of the following represents the correct order of acid strength?
- a $A > B > C$
 - b $B > A > C$
 - c $C > A > B$
 - d $C > B > A$
10. An acid buffer can be prepared by mixing solutions of:
- a sodium chloride and hydrochloric acid
 - b sodium borate and boric acid
 - c sodium sulfate and sulfuric acid
 - d sodium hydroxide and hydrochloric acid
11. Which of the following is not true about strong acid-strong base titration?
- a the pH is low at the beginning of the titration
 - b at the equivalence point, the pH is 7.00
 - c any indicator whose color changes in the pH range from about 4 to 10 can be used
 - d none of the above
12. Which of the following salts will yield a basic solution on dissolution in water?
- a a salt of weak acid and weak base
 - b a salt of strong acid and strong base
 - c a salt of weak acid and strong base
 - d a salt of strong acid and weak base
13. A more generalized acid-base concept is that of:
- a Brønsted and Lowry
 - b Arrhenius
 - c Lewis
 - d none of these
14. Which of the following anions is the weakest base?
- a NO_2^-
 - b NO_3^-
 - c CH_3COO^-
 - d PO_4^{3-}
15. Which of the following buffer solutions has a pH greater than 7?
- a $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$
 - b $\text{HCOOH}/\text{HCOOK}$

- c $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONH}_4$
 d $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$

Part II: Short Answer Questions

16. Define acid and base according to:
- Arrhenius concept
 - Brønsted-Lowry concept
 - Lewis concept
17. Given the following species, identify the acids and bases according to the Brønsted-Lowry concept.
- HNO_3
 - OCl^-
 - NH_2^-
 - NH_4^+
 - CH_3NH_3^+
18. Write the conjugate acids of the following bases.
- OH^-
 - Cl^-
 - OCl^-
 - CN^-
 - HCO_3^-
 - HPO_4^{2-}
 - HS^-
19. What are the conjugate bases of the following acids?
- H_2S
 - HCOOH
 - HSO_3^-
 - HSO_4^-
 - HS^-
 - HNO_2
 - HCN
20. Write the equation for the reaction of sulphuric acid and water, and identify the acid, the base, the conjugate acid and the conjugate base.
21. Identify the conjugate acid-base pairs in the following reactions using notation such as acid (1) and base (1)
- $\text{H}_2\text{S}(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{HS}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$
 - $\text{CN}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCN}(\text{aq}) + \text{OH}^-(\text{aq})$
 - $\text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_2\text{O}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - $\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
22. a What is meant by amphiprotic substance?
 b Write an equation for the autoionization of water that demonstrates that water is amphiprotic.
23. Which of the following are amphiprotic?
- OH^-
 - NH_3
 - H_2O
 - H_2S
 - NO_3^-
 - HCO_3^-
 - CH_3COO^-
 - HNO_3

24. Rank the base in each of the following groups in order of increasing base strength, and explain the reason for the order you assign.
- H_2O , OH^- , H^- , Cl^-
 - ClO_4^- , ClO^- , ClO_2^- , ClO_3^-
 - NH_2^- , HS^- , HTe^- , PH_2^-
 - BrO_2^- , ClO_2^- , IO_2^-
25. Which of the following acids are classified as Lewis acids but not as Brønsted-Lowry acids?
- HBrO_3
 - SbCl_3
 - HSO_4^-
 - AlF_3
26. Calculate $[\text{OH}^-]$ for each of the following solutions:
- $[\text{H}^+] = 0.005 \text{ M}$
 - $[\text{H}^+] = 1.3 \times 10^{-9} \text{ M}$
 - A solution in which $[\text{OH}^-]$ is 100 times greater than $[\text{H}^+]$.
27. Calculate the pH of each of the following:
- $[\text{H}^+] = 3.6 \times 10^{-3} \text{ M}$
 - $[\text{H}^+] = 0.047 \text{ M}$
 - $\text{pOH} = 5.33$
 - $[\text{OH}^-] = 6.7 \times 10^{-2} \text{ M}$
28. What is the pOH of each of the following solutions?
- $1.0 \times 10^{-2} \text{ M NaOH}$
 - $0.00520 \text{ M Ba(OH)}_2$
 - 0.0068 M LiOH
 - $3.51 \times 10^{-4} \text{ M HCl}$
29. Hydrogen cyanide, HCN, is a weak acid with a dissociation constant of 4.8×10^{-10} . Calculate the percent dissociation, the pH, and the OH^- concentration of a 0.15 M solution of HCN in water.
30. Calculate the $[\text{OH}^-]$ in a $1.0 \times 10^{-3} \text{ M}$ solution of the weak base methylamine (CH_3NH_2), whose $K_b = 4.4 \times 10^{-4}$. What percentage of the base has dissociated?
31. A 0.01 M butanoic acid solution is 3.9% dissociated at 298 K. Calculate the K_a value for butanoic acid.
32.
 - What is meant by the common-ion effect?
 - Give an example of a salt that can decrease the ionization of HCl in solution.
 - Explain why the ionization of a weak acid is suppressed by the presence of its conjugate base.



33. Describe the effect on pH (increase, decrease or no change) that results from each of the following additions.
- Sodium formate, NaCOOH , to a solution of formic acid, HCOOH .
 - Ammonium perchlorate, NH_4ClO_4 , to a solution of ammonia, NH_3 .
 - Potassium bromide, KBr , to a solution of potassium nitrite, KNO_2 .
 - Hydrochloric acid, HCl , to a solution of sodium acetate, NaCOOCH_3 .
34. Explain why a mixture of HCl and KCl does not function as a buffer, whereas a mixture of $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$ does.
35. Calculate the pH of the buffer system made up of $0.15 \text{ M NH}_3/0.35 \text{ M NH}_4\text{Cl}$.
36. The pH of a sodium acetate/acetic acid buffer is 4.5. Calculate the ratio of $[\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-]$.
37. A buffer is prepared by adding 20.0 g of acetic acid, CH_3COOH , and 20.0 g of sodium acetate; CH_3COONa , to enough water to form 2.00 L of solution.
- Determine the pH of the buffer.
 - Write the complete ionic equation for the reaction that occurs when a few drops of hydrochloric acid are added to the buffer.
 - Write the complete ionic equation for the reaction that occurs when a few drops of potassium hydroxide solution are added to the buffer.
38. A buffer is prepared by adding 1.00 g of acetic acid, CH_3COOH , and 1.50 g of sodium acetate, CH_3COONa , to enough water to form a 0.10 L solution.
- What is the pH of this buffer?
 - What is the pH after the addition of 1.00 mL of a 1.00 M HCl solution?
 - What is the pH after the addition of 1.00 mL of 1.00 M KOH solution?
39. How does the titration of a strong acid with a strong base differ from the titration of a weak acid with a strong base, with respect to the following points?
- Quantity of base required to reach the equivalence point.
 - pH at the beginning of the titration.
 - pH at the equivalence point.
 - pH after addition of a slight excess of base.
 - Choice of indicator for determining the equivalence point.
40. A 20.0 mL sample of 0.2 M HBr solution is titrated with 0.2 M NaOH solution. Calculate the pH of the solution after the following volumes of the base have been added; draw the titration curve.
- | | | |
|-----------|------------|-----------|
| a 15.0 mL | b 19.9 mL | c 20.0 mL |
| d 20.1 mL | e 35.0 mL. | |