CHEMISTRY

Distance Module-I

GRADE 12





CHEMISTRY GRADE 12

DISTANCE MODULE I



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CHEMISTRY Distance Module - I

GRADE 12

ACID-BASE EQUILIBRIA AND ELECTROCHEMISTRY

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Introduction to the module

Dear Learner, Grade 12 Chemistry includes two modules. Module 1 deals with Acid-Base Equilibria and Electrochemistry. Module 2 deals with Industrial Chemistry, Polymer and Introduction to Environmental Chemistry. For each module, an assignment for submission is provided. After you go through the contents of each module try to answer the questions. After completing the question submit the assignment to your tutor. Ask your tutor for her/his response and comments so that you can improve your study. The assignments are part of the total evaluation of the module. As a student enrolled in an independent study, you have taken on a dual role-that of a student and a teacher. As a student, you are responsible for mastering the lessons and completing the learning activities and assignments. As a teacher, you are responsible for checking your work carefully, noting areas in which you need to improve and motivate yourself to succeed.

Dear learner, this module contains two units, the first unit is acid base equilibria and the second unit is electrochemistry.

Acid-base reactions, in which protons are exchanged between donor molecules (acids) and acceptors (bases), form the basis of the most common kinds of equilibrium problems which you will encounter in almost any application of chemistry. In order to understand thoroughly the material in this unit, you are expected to be familiar with the following topics which are covered in the separate unit Introduction to Acid-Base Chemistry:

- The Arrhenius concept of acids and bases
- The Brønsted-Lowry concept, conjugate acids and bases
- Lewis acid base concepts
- Definition of pH and the pH scale
- Strong vs. weak acids and bases

A primary focus of Acid-Base Equilibria will give an emphasis on Aqueous equilibrium. A dominating factor of aqueous equilibrium is the ever present proton (H⁺) and hydroxide ion (OH⁻). Acid/Base theory and equilibria focus on the relationship of these two ions and how each affects the equilibria of a whole class of compounds known as **acids and bases**.

Acids and bases have been used as laboratory chemicals for centuries, as well as in the home. Common household acids include acetic acid (CH₃COOH, vinegar), citric acid (H₃C₄H₅O₇, in citrus fruits), and phosphoric acid (H_3PO_4 , a flavoring in carbonated beverages). Sodium hydroxide (NaOH, drain cleaner) and ammonia (NH₃, glass cleaner), are household bases. And acid-base chemistry occurs throughout the environment and organisms. You may have noticed that some acids (e.g., acetic and citric) have a sour taste. In fact, sourness was a defining property in the 17th century: an acid was any substance that had a sour taste; reacted with active metals, such as aluminum and zinc, to produce hydrogen gas; and turned certain organic compounds specific colors. Similarly, a base (like the amines in fish) was any substance that had a bitter taste and turned the same organic compounds different colors. Moreover, it was known that when an acid and a base react, each cancels the properties of the other in a process called **neutralization**. Although these early definitions described distinctive properties, they gave way to others based on molecular behavior. In this chapter, you will develop three definitions of acids and bases that allow you to understand ever-increasing numbers of reactions. In the process, you can apply the principles of chemical equilibrium to this essential group of substances.

The second unit of this module is electrochemistry. Electrochemistry deals with inter-conversion of electrical and chemical energy. Many chemical changes can be clearly related to the electrons that move from one species to another. Often, this electron exchange can be captured to do electrical work external to the chemical system (storage battery, fuel cell). Other times, electrical energy can be used to bring about chemical change (electrolysis, battery charging, etc.).

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Electrochemistry studies the electrical aspects of chemical reactions. Some redox reactions that have negative values of the free energy change (ΔG) can occur spontaneously, and release electrical energy. Non spontaneous redox reaction, on the other hand, can be made to occur by the application of an external source of electrical energy, through a process known as **electrolysis**

Electrochemistry can also help us in generating important thermodynamic data such as the standard cell potential and the equilibrium constant. Electrochemical processes also have important practical applications in the production of industrial chemicals. This unit mainly focuses on oxidationreduction reactions, Electrolysis of aqueous solutions, quantitative aspects of electrolysis, industrial application of electrolysis and volatic cells

In this module, the significance of these two disciplines in the study of chemistry and the practical usages will be discussed. At the end of each section you will find sets of self-test questions. Several activities are also included in the text. The answers for the self-test questions and activities are given at the ends of each unit.

Module Assessment Methods

The way the module is assessed should be based on how well each student performed throughout all of the sections. That is how well the students performed on all of the activities, self-test exercises and self-assessment (written assignment) that help the learners to exercise the basic emphasis of the module. Any answer for the activities, self-test exercise and selfassessment is given at the end of the module. Learner can self-check their answers and keep a record after receiving feedback for activities self-tests, and self-assessment exercises on the module. Finally, each unit concludes with an assignment that compiles and assesses the results of all the topics covered in each unit. The tutor should gather the written assignment and check the work of every student's assignment, record the achievement of each student and make sure that the suggested competencies for the module are achieved. Appreciate students working above the minimum requirement level and encourage them to continue working hard for the next level. Advocate the learners who are working below the minimum requirement to study by themselves, taking additional lesson time.

There are a number of symbols in the course materials so that it guides you as you study

₿

This tells you there is an overview of the unit and what the unit is about.



This tells you there is an in-text question to answer or think about in the text.

(P

This tells you to take note of or to remember an important point.

This tells you there is a self-test for you to do

-) This tells you there is a checklist.
-) This tells you there is a written assignment
- This tells you that this is the key to the answers for the self-tests.

UNIT ACID-BASE EQUILIBRIA

Introduction to unit 1

Dear learner, acids and bases are two extremes that describe chemicals, just like hot and cold are two extremes that describe temperature. Mixing acids and bases can cancel out their extreme effects; much like mixing hot and cold water. A substance that is neither acidic nor basic is neutral. Acidbase reactions, in which protons are exchanged between donor molecules (acids) and acceptors (bases), form the basis of the most common kinds of equilibrium problems which you will encounter in almost any application of chemistry. A primary focus of Acid-Base Equilibria will give an emphasis on Aqueous equilibrium.

A dominating factor of aqueous equilibrium is the ever present proton (H⁺) and hydroxide ion (OH⁻). Acid/Base theory and equilibria focus on the relationship of these two ions and how they each affect the equilibria of a whole class of compounds known as **acids and bases**.

Dear learner, in order to understand thoroughly the material in this unit, you are expected to be familiar with the following topics which will be covered in the next sections. These topics are the Arrhenius concept of acids and bases, the Brønsted-Lowry concept, conjugate acids and bases, Lewis concept of acids and bases, Definition of pH and the pH scale. Strong verses weak acids and bases etc.

Objectives

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

- describe the draw backs of Arrhenius acid base concepts
- define Bronsted-Lowery and Lewis concepts of acids and bases
- describe the dissociation of water, weak mono-protic and polyprotic acids, and weak bases
- Solve equilibrium problems involving concentration of reactants and products, k_a, k_b, pH and pOH
- discuss the common ion effect, buffer solution, hydrolysis of salts, acidbase indicators and acid-base titrations
- explain how buffering action affects our daily lives using examples
- determine the equivalents of acid or base that are required to neutralize specific amount of acid or base
- predict, in qualitative terms, whether a solution of a specific salt will be acidic, basic or neutral.
- explain how to solve problems involving concentration and pH of acid-base titration
- Write chemical equations to show differences in the three definitions of acids and bases.

Unit Content

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ACID-BASE EQUILIBRIA

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The Required Study Time

5 weeks

If you set an average of one hour per day, you will be able to complete unit one by the end of the assigned week. Try to do all the learning activities. And compare your answers with the ones provided at the end of the Module.

If you do not get a particular exercise right in the first attempt, you should not get discouraged, but instead, go back and attempt it again. If you still do not get it right after several attempts, then you will seek help from your friend or even your tutor.

Unit Learning Strategies

Individual study (self-study) is the advised methodology for this unit, and for individuals with internet access, visual-based learning is also advised. Activities are presented at the start of each unit part. The students are required to think critically about the activities and the given exercise and validate their findings by contrasting them with the solution provided at the conclusion of the module.

You can recall what you learnt in a prior module or unit thanks to the activity. Please evaluate yourself by completing the self-test exercises and rating the check list that is provided at the end of each segment. See the feedback provided at the module's end for the solution to the self-test exercise. Please visit the module to read the provided notes again and attempt to answer the questions once more if you didn't meet the required minimum standard for the activities and self-test exercise.

Section 1.1: ACID-BASE CONCEPTS

Dear learner, the concepts of acids and bases are probably among the most familiar chemistry concepts. The reason is that acids and bases have been used as laboratory chemicals for centuries, as well as in the home. Common household acids include acetic acid (CH_3COOH , vinegar), citric acid ($H_3C_6H_5O_7$, in citrus fruits), and phosphoric acid (H_3PO_4 , a flavoring in carbonated beverages). Sodium hydroxide (NaOH, drain cleaner) and ammonia (NH_3 , glass cleaner), are household bases.

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, you 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.

Objectives

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

- define acid by the Bronsted-Lowry concept;
- give examples of Bronsted-Lowry acids
- define base by the Bronsted-Lowry concept
- give examples of Bronsted-Lowry bases.
- explain what conjugate acids and conjugate bases are
- identify the acid-base conjugate pairs from the 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 acid by the Lewis concept

- give examples of Lewis acids
- define base by the Lewis concept
- give examples of Lewis bases
- calculate pH from $\left\lceil H^+ \right\rceil$ and $\left\lceil H^+ \right\rceil$ from pH
- calculate pOH from $\left\lceil OH^{-} \right\rceil$ and $\left\lceil OH^{-} \right\rceil$ from pOH

1.1.1 Arrhenius concept of acids and bases

Activity 1.1

Reflect on the following questions.

- 1. Explain Arrhenius acid and base concepts using appropriate examples?
- 2. Does hydrogen ion exist freely in water?
- 3. What are the drawbacks of the Arrhenius' concepts of acids and bases?

The Swedish chemist Svante Arrhenius framed the first successful concept of acids and bases. He defined acids and bases in terms of the effect these substances have on water. According to Arrhenius, acids are substances that increase the concentration of H^+ (proton ion) in aqueous solution, and bases increase the concentration of OH^- (a hydroxide ion) in aqueous solution.

In Arrhenius's theory, a strong acid is a substance that completely ionizes in aqueous solution to give H_3O^+ (aq) and an anion. An example is perchloric acid, $HClO_4$

 $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$

Other examples of strong acids are H_2SO_4 , HI, HBr, HCl, and HNO_3 . A strong base completely ionizes in aqueous solution to give OH^- and a cation. Sodium hydroxide is an example of a strong base.

 $NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$

The principal strong bases are the hydroxides of Group IA elements and Group IIA elements (except Be). Despite its early successes and continued usefulness, the Arrhenius theory does have limitations.

1.1.2 Brønsted-Lowry Concept of Acids and Bases

) Activity 1.2

From what you have learnt in Grade 10 chemistry, reflect the following questions

- 1. Give two Brønsted-Lowry bases that are not Arrhenius bases.
- 2. How does Brønsted-Lowry concept of acids and bases differ from Arrhenius definition? What are the similarities?
- 3. 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?

In 1923, J. N. Brønsted in Denmark and T. M. Lowry in Great Britain independently proposed a new acid base theory. They pointed out that acid-base reactions can be seen as proton-transfer reactions and those acids and bases can be defined in terms of this proton (H) transfer. According to their concept, an acid is a proton donor and a base is a proton acceptor. Let's use the Brønsted–Lowry theory to describe the ionization of ammonia in aqueous solution



In this reaction water acts as an **acid**. It gives up a proton (H⁺) to NH_3 , a base. As a result of this transfer the polyatomic ions NH_4^+ and OH^- are formed- the same ions produced by the ionization of the hypothetical NH_4OH of the Arrhenius theory.

However, they cannot be called Arrhenius bases since in aqueous solution they do not dissociate to form OH^- . The advantage of this definition is that it is not limited to aqueous solutions. Bronsted-Lowry acids and bases always occur in pairs called **conjugate acid base pairs**.

1.1.3 Conjugate acid-base pairs

?) How are a Conjugate acid and a Conjugate base formed?

Conjugate acid-base pairs can be defined as an acid and its conjugate base or a base and its conjugate acid. The conjugate base of a Brønsted-Lowry acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted-Lowry base. Every Brønsted-Lowry acid has a conjugate base, and every Brønsted- Lowry base has a conjugate acid.

For example, the chloride ion (Cl^{-}) is the conjugate base formed from the acid HCl, and H_2O is the conjugate base of the acid H_3O^{+} . Similarly, the ionization of acetic acid can be represented as

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In the above reaction, CH_3COOH acts as an acid. It gives up a proton, H^+ , which is taken up by H_2O . Thus, H_2O acts as a base. In the reverse reaction, the hydronium ion, H_3O^+ , acts as an acid and CH_3COO^- acts as a base. When CH_3COOH loses a proton, it is converted into CH_3COO^- . Notice that the formulas of these two species differ by a single proton, H^+ . Species that differ by a single proton (H^+) constitute a conjugate acid-base pair. Within this pair, the species with the added H^+ is the acid, and the species without the H^+ is the base. For any conjugate acid-base pair,

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

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

	Conjug	ate pair				
Acid	+	Base	\rightleftharpoons	Base	+	Acid
		- E				1
			C	onjugate aci	d - base p	pair
HF	+	H_2O		F-	+	$H_{3}O^{+}$
НСООН	+	CN⁻		HCOO-	+	HCN
NH_4^+	+	CO32-		NH_3	+	HCO3-
$H_2PO_4^-$	+	OH-		HPO ₄ ²⁻	+	H_2O
H_2SO_4	+	$N_{2}H_{5}^{+}$		HSO ₄ -	+	N ₂ H ₆ ²⁺
HPO ₄ ²⁻	+	SO32-		PO ₄ ³⁻	+	HSO ₃ -

Table 1.1The conjugate pairs in some Acid-Base Reactions.

Example 1.1

 For each of the following reactions, which occur in aqueous solution, identify the Brønsted-Lowry acids and bases and their respective conjugates in each of the following reactions.

a. $NH_3 + H_2PO_4^- \rightleftharpoons NH_4^+ + HPO_4^{2-}$

b. $HCl + H_2PO_4^- \rightleftharpoons Cl^- + H_3PO_4$

Solution:

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

a. $H_2PO_4^-$ is converted to HPO_4^{2-} by donating a proton. So, $H_2PO_4^-$ is an acid, and HPO_4^{2-} is its conjugate base. NH_3 accepts the proton lost by the $H_2PO_4^-$. As a result, NH_3 is a base, and NH_4^+ is its conjugate acid.

 $\begin{array}{c} NH_{3}+H_{2}PO_{4}^{-}\rightleftharpoons NH_{4}^{+}+HPO_{4}^{2-}\\ Base Acid Acid Base \end{array}$

b. $H_2PO_4^-$ accepts a proton from *HCl*. Therefore, $H_2PO_4^-$ is a base and H_3PO_4 is its conjugate acid. *HCl* donates a proton to $H_2PO_4^-$. Thus, *HCl* is an acid, and *Cl⁻* is its conjugate base

 $\begin{array}{c} HCl + H_2PO_4^{-} \rightleftharpoons Cl^{-} + H_3PO_4\\ Acid & Base \end{array} \xrightarrow{} Cl^{-} + H_3PO_4\\ Acid & Acid \end{array}$

Strengths of Conjugate Acid-Base Pairs

The net direction of an acid-base reaction depends on relative acid and base strengths: A reaction proceeds to the greater extent in the direction in which a stronger acid and stronger base form a weaker acid and weaker base. 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 (chart 1.1) shows the strength of conjugate acid-base pairs.

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Chart 1.1 Strengths of Conjugate Acid-Base Pairs.

1.1.4 Auto ionization of substances

What is auto ionization? Do you familiar with it?

Molecular auto ionization (or self-ionization) is a reaction between two identical neutral molecules, especially in a solution, to produce an anion and a cation. If a pure liquid partially dissociates into ions, it is said to be self-ionizing. Water, as you know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base. Water functions as a base in reactions with acids such as HCI and CH_3COOH , and it

functions as an acid in reactions with bases such as NH_3 . Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent:





This reaction is sometimes called the **auto ionization of water**. 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

Do you think that a molecule or an ion can be both a donor and acceptor of protons?

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Molecules or ions that can either donate or accept a proton, depending on the other reactant, are called **amphiprotic species**. For example, $HCO_3^$ acts as an acid in the presence of OH^- but as a base in the presence of HF. The most important amphiprotic species is water itself. When an acid donates a proton to water, the water molecule is a proton acceptor, and hence a base. Conversely, when a base reacts with water, a water molecule donates a proton, and hence acts as an acid.

Consider, for example, the reactions of water with the base NH_3 and with

the acid CH_3COOH (acetic acid)



In the first case, water reacts as an acid with the base NH_3 . In the second case, water reacts as a base with the acid CH_3COOH .

Lewis concept of acids and bases

Activity 1.3

Please look and reflect on the following questions.

- What is the main difference between Lewis acid -base and Brønsted-Lowry acid – base concepts?
- 2. Are all Brønsted-Lowry acids and bases are also acids and bases according to Lewis concept?
- 3. Is there any limitation to the Brønsted-Lowry definition of acids and bases? Explain if any

G. N. Lewis, who proposed the electron-pair theory of covalent bonding, realized that the concept of acids and bases could be generalized to include reactions of acidic and basic oxides and many other reactions, as well as proton-transfer reactions.

According to this concept, the Lewis acid-base definition holds that

- > A base is any species that donates an electron pair to form a bond.
- > An acid is any species that accepts an electron pair to form a bond.

Consider, for example, the reaction of boron trifluoride with ammonia



The boron atom in boron trifluoride, BF_3 , has only six electrons in its valance 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, you should look for:

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

Example 1.2

- 1. Identify the acid and the base in each Lewis acid-base reaction.
 - a. $BH_3 + (CH_3)_2 S \rightarrow H_3 BS(CH_3)_2$
 - b. $CaO + CO_2 \rightarrow CaCO_3$

C. $BeCl_2 + 2Cl^- \rightarrow BeCl_4^{2-}$

Solution:

- a. In BH_3 , boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair of electrons. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3 . The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3 .
- b. CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
- c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus, the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.
- 2. Identify the acid and the base in each of Lewis acid–base reaction. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O : BF_3$

 $H_2O + SO_3 \rightarrow H_2SO_4$

Solution:

Lewis base: $(CH_3)_2O$; Lewis acid: BF_3

Lewis base: H_2O ; Lewis acid: SO_3

Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand I can.....

•	define acids, bases and Amphiprotic species	
•	describe Arrhenius concepts of bases and acids	
•	describe Bronsted- Lowery concepts of bases and acids	
•	describe Lewis concepts of bases and acids	
•	identify the conjugate pairs in some Acid-Base reactions	
•	describe auto-ionization of substances	

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Self-Test Exercise 1.1

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.
$$HBr(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$$

b.
$$NaCl(s) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq)$$

C.
$$NH_3(l) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$

d.
$$NaOH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq)$$

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

 $\texttt{a.} \ HClO_2 + H_2O \rightleftharpoons ClO_2^- + H_3O^+$

b. $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$

C. $H_2O + SO_3^{2-} \rightleftharpoons OH^- + HSO_3^-$

- 3. Define each of the following terms.
 - a. auto ionization b. amphiprotic species
- 4. Write equations to show the amphiprotic behavior of

a. $H_2 P O_4^{-}$

5. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated

b. *H*₂*O*

a. Cl^{-} , NO_{3}^{-} , $CH_{3}COO^{-}$, and NH_{3}

b. $HClO_4$, CH_3COOH , HNO_3 and HCl

- 6. What is the weakness of the Brønsted-Lowry acids and bases theory?
- 7. Write the self-ionization of ammonia.
- 8. Identify Lewis acids and Lewis bases in each of the following reactions.

a. $\mathrm{H}^+ + \mathrm{OH}^- \rightleftharpoons H_2 O$	d. $OH^- + Al(OH)_3 \rightleftharpoons Al(OH)_4^-$
b. $Cl^- + BCl_3 \rightleftharpoons BCl_4^-$	e. $CO_2 + H_2O \rightleftharpoons H_2CO_3$
$C. K^+ + 6H_2 O \rightleftharpoons K(H_2 O)_6^+$	f. $Ni + 4CO \rightleftharpoons Ni(CO)_4$

Section 1.2: Ionic Equilibria of Weak Acids and Bases

Dear learner, do you know that weak acid and base equilibrium refer to the equilibrium in weak acid and base reactions because of their partial ionization in a solution? Acid - base equilibria involve the transfer of protons between substances. Therefore, substances can be classified as acids or bases depending on their interaction with protons.

Objectives

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 why water is a weak electrolyte
- use K_w to calculate $\left\lceil H_3 O^+ \right\rceil$ or $\left\lceil OH^- \right\rceil$ in aqueous solution
- 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 $[H^+]$ 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 $[OH^-]$ and pOH of a basic solution from a given value of K_b and the initial concentration of the solution.

1.2.1 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?

Although pure water is often considered a non-electrolyte (nonconductor of electricity), precise measurements do show a very small conduction. This conduction results self-ionization (or auto-ionization) of water, a reaction in

which two like molecules react to give ions. The H_2O molecule can act as either an acid or a base; it is amphiprotic. It should come as no surprise that amongst themselves water molecules can produce H_3O^+ and OH^- ions via the following self-ionization reaction or auto-ionization reaction:

 $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$



Like any equilibrium process, the auto-ionization of water is described quantitatively by equilibrium constant:

$$K_{c} = \frac{\left[H_{3}O^{+}\right]\left[OH^{-}\right]}{\left[H_{2}O\right]^{2}}$$

Because the concentration of ions formed is very small and the concentration of H_2O remains essentially constant, about 56 M at 25°C, we multiply K_c by $[H_2O]^2$ to obtain a new equilibrium constant, the ion-product constant for water, K_w :

$$\left[H_2O\right]^2 K_c = \text{constant} = \left[H_3O^+\right]\left[OH^-\right]$$

We call the equilibrium value of the ion product $[H_3O^+][OH^-]$, the ionproduct constant for water, K_w . At 25°C, the value of K_w is 1.0 x 10⁻¹⁴. Like any equilibrium constant, K_w varies with temperature. At body temperature (37°C), K_w equals 2.5 x 10⁻¹⁴.

$$K_w = [H_3O^+][OH^-] = 1.0 \ x \ 10^{-14} \ at \ 25^{\circ}C$$

Because we often write $H^+(aq)$ for $H_3O^+(aq)$, the ion-product constant for water can be written

$$K_{w} = \left[H_{3}O^{+}\right]\left[OH^{-}\right]$$

Using K_w , you can calculate the concentrations of H_3O^+ and OH^- ions in pure water. These ions are produced in equal numbers in pure water, so their concentrations are equal. Let $x = [H_3O^+] = [OH^-]$. Then, substituting into the equation for the ion-product constant, $K_w = [H_3O^+][OH^-]$ you get at 25 °C, $1.0 \times 10^{-14} = x^2$ hence x equals 1.0×10^{-7} .

Thus, the concentrations of $\rm H_3O^+$ and $\it OH^-$ are both1.0 x 10-7 M in pure water.

If you add an acid or a base to water, the concentrations of H_3O^+ and OH^- will no longer be equal. The equilibrium-constant equation $K_w = [H_3O^+][OH^-]$ will still hold. In any aqueous solution at 25°C, no matter what it contains, the product of $[H_3O^+]$ and $[OH^-]$ must always equal 1.0 × 10^{-14} . The equilibrium nature of auto-ionization allows us to define "acidic" and "basic" solutions in terms of relative magnitudes of $[H_3O^+]$ and $[OH^-]$:

- i. a neutral solution, where $[H_3O^+] = [OH^-]$.
- ii. an acidic solution, where $[H_3O^+] > [OH^-]$.
- iii. a basic solution, where $\left[OH^{-}\right] > \left[H_{3}O^{+}\right]$

Activity 1.4

Answer the following concepts.

- 1. Many substances undergo auto-ionization in analogous to water. For example, the auto-ionization of liquid ammonia is: $2NH_3 \rightleftharpoons NH_4^+ + NH_2^$
 - a. Write K_c expression for auto-ionization of ammonia that is analogous to the K_w expression for water.
 - b. Name the strongest acidss and bases that can exist in liquid ammonia?
 - c. For water, a solution with $[OH^{-}] < [H_3O^{+}]$ is acidic. What are the analogous relationships in liquid ammonia?

Example 1.3

1. A research chemist adds a measured amount of HCl gas to pure water at 25 °C and obtains a solution with $[H_3O^+] = 3.0 \times 10^{-4}$ M. Calculate $[OH^-]$. . Is the solution neutral, acidic, or basic?

Solution: We use the known value of K_w at 25°C (1.0 x 10⁻¹⁴) and the given $[H_3O^+]$ (3.0x10⁻⁴M) to solve for $[OH^-]$. Then we compare $[H_3O^+]$ with $[OH^-]$ to determine whether the solution is acidic, basic, or neutral Calculate for the $[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}} = 3.3 \times 10^{-11} M$. Because $[H_3O^+] > [OH^-]$, the solution is acidic

1.2.2 The pH scale

It is a well-known fact that whether an aqueous solution is acidic, neutral, or basic depends on the hydronium-ion concentration. You can quantitatively describe the acidity by giving the hydronium-ion concentration. But because these concentration values may be very small, it is often more convenient to give the acidity in terms of pH, which is defined as the negative of the logarithm of the molar hydronium-ion concentration. pH is a measure of the hydronium ion content of a solution. It is also restated in terms of $[H_3O^+]$.

$$pH = -\log[H_3O^+]$$
 or $pH = -\log[H^+]$

Thus, in a solution that has $\left[H_3O^+\right] = 2.5 \ge 10^{-3} M$

$$pH = -\log(2.5 \times 10^{-3}) = 2.60$$

Note that the negative logarithm gives us positive numbers for pH. Like the equilibrium constant, the pH of a solution is a dimensionless quantity.

To determine the $[H_3O^+]$, that corresponds to a particular pH value, you do an inverse calculation. In a solution with pH = 4.5,

 $\log[H_3O^+] = -4.50$ and $[H_3O^+] = 10^{-4.50} = 3.2 \times 10^{-5} M$ The *pH* of a solution is measured by a *pH* -meter.



Figure 1.1 *pH* -meter.

A *pH* meter (figure 1.1) is commonly used in the laboratory to determine the *pH* of a solution. Although many *pH* meters have scales marked with values from 1 to 14, *pH* values can, in fact, be greater than 1 and less than 14. *pH* value 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*. For neutral solution, *pH* =

For acidic solutions pH < and

For basic solutions pH > 7

Activity 1.5

Check the color change of the following substances, using a litmus paper.

Substance	Color change	Acidic, Basic or Neutral
Beer		
Milk of magnesia		
(Magnesium hydroxide solution)		
Tomato juice		
Lemon juice		
Drinking water		

The pH notation has been extended to other exponential quantities. A pOH scale analogous to the pH scale can be devised using the negative logarithm of the hydroxide ion concentration of a solution. Thus, you can define pOH as:

 $pOH = -\log[OH^-]$

If you are given the pOH value of a solution and asked to calculate the OH^- ion concentration, we can take the antilog of the above equation as follows

$$\left[OH^{-}\right] = 10^{-pOH}$$

An important expression between pH and pOH can be obtained by considering the ion product for water at 25°C. $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ Taking the negative logarithm of both sides, you can obtain

-
$$(\log [H_3 O^+] + \log [OH^-]) = -\log(1.0 \times 10^{-14})$$

$$-\log\left[H_{3}O^{+}\right] + -\log\left[OH^{-}\right] = 14$$

From the definition of *pH* and *pOH* we obtain: pH + pOH = 14

Thus, in general, the sum of the pH and pOH values must equal to pK_w . This equation provides us with another way to express the relationship between

the H^+ ion concentration and the OH^- ion concentration.

Example 1.4

Calculate:

a. the *pH* and *pOH* of a juice solution in which $[H_3O^+]$ is 5.0×10^{-3} M

```
b. the [H_3O^+] and [OH^-] of human blood at pH = 7.40
Solution:
```

Q.
$$[H_3O^+] = 5.0 \ge 10^{-3}M$$

 $pH = ? \text{ and } pOH = ?$
 $pH = -\log[H_3O^+] = -\log(5.0 \ge 10^{-3})$
 $= 3 - \log 5.0 = 2.3$
 $pH + pOH = 14$
 $pOH = 14 - pH$
 $pOH = 14 - 2.3$
 $= 11.7$
b. $pH = 7.40, \ pOH = 14 - 7.40 = 6.6$
 $[H_3O^+] = ? \ [OH^-] = ?$
 $pH = -\log[H_3O^+] \ and \ pOH = -\log[OH^-]$
 $\log[H_3O^+] = -7.40 \ and \ \log[OH^-] = -6.6$
 $[H_3O^+] = 10^{-7.40} = 4.0 \ge 10^{-8}M \ and \ [OH^-] = 10^{-6.6} = 2.51 \le 10^{-7}M$

Measures of the strength of acids and bases in aqueous solution The strength of acids and bases depends on a number of factors Some of the ways to compare the strengths of acids and bases are the concentration of hydrogen and hydroxide ions, pH and pOH, percent dissociation, K_a and K_b for the reaction describing its ionization in water.

Concentration of hydrogen and hydroxide ions

How do the concentration of hydrogen and hydroxide ions affect acid and base strength?

A strong acid is one that completely dissociates in water to release proton. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions (H_3O^+) than do weaker acids. Examples of the strong acids are: hydrochloric acid (*HCl*)

, nitric acid (HNO_3), perchloric acid ($HClO_4$), and sulfuric acid (H_2SO_4). Each of these acids ionizes essentially 100% in solution. By contrast, however, a weak acid, being less willing to donate its proton, will only partially dissociate in solution. 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. The net direction of an acid-base reaction depends on relative acid and base strengths: a reaction proceeds to the greater extent in the direction in which a stronger acid and stronger base form a weaker acid and weaker base.

1.2.3 *pH* and *pOH*

If the pH of a solution at 25°C is 2, is it acidic, neutral or basic?

One way to determine the strength of acids is using the pH values. The acid strength increase with smaller pH value, 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 strength of base increases with decreasing the pOH value.

1.2.4 Percent Ionization

How is the percent ionization and acid and base strength related?

Another measure of the strength of an acid is its **percent ionization**, which is defined as the proportion of ionized molecules on a percentage basis. Mathematically:

 $Percent \ ionization = \frac{Ionized \ acid \ concentration \ at \ equilibrium}{Initial \ concentration \ of \ acid} \ x \ 100 \ \%$

The strength of an acid depends on the percentage of the acid molecules that dissociate in water solution.

As with acids, the measure of the strength of a base is its **percent ionization**, which is defined as the proportion of ionized molecules on a percentage basis. Mathematically:

 $percent \ ionization = \frac{Ionized \ base \ concentration \ at \ equilibrium}{Iniotial \ concentration \ of \ base} \ x \ 100 \ \%$

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The percent ionization increases with base strength.

Strong acids and strong bases ionize nearly completely in water. But weak acids and weak bases dissociate partially in water, and their percent of ionization is small.

Dissociation (Ionization) Constants

Acid ionization Constant, K_a

) What is the relationship between strength of acids with their aciddissociation constant values?

The acid ionization constant or dissociation constant is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for the reaction of dissociation of acid into its conjugate base and hydrogen ion. Acid dissociation constant of weak acid *HA* like acetic acid, formic acid can be written as:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

the dissociation-constant expression can be written as:

$$K = \frac{\left[H_3 O^+\right] \left[A^-\right]}{\left[H_2 O\right] \left[HA\right]}$$

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

$$K[H_2O] = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

The product of the two constants, K and $[H_2O]$, 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:

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[A^{-}\right]}{\left[HA\right]}$$

Acids are classified as either strong or weak, based on their ionization in water. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. The ionization-constants of some weak monoprotic acids are tabulated in table 1.2.

Name of the Acid	Formula	K _a
Acetic acid	CH ₃ COOH	1.8 × 10 ⁻⁵
Ascorbic acid	$C_{6}H_{8}O_{6}$	8.0 × 10 ⁻⁵
Benzoic Acid	C ₆ H₅COOH	6.5 × 10⁻⁵
Formic acid	НСООН	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

Table 1.2 Ionization constant of some weak monoprotic acids at 25°C.
Example 1.5

1. A 0.250 M aqueous solution of butyric acid is found to have a pH of 2.72. Determine K_a for butyric acid

Solution:

	$CH_3(CH_2)_2COOH(aq$	$H_1 \rightarrow H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + H_2O(l) $	$CH_3(CH_2)_2COO^-$	(aq)
Initial conc.	0.250 M			
Changes	- x	$+_{\rm X}$	$+_{\rm X}$	
equilib. conc.	0.250 M – x	Х	Х	

x is a known quantity, It is the $[H_3O^+]$ in solution, which we can determine from the pH.

 $\log \left[H_3 O^+ \right] = -pH = -2.72$ $\left[H_3 O^+ \right] = 10^{-2.72} = 1.9 \ x \ 10^{-3} M$

Now we can solve the following expression for K_a by substituting in the value

$$x = 1.9 \times 10^{-3} M$$

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[CH_{3}(CH_{2})_{2}COO^{-}\right]}{\left[CH_{3}(CH_{2})_{2}COOH\right]} = \frac{x.x}{0.250 - x}$$

$$K_{a} = \frac{(1.9 \times 10^{-3})(1.9 \times 10^{-3})}{0.250 - 1.9 \times 10^{-3}} = 1.5 \times 10^{-5}$$

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

HF is given by $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

Solution: The species that can affect the pH of the solution are HF, and the conjugate base ,

Let x be the equilibrium concentration of H_3O^+ and F^- ions in molarity (**M**). Thus

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Initial conc. 0.50		
Changes – x	$+_{\mathbf{X}}$	$+_{\mathbf{X}}$
Equil. conc. $0.50 - x$	Х	Х
$K = \frac{\left[H_3 O^+\right] \left[F^-\right]}{\left[F^-\right]}$		

$$K_a = \frac{\left[H_3O^+\right]\left[F^-\right]}{\left[HF\right]}$$

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

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

Rearranging this expression provides: $x^2 + (6.8 \times 10^{-4}) \times -3.4 \times 10^{-4} = 0$ 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

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

Rearranging this equation gives:

$$x^2 = (0.50)(6.8 \ x \ 10^{-4}) = 3.4 \ x \ 10^{-4}$$

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

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

$$[HF] = (0.50 - 0.018)M = 0.48 M$$

 $[F^{-}] = [H_3O^{+}] = 0.018 M$

and the pH of the solution is $pH = -\log(0.018) = 1.74$

How good is this approximation? Because K_a values for weak acids are generally known to an accuracy of only ± 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%.

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

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3. What is the percent ionization of acetic acid in a 0.100M solution of

acetic acid, CH_3COOH ?

Solution:

 $\begin{array}{ccc} CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq), \ K_a = 1.8 \ x \ 10^{-5} \\ \mbox{Initial conc.} & 0.100 \ M & ---- & ---- \\ \mbox{Changes} & -x & +x & +x \\ \mbox{Equilib conc.} & 0.100 \ M - x & x & x \end{array}$

x is a known quantity, it is $[H_3O^+]$ in solution, which we can determine from

the K_a

 $K_{a} = \frac{\left[H_{3}O^{+}\right]\left[CH_{3}COO^{-}\right]}{\left[CH_{3}COOH\right]}$

Substituting the concentration of CH_3COOH , H_3O^+ and CH_3COO^- , in terms of x, gives:

$$K_a = \frac{(x)(x)}{(0.100 - x)}$$

1.8 x 10⁻⁵ = $\frac{x^2}{0.100 - x}$

Since CH_3COOH is a weak acid, and weak acids ionize only to a slight extent, **x** must be small compared to 0.10. Therefore, you can make the approximation: $0.10 - x \approx 0.10$.

Now, the equation becomes $(1.8 \times 10^{-5})(0.100) = x^2$

 $x = \sqrt{1.8 \ x \ 10^{-6}} = 1.342 \ x \ 10^{-3}$

Percent ionization = $\frac{1.342 \times 10^{-3}}{0.100} \times 100 \% = 1.342 \%$

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.

Base dissociation constant, K_b

Equilibria involving weak bases are treated similarly to those for weak acids.

Ammonia, for example, ionizes in water as follows:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The corresponding equilibrium constant is:

$$K_{c} = \frac{\left[NH_{4}^{+}\right]\left[OH^{-}\right]}{\left[NH_{3}\right]\left[H_{2}O\right]}$$

Because the concentration of H_2O is nearly constant, you can rearrange this equation as you did for acid ionization.

$$K_{b} = K_{c} \left[H_{2}O \right] = \frac{\left[NH_{4}^{+} \right] \left[OH^{-} \right]}{\left[NH_{3} \right]}$$

where K_b is the base dissociation constant.

In general, a weak base B with the base ionization

 $B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$

has a base-ionization constant, K_b (the equilibrium constant for the ionization of a weak base), equal to:

$$K_{b} = \frac{\left[HB^{+}\right]\left[OH^{-}\right]}{\left[B\right]}$$

Note that K_b values for strong bases are large, while K_b values for weak bases are small.

Table	1.3 shows the	K_b values	of some	common	weak bases	at 25°C.

Base	Formula	K_b
Ammonia	NH ₃	1.8 × 10–5
Aniline	$C_6H_5NH_2$	4.0 × 10–10
Ethylamine	$C_2H_5NH_2$	4.7 × 10–4
Hydrazine	C_2H_4	1.7 × 10–6
Hydroxylamine	NH ₂ OH	1.1 × 10–6
Methylamine	CH ₃ NH ₂	4.4 × 10–4
Pyridine	C_5H_5N	1.7 × 10–9

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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
$$\left[OH^{-} \right]$$
 first, instead of $\left[H^{+} \right]$

Example 1.6

1. What is the hydroxide-ion concentration of a 0.20 M solution of ammonia in water? $K_{\rm b}$ = 1.8 × 10⁻⁵

Solution:

	$NH_3(aq) +$	$H_2O(l) \rightleftharpoons NH_4^+(aq)$	$(q) + OH^{-}(aq)$	<u>(</u>)
initial conc.	0.20 M			
changes	- X	$+_{\mathbf{X}}$	$+_{\mathbf{X}}$	
equlib.conc.	0.20M-x	Х	Х	

The equilibrium equation for the reaction is given by: $K_b = \frac{\left[NH_4^+ \right] \left[OH^- \right]}{NH_3}$ Substituting the concentration of NH_3 , NH_4^+ and OH^- in terms of x, gives:

$$K_b = \frac{(x)(x)}{(0.20 - x)}$$
$$1.8 \ x \ 10^{-5} = \frac{x^2}{0.20 - x}$$

Since NH_3 is a weak base, and weak bases ionize only to a slight extent, x must be small compared to 0.20. Therefore, you can make the approximation: $0.20 - x \approx 0.20$

Now, the equation becomes $(1.8 \times 10^{-5})(0.20) = x^2$

 $\mathbf{x} = \sqrt{3.6 \ x \ 10^{-6}} = 1.897 \ x \ 10^{-3}$

The hydroxide ion concentration is $\,1.897\,\times\,10^{\text{-3}}$ M

🕖 CHECKLIST - 1. 2

Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand

I can.....

- define percent ionization
- describe how the concentration of hydrogen and hydroxide ions affect acid and base strength
- give mathematical expression for ion product constant for water
- give mathematical expression for base and acid dissociation constant
- describe the relationship between strength of acids with their acid dissociation constant values
- calculate the pH of weak acids
- describe how the percent ionization and acid strength related
- determine the acid strength of acids using pH values.
- determine the base strength of bases using pOH values
- describe how the concentration of hydrogen and hydroxide ions affect acid and base strength.

Self-Test Exercise 1.2

1. Calculate $[H^+]$ or $[OH^-]$, as required, for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

a.
$$[H^+] = 1.0 \times 10^{-7} M$$

b.
$$[OH^{-}] = 1.0 \times 10^{-4} M$$

c. $[OH^{-}] = 1.0 \times 10^{-8} M$

2. Calculate the concentration of OH^- in a solution in which

a.
$$\begin{bmatrix} H_3 O^+ \end{bmatrix} = 2.0 \times 10^{-5} M$$

b. $\begin{bmatrix} H_3 O^+ \end{bmatrix} = \begin{bmatrix} OH^- \end{bmatrix}$
c. $\begin{bmatrix} H_3 O^+ \end{bmatrix} = 10^2 \times \begin{bmatrix} OH^- \end{bmatrix}$

Γ	٦

- 3. Calculate $[H_3O^+]$ in a solution that is at 25°C and has $[OH^-] = 6.7 \times 10^{-2} M$. Is the solution neutral, acidic, or basic?
- 4. Why water is a weak electrolyte?
- 5. A solution formed by dissolving an antacid tablet has a pH of 9.18 at

25°C. Calculate $\left[H^{+}\right]$, $\left[OH^{-}\right]$ and pOH.

6. 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 $[H^+]$, $[OH^-]$, *pH* and *pOH* of the three solutions.

- 7. Calculate the percent ionization of a 0.10M solution of acetic acid with a pH of 2.89
- 8. Calculate the pH of a 0.10 M solution of acetic acid. $K_a = 1.8 \times 10^{-5}$
- 9. for a 0.036 M HNO₂ solution.
 - a. Write a chemical equation that shows the ionization of nitrous acid in water.
 - b. Calculate the equilibrium concentration of hydrogenions at 25°C, using the approximation method. Then check whether the approximation is valid or not.
 - c. If the approximation is invalid, use the quadratic formula to calculate the concentration of hydrogen ions.
 - d. Calculate the pH of the solution.
- 10. For a 0.040 M ammonia solution:
 - a. Write a chemical equation that shows the ionization of ammonia in water.
 - b. Calculate the equilibrium concentration of ammonia, ammonium ions and hydroxide ions, using the approximation method. Check whether the approximation is valid or not.
 - c. If the approximation is invalid, use the quadratic formula to calculate the concentration of ammonia, ammonium ions and hydroxide ions.
 - d. Calculate the pOH and pH of the solution.

Section 1.3: Common ion Effect and Buffer Solution

Dear learner, do you know the "Common Ion Effect?": The dissociation of a weak electrolyte is decreased by adding to the solution a strong electrolyte (i.e. a salt) that has an ion in common with the weak electrolyte.

Solutions that resist a change in pH upon addition of small amounts of acid or base are called "Buffered" solutions (or just "Buffers")

Objective

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 CH₃COOH / CH₃COONa

1.3.1 The Common ion Effect

Activity 1.6

In Grade 11 Chemistry, you learned Le Chatelier's principle. Based on your knowledge of grade 11 chemistry analyze the following questions.

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

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The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion that takes part in the equilibrium. The common-ion effect occurs when a given ion is added to an equilibrium mixture that already contains that ion.

Consider a solution of acetic acid, CH_3COOH , in which you have the following acid-ionization equilibrium:

 $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$



Suppose you add HCI (aq) to this solution. What is the effect on the acid-ionization equilibrium?

Because HCl (aq) is a strong acid, it provides H_3O^+ ion, which is present on the right side of the equation for acetic acid ionization. According to LeChâtelier's principle, the equilibrium composition should shift to the left

$$CH_3COOH(aq) + H_2O(l) \leftarrow CH_3COO^-(aq) + H_3O^+(aq)$$

added

The degree of ionization of acetic acid is decreased by the addition of a strong acid. This repression of the ionization of acetic acid by *HCl* (aq) is an example of the common-ion effect. Another example is, if sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions, we can represent the effect of acetate salts on the acetic acid equilibrium as:



Section 1.3: Common ion Effect and Buffer Solution

Buffer Solutions

How does a buffer solution resist a pH change?

A buffer is commonly defined as a solution that resists changes in pH when a small amount of acid or base is added or when the solution is diluted with pure solvent. This property is extremely useful in maintaining the pH of a chemical system at an optimum value to appropriately influence the reaction kinetics or equilibrium processes. A buffer solution actually is a mixture of a weak acid and its conjugate base or a mixture of a weak base and its conjugate acid. The conjugate forms are commonly referred to as "salts". Comparison of buffered and unbuffered solutions are given in table 1.4

	Initial pH of	pH after addition	pH after
	1.0 L sample	of 0.010 mol	addition of
		NaOH	0.010 mol HCI
Un buffered solution:	4.8	12.0	2.0
1.28 × 10 ⁻⁵ M HCl			
Buffered solution:			
0.099M <i>CH</i> ₃ COOH	4.8	4.8	4.7
0.097M <i>CH</i> ₃ COONa			

Table 1.4 Comparison of buffered and un buffered solutions.

A buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that may be added to it. Similarly it must contain a large concentration of base to react with any added H^+ ions. Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair (a weak acid and its conjugate base or a weak base and its conjugate acid).

A simple buffer solution can be prepared by adding comparable amounts of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) to water. The equilibrium concentrations of both the acid and the conjugate base (from CH_3COONa) are assumed to be the same as the starting concentrations. This is so because CH_3COOH is a weak acid and the extent of hydrolysis of the CH_3COO^- ion is very small and the presence of CH_3COO^- ions suppresses the ionization of CH_3COOH , and the presence of CH_3COOH suppresses the hydrolysis of the CH_3COO^- ions

A solution containing these two substances has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociates

completely in water: $CH_3COONa(s) \xrightarrow{H_2O} CH_3COO^-(aq) + Na^+(aq)$

If an acid is added, the H^+ ions will be consumed by the conjugate base in the buffer, CH_3COO^{-} , according to the equation

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

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 stomachs has a pH of about 1.5. These pH values, which are crucial for the proper functioning of enzymes and the balance of osmotic pressure, are maintained by buffers in most cases. The pH of a buffer solution can be estimated with the help of Henderson–Hasselbalch equation when the concentration of the acid and its conjugate base, or the base and the corresponding conjugate acid, are known. The Henderson-Hasselbach equation is derived from the definition of the acid dissociation constant as follows.

Consider the hypothetical compound HA in water. The dissociation equation and K_a expression are $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

The key variable that determines $[H O^+]$ is the concentration ratio of acid species to base species, so, rearranging to isolate $[H_3O^+]$ gives

$$\left[H_3O^+\right] = K_a \ x \ \frac{\left[HA\right]}{\left[A^-\right]}$$

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Taking the negative logarithm of both sides gives

$$-\log\left[H_{3}O^{+}\right] = -\log K_{a} - \log \left(\frac{\left[HA\right]}{\left[A^{-}\right]}\right)$$

from which definitions gives $pH = pK_a - \log\left(\frac{[HA]}{[A^-]}\right)$

Rearranging the equation gives

$$pH = pK_a + \log\left(\frac{\left[A^{-}\right]}{\left[HA\right]}\right)$$

Generalizing the previous equation for any conjugate acid-base pair gives the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[Conjugate \ base]}{[weak \ acid]}\right)$$

Similarly, for a weak base dissociation:

$$pOH = pK_b + \log\left(\frac{[Conjugate \ acid]}{[weak \ base]}\right)$$

Example 1.8

What is the pH of a buffer solution consisting of 0.035M NH_3 and 0.050

M NH_4^+ (K_a for NH₄⁺ is 5.6 x 10⁻¹⁰)? The equation for the reaction is:

 $NH_4^+ \rightleftharpoons H^+ + NH_3$

Assuming that the change in concentrations is negligible in order for the system to reach equilibrium, the Henderson-Hasselbalch equation will be:

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$
$$pH = 9.23 + \log\left(\frac{0.035}{0.050}\right) pH = 9.095$$

A buffer is made by mixing 0.060 M $\it NH_3$ with 0.040 M $\rm NH_4Cl.$ What is the pH

of this buffer? $K_b = 1.8 \ x \ 10^{-5}$

Solution: The buffer contains a base and its conjugate acid in equilibrium. The equation is

 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Assuming that the change in concentrations is negligible in order for the system to reach equilibrium, the Henderson-Hasselbalch equation will be:

$$pOH = pK_{b} + \log\left(\frac{[Conjugate \ acid]}{[weak \ base]}\right)$$

$$pOH = pK_{b} + \log\left(\frac{NH_{4}^{+}}{NH_{3}}\right)$$

$$pOH = 4.745 + \log\left(\frac{0.04}{0.06}\right)$$

$$pOH = 4.745 - 0.1761$$

$$= 4.5689$$

$$pH = 14 - pOH$$

$$= 14 - 4.5689$$

$$= 9.4311$$

CHECKLIST - 1.3

Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand I can.....

- define common ion effect and buffer solution
- describe how a buffer solution resists a pH change
- give mathematical expression for Henderson-Hasselbalch equation
- Compare buffered and unbuffered solutions

Self-Test Exercise 1.3

- 1. Calculate the pH of a solution containing 0.20 M CH_3COOH and 0.30 M CH_3COONa
- 2. What would be the pH of a 0.20 M CH_3COOH solution if no salt were present?
- 3. Calculate the pH:
 - a. of a buffer solution containing 0.1 M CH₃COOH and a 0.1 M solution of CH₃COONa
 - 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.

Section 1.4: Hydrolysis of Salts

Dear learner, hydrolysis is a common form of a chemical reaction where water is mostly used to break down the chemical bonds that exist between particular substances. Hydrolysis is derived from a Greek word **hydro** meaning water and **lysis** meaning break or to unbind. Usually in hydrolysis the water molecules get attached to two parts of a molecule. One molecule of a substance will get H^+ ion and the other molecule receives the OH^- group. The term salt hydrolysis describes the "interaction of anion and 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.

Objectives

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.

1.4.1 Hydrolysis of Salts of Strong Acids and Strong Bases

The reaction between a strong acid (say, *HCl*) and a strong base (say, *NaOH*) can be represented by

 $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ or in terms of the net ionic equation

 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

The anions derived from strong acids are weak conjugate bases and do not undergo hydrolysis. The cations derived from strong bases are weak conjugate acids and also do not hydrolysis. For the above reaction, chloride ions, Cl^- , and sodium ions, Na^+ , do not hydrolyze, It involves only ionization of water and no hydrolysis. The solution of the salt will be **neutral (***pH* **=7)**.

Hydrolysis of Salts of weak acids and strong bases

Consider the neutralization reaction between acetic acid (a weak acid) and sodium hydroxide (a strong base):

 $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(aq)$

This equation can be simplified to:

 $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(aq)$

The acetate ion undergoes hydrolysis as follows:

 $CH_3COO^{-}(aq) + H_2O(aq) \rightarrow CH_3COOH(aq) + OH^{-}(aq)$

Therefore, at the equivalence point, when only sodium acetate present, the pH will be greater than 7 as a result of the excess OH^- ions formed. Note that this situation is analogous to the hydrolysis of sodium acetate (CH_3COONa) . Solutions of these salts are basic because the anion of the weak acid is a moderately strong base and can be hydrolyzed.

1.4.2 Hydrolysis of Salts of strong acids and weak bases

When you neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a strong acid. For example, ammonium chloride, NH_4Cl , is a salt formed by the reaction of the weak base ammonia with the strong acid HCl: $NH_3(aq)+HCl(aq) \rightarrow NH_4Cl(aq)$

A solution of this salt contains ammonium ions and chloride ions. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration: $NH_4^+(aq) + H_2O(1) \rightarrow H_3O^+(aq) + NH_3(aq)$

1.4.3 Hydrolysis of Salts of weak acids and weak bases

Solutions of a salt formed by the reaction of a weak acid and a weak base involve both cationic and anionic hydrolysis. To predict whether the solution is acidic or basic you need to compare the K_a of the weak acid and the K_b of the weak base. If the K_a is greater than the K_b , the solution is acidic, and if the K_a is less than the K_b , the solution is basic. If they are equal the solution is neutral. As an example consider solutions of ammonium formate, NH_4CHO_2 . These solutions are slightly acidic, because the K_a for NH_4^+ (5.6x 10^{-10}) is somewhat larger than the K_b for format ion, CHO_2^- (5.9x 10^{-11}).



In the following table you are given K_a and K_b values of some cations and anions, respectively. After completing your work reflect the answer for yourself.

Anion	K_b	Cation	K _a
F^-	1.4 × 10 ⁻¹¹	$\mathrm{N}H_4^{+}$	5.6 × 10 ⁻¹⁰
CNS^-	2.0 × 10 ⁻⁵		
CH₃COO⁻	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.

CHECKLIST - 1.4

Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand

l can.....

- define hydrolysis
- describe the Hydrolysis of Salts of Strong Acids and Strong Bases
- describe the Hydrolysis of Salts of weak acids and strong bases
- describe the Hydrolysis of Salts of strong acids and weak bases
- describe the Hydrolysis of Salts of weak acids and week bases
- predict whether the solution is acidic or basic by comparing the Ka
 of the weak acid and the Kb of the weak base

Self-Test Exercise 1.4

Consider Na₂CO₃ and answer the following:

- 1. what are the parent acid and base of this salt?
- 2. Which ions of the salt can be hydrolyzed?
- 3. What will be the nature of Na₂CO₃ solution? Will it be acidic, basic or neutral?

Section 1.5: Acid–Base Indicators and Titrations

Dear learner, an acid-base titration is an experimental technique used to acquire information about a solution containing an acid or base. Hundreds of compounds both organic and inorganic can be determined by a titration based on their acidic or basic properties. Acid is titrated with a base and base is titrated with an acid. That is an acid-base titration is the addition of a volume of base of known concentration to acid of unknown concentration (or addition of acid to base). The endpoint is usually detected by adding an indicator. An acid – base titration involves strong or weak acids or bases. Specifically, an acid – base titration can be used to figure out the following.

- The concentration of an acid or base
- Whether an unknown acid or base is strong or weak.
- pK_a of an unknown acid or pK_b of the unknown base.

Objectives

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;
- distinguish between end point and equivalent point; and
- discuss the different types of titration curves

1.5.1 Acid–Base Indicators

How do acid-base indicators change color?

Acid-base indicators are weak organic acids (denoted here as HIn) or weak organic bases (In^-) that indicate whether a solution is acidic, basic or neutral. The color of the indicator depends on the pH of the solution to which it is added. When just a small amount of indicator is added to a solution, the indicator does not affect the pH of the solution. Instead, the ionization equilibrium of the indicator is affected by the prevailing $[H_3O^+]$ in the solution

 $\underset{Acid \ colour}{HIn} + H_2 O \rightleftharpoons H_3 O^+ + \underset{Base \ colour}{In^-}$

If the indicator is in a sufficiently acidic medium[increasing $[H_3O^+]$], the equilibrium, according to Le Châtelier's principle, shifts to the left and the predominant color of the indicator is that of the non-ionized form (*HIn*).

On the other hand, in a basic medium [decreasing $[H_3O^+]$] the equilibrium shifts to the right and the color of the solution will be blue due to that of the conjugate base (In^-).

An acid-base indicator is usually prepared as a solution (in water, ethanol, or some other solvent). In acid-base titrations, a few drops of the indicator solution are added to the solution being titrated. In other applications, porous paper is impregnated with an indicator solution and dried. When this paper is moistened with the solution being tested, it acquires a color determined by the pH of the solution. This paper is usually called pH test paper.

Indicator change	Acid	Base	pH range of
malcalor change	Color	Color	Color
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
Phenolphthalein	Colorless	Pink	8.2 – 10.0

Example 1.9

1. What is the pH of a buffer prepared with 0.40 M CH_3COOH and 0.20 M

 CH_3COO^- if the K_a of CH_3COOH is 1.8 x 10 ⁻⁵?. Which type of indicator is used to check the acidity or basicity of this solution?

Solution:

$$\left[H_{3}O^{+}\right] = K_{a} x \frac{\left[CH_{3}COOH\right]}{\left[CH_{3}COO^{-}\right]} = 1.8 x 10^{-5} M x \frac{0.40}{0.20}$$

 $[H_3O^+] = 3.6 \ x \ 10^{-5} M$

 $pH = -\log(3.6 \ x \ 10^{-5}) = 4.44$

The pH value indicates that the solution is acidic. You can refer the type of indicators from Table 1.5.

1.5.2 Equivalents of Acids and Bases

Activity 1.8

Attempt the following questions.

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

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An equivalent is the amount of a substance that reacts with an arbitrary amount (typically one mole) of another substance in a given chemical reaction. In a more formal definition, the equivalent is the amount of a substance needed to react with or supply one mole of hydrogen ions (H⁺) in an acid–base reaction.

For example for Sulfuric acid (H_2SO_4) an equivalent is 2.

For bases, it is the number of hydroxide ions (OH^-) ions provided for a reaction, for example for barium hydroxide $(Ba(OH)_2)$ equivalents is equal to 2.

The normality of a solution refers to the number of equivalents of solute per Liter of solution.

Normality = $\frac{Number of equivalents of solutes}{Liters of solution}$

The definition of chemical equivalent depends on the substance or type of chemical reaction under consideration. Because the concept of equivalents is based on the reacting power of an element or compound, it follows that a specific number of equivalents of one substance will react with the same number of equivalents of another substance. When the concept of equivalents is taken into consideration, it is less likely that chemicals will be wasted as excess amounts. Keeping in mind that normality is a measure of the reacting power of a solution; you can use the following equation to determine normality. Thus, according to the definition of normality, the number of equivalents is the normality multiplied by the volume of solution, in litters. If we add enough acid to neutralize a given volume of base, the following equation holds:

 $N_1 V_1 = N_2 V_2$

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 1.10
1. What volume of 2.0 N <i>NaOH</i> is required to neutralize 25.0 mL of 2.70 N
H_2SO_4 ?
Solution:
$N_1 V_1 = N_2 V_2$
$V_2 = \frac{N_1 V_1}{N_2}$
$V_2 NaOH = \frac{(2.7N H_2SO_4)(25.0 mL H_2SO_4)}{2.0N NaOH}$
$= 33.8 \ mL$

1.5.3 Acid–Base Titrations

) What does an acid base titration mean?

An acid-base titration is a procedure for determining the amount of acid (or base) in a solution by determining the volume of base (or acid) of known concentration that will completely react with it. In a titration, one of the solutions to be neutralized say, the acid is placed in a flask or beaker, together with a few drops of an acid base indicator (Figure 1.2). The other solution (the base) used in a titration is added from a burette and is called the titrant. The titrant is added to the acid (Titrand or analyte), first rapidly and then drop by drop, up to the equivalence point. The equivalence point of the titration is the point at which the amount of titrant added is just enough to completely neutralize the analyte solution. At the equivalence point in an acid-base titration, moles of base are equal to moles of acid and the solution contains only salt and water. The equivalence point is located by noting the color change of the acid base indicator. The point in a titration at which the indicator changes color is called the end point of the indicator. The end point must match the equivalence point of the neutralization. That is, if the indicators end point is near the equivalence point of the neutralization, the color change marked by that end point will signal the attainment of the equivalence point.

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This match can be achieved by use of an indicator whose color change occurs over a pH range that includes the pH of the equivalence point. Knowing the volume of titrant added allows the determination of the concentration of the unknown analyte using the following relation

volume of base x concentration of base = volume of acid x unknown concentration of acid

unknown concentration of $acid = \frac{volume \ of \ base \ x \ concentration \ of \ base}{volume \ of \ acid}$



Figure 1.2 The Techniques of Titration.

Experiment 1.1

Dear learner, to understand about the Acid-base Titration very well, perform the follow-ing experiment. To conduct the experiment, visit a nearby high school and request a teacher who is teaching Grade 12 chemistry to help you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory. If you couldn't find a high school in your area, request your tutor to get support and advices.

Title: 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 1.1).
- 2. Using a funnel, introduce 0.1 N sodium hydroxide solutions into the burette. Allow some of the solution to flow out and make sure that there are no air bubbles in the solution (why?).
- 3. Record level of the solution, corresponding to the bottom of the meniscus, to the nearest 0.1 mL.
- 4. Measure exactly 10 mL of hydrochloric acid solution (given) with the help of a10 mL pipette and add it into a clean 150 mL Erlenmeyer flask and add two or three drops of phenolphthalein indicator.
- 5. 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 stopcock 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 color comes which disappears on swirling.
- Add more sodium hydroxide drop wise until the pink color persists for a few seconds.
- Find the difference between the initial level and the end point level of the burette.

Observations and analysis:

- 1. Color 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 difference between equivalence point and end point for a chemical reaction (acid base titeration)?



Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand

l can.....

- define acid base indicators, acid base titrations an acid base titration curve
- describe how acid-base indicators change color
- give mathematical expression for normality
- calculate the equivalents of acids and bases
- identify the color change of some common indicators

Self-Test Exercise 1.5

Reflect on the following questions.

- 1. How is an indicator selected for detecting the pH change in acid-base titrations?
- 2. If 83 mL of 0.45 M NaOH solution neutralizes a 235 mL HCl solution. Calculate the molarity of the HCl solution.
- 3. A 25.0-mL solution of 0.100 M acetic acid is titrated with a 0.200 M NaOH solution. Calculate the pH of the solution before the addition of NaOH $(K_{a}$ for acetic acid is 1.77 x 10⁻⁵.)
- 4. A 108.6 mL sample of 0.100 M methylamine (CH₃NH₂, K_b = 4.4 x 10⁻⁴) is titrated with 0.250 M HNO₃. Calculate the pOH and pH of the solution before the addition of HNO₃.
- 5. Give the reason for the following statement: The addition of CH_3COONa to CH_3COOH increases the pH whereas the addition of NH_4CI to aqueous ammonia solution (NH_4OH) decreases the pH of the system.

Unit Summary

- By the Arrhenius definition, an Arrhenius acid produces H^+ and an Arrhenius base produces OH^- in aqueous solutions. And an acid-base reaction (neutralization) is the reaction of H^+ and OH^- to form H_2O . The Arrhenius definition of acids and bases has many limitations but still we cannot ignore it.
- The Brønsted-Lowry acid-base definition does not require that bases contain OH⁻ in their formula or that acid-base reactions occur in aqueous solution. An acid is a species that donates a proton and a base is one that accepts it, so an acid-base reaction is a proton-transfer process. When an acid donates a proton, it becomes the conjugate base; when a base accepts a proton, it becomes the conjugate acid. In an acid-base reaction, acids and bases form their conjugates. A stronger acid has a weaker conjugate base, and vice versa.

- Brønsted-Lowry bases include NH_3 and amines and the anions of weak acids. All produce basic solutions by accepting H^+ from water, which yields OH^- , thus making $[H_3O^+] < [OH^-]$
- The Lewis acid-base definition focuses on the donation or acceptance of an electron pair to form a new covalent bond in an adduct, the product of an acid-base reaction. Lewis bases donate the electron pair, and Lewis acids accept it. Thus, many species that do not contain H^+ act as Lewis acids; examples are molecules with electron-deficient atoms and those with polar double bonds. Metal ions act as Lewis acids when they dissolve in water, which acts as a Lewis base, to form the adduct, a hydrated cation
- Pure water auto ionizes to a small extent in a process whose equilibrium constant is the ion product constant for water, K_w (1.0 x 10⁻¹⁴ at 25 °C). $\begin{bmatrix} H_3O^+ \end{bmatrix}$ and $\begin{bmatrix} OH^- \end{bmatrix}$ are inversely related: in acidic solution, $\begin{bmatrix} H_3O^+ \end{bmatrix}$ is greater than $\begin{bmatrix} OH^- \end{bmatrix}$; the reverse is true in basic solution; and the two are equal in neutral solution. To express small values of $\begin{bmatrix} H_3O^+ \end{bmatrix}$, we use the pH scale ($pH = -\log[H_3O^+]$). Similarly, $pOH = -\log[OH^-]$ and $pK = -\log K$
- A high *pH* represents a $low[H_3O^+]$. In acidic solutions, *pH* < 7; in basic solutions, *pH* > 7; and in neutral solutions *pH* = 7. The sum of *pH* and pOH equals *pK*_w (14.00 at 25 °C).
- Acid strength depends on $[H_3O^+]$ relative to [HA] in aqueous solution. Strong acids dissociate completely and weak acids slightly.
- The extent of dissociation is expressed by the acid-dissociation constant, K_a . Most weak acids have K_a values ranging from about 10⁻²to 10⁻¹⁰.
- The *pH* of a buffered solution changes much less than the *pH* of an unbuffered solution when $[H_3O^+]$ or OH^- is added.
- An acid-base reaction proceeds to the greater extent in the direction in which a stronger acid and base form a weaker base and acid.
- Two common types of weak-acid equilibrium problems involve finding K_a from a given concentration and finding a concentration from a given K_a .

- The extent to which a weak base accepts a proton from water to form OH^- is expressed by a base-dissociation constant, K_b .
- By multiplying the expressions for K_a of HA and K_b of A^- , we obtain K_w . This relationship allows us to calculate either K_a of BH^+ or K_b of A^- .
- A buffer consists of a weak acid and its conjugate base (or a weak base and its conjugate acid). To be effective, the amounts of the components must be much greater than the amount of $[H_3O^+]$ or OH^- added.
- The buffer-component concentration ratio determines the pH; the ratio and the pH are related by the Henderson-Hasselbalch equation.
- When $[H_3O^+]$ or OH^- is added to a buffer, one component reacts to form the other; thus $[H_3O^+]$ (and pH) changes only slightly.
- A concentrated (higher capacity) buffer undergoes smaller changes in pH than a dilute buffer. When the buffer pH equals the pK_a of the acid component, the buffer has its highest capacity.

Self-assessment Questions for Unit 1

Multiple Choice Questions

- 1. Which of the following is a Brønsted-Lowry base but not an Arrhenius base?
 - A. NH_3 C. Ca(OH)₂
 - B. NaOH D. KOH
- 2. Use the following acid ionization constants to identify the correct decreasing order of base strength.

HF	HNO ₂	HCN
K _a = 7.2 x 10 ⁻⁴	K _a = 4.5 x 10 ^{−4}	K _a = 6.2 x 10 ⁻¹⁰
A. $CN^{-} > NO_{2}^{-} > F^{-}$	C.	$NO_{2}^{-} > F^{-} > CN^{-}$
B. b. $F > NO_2 > CN$	D.	NO ₂ -> CN->F-

3. In the Brønsted–Lowry definition of acids and bases, an acid _____

a. is a proton donor.

c. is a proton acceptor.

- b. breaks stable hydrogen bonds.
- d. corrodes metals.

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- - 4. Which of the following is the conjugate acid of the hydrogen phosphate ion, HPO²⁻?
 - C. H₂PO₄ A. H₃PO₄ D. H₃O⁺ B. PO,^{3−}
 - 5. Which one of the following is not a conjugate acid-base pair?
 - A. NH_3 and NH_4^+ C. NH_3 and NH_2^-
 - B. HS⁻ and H₂S D. H₃O⁺ and OH⁻
 - 6. Which one of the following is not a conjugate acid-base pair?
 - A. NH_3 and NH_2^- C. HNO_3 and HNO_2
 - B. $H_2PO_4^{-}$ and HPO_4^{2-} D. H₂O and OH-

7. Which one of the following is **not** a strong acid?

- A. nitric acid, HNO₃ C. sulfuric acid, H_2SO_4
- B. carbonic acid, H_2CO_3 D. perchloric acid, HClO₄
- 8. Each of the following pairs contains one strong acid and one weak acid EXCEPT:
 - A. H_2SO_4 and H_2CO_3 C. HBr and H_3PO_2
 - D. HSO_4^- and HCNB. HNO_3 and HNO_2
- 9. When $[H^+] = 4.0 \times 10^{-9}$ M in water at 25°C, then _____ C. pH = 7.00. A. pH = 9.40. D. pH = 6.40 B. pH = 8.40.
- 10. A solution with an [OH⁻] concentration of 1.20×10^{-7} M has a pOH and pH of _____
 - A. 6.92 and 7.08 C. 1.00 and 13.00
 - B. 7.08 and 6.92 D. 5.94 and 8.06

Section 1.5: Acid-Base Indicators and Titrations

11. The acidic ingredient in vinegar is acetic acid. The pH of vinegar is around 2.4, and the molar concentration of acetic acid in vinegar is around 0.85 M. Based on this information, determine the value of the acid ionization constant, Ka, for acetic acid.

Α.	2.5x10⁻⁵	C.	5.0 x 10 ⁻⁵
		•••	010 / 10

- B. 1.9 x 10⁻⁵ D. 7.4 x 10⁻³
- 12. A cup of coffee has a hydroxide ion concentration of 1.0×10^{-10} M. What is the pH of this coffee?

Α.	6	C.	4
Β.	7	D.	2

13. What is the concentration of [OH-] in a 0.20 M solution of ammonia? The $K_{\rm b}$ value for ammonia is 1.8×10^{-5} .

- A. 3.6×10^{-6} M C. 1.9×10^{-3} M
- B. 1.8×10^{-5} M D. 4.2×10^{-4} M
- 14. Which of the following is **not** true about Lewis base?
 - A. Lewis bases are cationic in nature
 - B. Lewis base strength generally depends on the $\ensuremath{\mathsf{pK}}_{\ensuremath{\mathsf{a}}}$ of the corresponding parent acid
 - C. Lewis bases are electron-rich species
 - D. Water is an example of a Lewis base.
- 15. Which one of the following salts form an aqueous solution with pH = 7?
 - A. Na₂S C. NaBr
 - B. NaNO₂ D. Na₂CO₃

S) Written Assignment for unit 1

Short Answer Questions

- Define acids and bases based on the concept of: a. Arrhenius b. Brønsted-Lowry c. Lewis
- 2. In each of the following equations, identify the reactant that is a Brønsted–Lowry acid and the reactant that is a Brønsted–Lowry base:
 - $A. \quad HBr(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$
 - B. $CN^{-}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{-}(aq)$
- 3. Identify the Bronsted -Lowery acid base pairs in each of the following equations.
 - A. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
 - B. $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq)$
 - C. $H_3PO_4(aq) + NH_3(aq) \rightleftharpoons H_2PO_4^-(aq) + NH_4^+(aq)$
- 4. According to the Lewis theory, each of the following is an acid base reaction. Which species is the acid and which is the base?

A.
$$BF_3 + F^- \rightarrow BF_4^-$$

B. $OH^-(aq) + CO_2(aq) \rightarrow HCO_3^-(aq)$

- 5. Classify each of the following compounds as a strong acid, weak acid, strong base, or weak base:
 - A. KOH
 C. $C. H_2 SeO_4$

 B. $(CH_3)_2 CHCOOH$ D. $CH_3)_2 CHNH_2$
- 6. Which of the following are amphiprotic?

OH-	E.	NO_3^-
NH ₃	F.	HCO3-
H ₂ O	G.	CH3COO-
H ₂ S	Η.	HNO ₃
	OH^- NH_3 H_2O H_2S	OH ⁻ E. NH ₃ F. H ₂ O G. H ₂ S H.

7. A research chemist adds a measured amount of HCI gas to pure water at 25 °C and obtains a solution with $[H_3O^+] = 53.0 \times 10^{-4}M$. Calculate $[OH^-]$. Is the solution neutral, acidic, or basic?

- Calculate the percent ionization of a 0.125 M solution of nitrous acid (a weak acid), with a pH of 2.09
- 9. A vinegar solution has a $[OH^-] = 5.0 \times 10^{-12} \text{ M}$ at 25 °C. What is the $[H_3O^+]$ of the vinegar solution? Is the solution acidic, basic, or neutral?
- 10. The K_a for acetic acid, $HC_2H_3O_2$, is 1.8×10^{-5} . What is the pH of a buffer prepared with $1.0 \text{ M HC}_2H_3O_2$ and $1.0 \text{ M C}_2H_3O_2^-$? $HC_2H_3O_2(aq) + H_2O(aq) \rightleftharpoons H_3O + (aq) + C_2H_3O_2^-(aq)$

Answer key to Activities of Unit 1

Activity 1.1

- 1. According to Arrhenius, acids are substances that increase the concentration of H^+ (proton ion) in aqueous solution, and bases increase the concentration of OH^- (a hydroxide ion) in aqueous solution. In Arrhenius's theory, a strong acid is a substance that completely ionizes in aqueous solution to give H_3O^+ (aq) and an anion. An example is perchloric acid, $HClO_4$. $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$.
- 2. Other examples of strong acids are H_2SO_4 , HI, HBr, HCl, and HNO_3 . A strong base completely ionizes in aqueous solution to give $OH^$ and a cation. Sodium hydroxide is an example of a strong base. $VaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$
- 3. No
- 4. The theory can be applied only to reactions that occur in water, because it defines acids and bases in terms of what happens when compounds dissolve in water. It does not give any reason why some compounds, such as HCl, dissolve in water to give acidic solutions, whereas others such as CH_4 do not. The theory states that only compounds that contain OH^- ions can be classified as Arrhenius bases. It cannot explain why other compounds, such as Na_2CO_3 , have the characteristic properties of bases.

a Activity 1.2

- 1. All Arrhenius bases commonly contain only one Brønsted-Lowry bases, which is the OH^- . NaOH, KOH etc. are not Brønsted-Lowry bases. Only the OH^- they release is a base. For example, NH_2^- , S⁻², F^- , CN^- are Brønsted-Lowry bases.
- 2. All Arrhenius acids, such as HCl, HBr; , HI, $HClO_4$, are Brønsted-Lowery acids. But, the reverse is not true. This is because Brønsted-Lowry acids include all substances that can donate a proton (H^+) in aqueous solution or in any other medium or in the gaseous state. Inform them that conjugate acids formed after bases accept a proton are Brøonsted-Lowry acids such as H_3O^+ , NH_4^+ etc.
- 3. Mention the inverse relationship between the strengths of acids and their conjugate bases. The conjugate bases of strong acids tend to be relatively weak bases and the conjugate bases of weak acids tend to be strong bases. Similarly, the stronger the base the weaker is its conjugate acid and the weaker the base, the stronger is its conjugate acid.



- 1. Brønsted-Lowry acids are proton (H^+) donors. The Lewis concept of acids considers H^+ as one kind of acid only. According to the Lewis concept, an acid is any species that has a vacant orbital or unfilled shell and can form a coordinate covalent (dative) bond by sharing an electron pair from any other species. The Brønsted-Lowry concept considers species as bases only if they can accept a proton (H^+). For the base to accept a proton, it should have a lone pair of electrons. Thus, Brønsted-Lowry bases are also Lewis bases. However, Lewis bases include all species having a lone pair of electrons and are capable of forming a dative bond by supplying the lone pair not only with H^+ , but also with other species.
- 2. Yes
- 3. The Brønsted-Lowry concept restricted the definition of acids and bases to proton transfer only. It doesn't explain why species like CO_2 , SO_2 , Cu^{2+} etc. function as acids even if they do not contain a proton.

Crivity 1.4

- $\text{a.} \quad \text{K}_{c} = \frac{[\text{NH}_{4}^{+}][\text{NH}_{2}^{-}]}{[\text{NH}_{3}]^{2}}$
- b. In liquid ammonia, $\mathrm{NH_4^+}^+$ is the strongest acid, and $\mathrm{NH_2^-}$ is the strongest base.
- c. A solution with $[NH_4^+] > [NH_2^-]$ is acidic.

Activity 1.5

Substance	Color change	Acidic, Basic or Neutral
Beer	Red color	Acidic
Milk of magnesia	Blue color	Basic
Tomato juice	Red color	Acidic
Lemon juice	Red color	Acidic
Drinking water	Colorless	Maybe acidic, basic or neu-
	C01011633	tral



- 1. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The reaction is exothermic.
- a. The equilibrium shifts to the left, favouring the reverse reaction and increasing the concentration of reactants while reducing the concentration of products. The position of equilibrium moves to the left
 - b. The position of equilibrium moves to the right
 - c. The position of equilibrium moves to the right
 - d. The position of equilibrium moves to the left
 - e. increasing the temperature favors the endothermic reaction. but decreasing the temperature favors the exothermic reaction, thus replacing the heat that was removed. Since the given reaction is exothermic, increasing temperature caused a shift in the equilibrium to the left, favoring reactants.
- f. Changing the pressure or volume will only affect the reaction if the reaction involves gaseous reactants and/or products. Increasing the pressure (typically by reducing volume) results in the position of equilibrium moving towards the side with fewest moles of gas molecules. Thus, decreasing pressure favors reactant formation.
- g. Adding a catalyst will not affect the position of an equilibrium. A catalyst speeds up both the forward and the reverse reactions, so there is no uneven change in reaction rates. Generally, a catalyst will help a reaction to reach the point of equilibrium sooner, but it will not affect the equilibrium otherwise.

Crivity 1.7

To answer the activities it is better to know the general principle that, if $K_a > K_b$, the salt solution is acidic, and if $K_b > K_a$, the salt solution is basic, and if $K_a = K_b$ the salt solution is neutral. So, the solution of NH_4F is acidic because $K_a > K_b$, the solution of NH_4CNS is basic because $K_b > K_a$, and the solution of CH_3COONH_4 is neutral because $K_a = K_b$.

Activity 1.8

1. An equivalent of an acid is the mass of the acid that releases one mole of H^+ in solution or reacts with one mole of OH^- completely. Likewise, an equivalent of a base is the mass of the base that produces one mole of OH^- or accepts one mole of H^+ . For an oxidation-reduction reaction, one equivalent is the quantity of a substance that will react with or yield 1 mol of electrons. Note that the equivalent is defined in terms of a reaction, not merely in terms of the formula of a compound. The difference between equivalent mass and molecular mass of a substance is that equivalent mass of a substance is the mass in grams of 1 equivalent of the substances. As an example consider the dissociation of sulphuric acid in water. $H_aSO(aq) \rightarrow 2H^+(aq) + SO^{2^-}(aq)$ From the equation, it can be noted that one mole of H_2SO_4 releases two mole of H^+ . Thus, one mole of H_2SO_4 is 98 g/mol while its equivalent mass is 49 g/equivalent. From this, we can conclude that

Equivalence mass(g) = $\frac{\text{molar mass } (g)}{\text{number of equivalents per mole}}$

2. The difference between molarity and normality in relation to the difference between equivalent mass and molecular mass is given as follows:

Normality = Molarity x Number of equivalents

It is also known that during an acid-base neutralization reaction, one equivalent of an acid can neutralize one equivalent of the base. When neutralization is complete, the number of equivalents of the acid is exactly equal to that of the base. The formula; $N_1V_1 = N_2V_2$ proves this fact.



ਡ) Self-test exercise 1.1

- 1. a. Arrhenius acid
 - b. Cannot be classified as an Arrhenius acid or an Arrhenius base
 - c. Arrhenius base

2. a.
$$HClO_2 + H_2O \rightleftharpoons ClO_2^- + H_3O^+$$

- b. $\operatorname{OCl}^{-} + \operatorname{H}_{\operatorname{acid}} \xrightarrow{} \operatorname{HOCl} + \operatorname{OH}^{-}_{\operatorname{conjugate acid}} + \operatorname{OH}^{-}_{\operatorname{conjugate base}}$ $\operatorname{H}_{2}O + \operatorname{SO}_{3}^{2^{-}} \rightleftharpoons \operatorname{OH}^{-}_{\operatorname{conjugate acid}} + \operatorname{HSO}_{3}^{-}_{\operatorname{conjugate base}}$ C.
- 3. a. Auto-ionization is a reaction that involves the transfer of a proton from one molecule to another molecule of the same substances.
 - b. Amphiprotic species are molecules or ions that can act as a proton donor or proton acceptor.
- 4. a. $H_2PO_4^- + H_2O \rightarrow HPO_4^{-2-} + H_3O^+$

b. $H_2O + H_2PO_4^- \rightarrow OH^- + H_2PO_4$

- 5. a. $HClO_4 > HCl > HNO_3 > CH_3COOH$ b. $OH^{\dagger} > NH_{ii} > CH COO^{\dagger} > NO^{\dagger} > Cl^{\dagger}$
- 6. It restricted an acid-base concept only to proton transfer

7.
$$NH_3 + NH_3 \Longrightarrow NH_4^+ + NH_2^-$$

8. C. $H_{\text{Lewis acide}}^+ + OH_{\text{Lewis base}}^- \rightleftharpoons H_2O$

b. $\operatorname{Cl}_{\operatorname{Lewis \, base}}^{-} + \operatorname{BCl}_{3} \rightleftharpoons \operatorname{BCl}_{4}^{-}$

C.
$$K_{\text{Lewis acid}}^{+} + \frac{6H_2O}{K(H_2O)^{+}} \rightleftharpoons K(H_2O)^{+}$$

d.
$$OH^{-}_{\text{Lewis base}} + Al(OH)_{3} \rightleftharpoons Al(HO)_{4}^{-}$$

e.
$$\operatorname{CO}_2 + \operatorname{H}_2 \operatorname{O}_3 \rightleftharpoons \operatorname{H}_2 \operatorname{CO}_3$$

f.
$$Ni_{\text{Lewis acide}} + 4CO_{\text{Lewis acide}} \rightleftharpoons Ni(CO)_4$$



- 1. a. $[OH^{-}] = 1.0 \text{ x} 1 \text{ } 0^{-7} \text{M}$, neutral
 - b. $[H^+] = 1.0 \text{ x } 10^{-10} \text{ M}$, basic
 - c. $[H^+] = 1.0 \times 10^{-4} M$, acidic
- 2. a. 5.0×10^{-10} M b. 5.0×10^{-7} M c. 1.0×10^{-8} M
- 3. 1.49 x 10⁻¹² , basic
- 4. Because, it dissociates only slightly.
- 5. $[H^+] = 6.6 \times 10^{-10}$

 $[OH^{-}] = 1.5 \times 10^{-5}$ pOH = 4.82

6. For 2.0 M HNO₃

 $[H^+] = 2.0 M$ pH = -0.30 pOH = 14.30 $[OH^-] = 5.0 \times 10^{-5} M$

For 0.30 M HNO₃

 $[H^+] = 0.3 \text{ M}, \text{ pH} = 0.52, \text{ pOH} = 13.48, [OH^-] = 3.3 \times 10^{-14} \text{ M}$

For 0.0063 M HNO₃

 $[H^+] = 0.0063 \text{ M}, \text{ pH} = 2.20, \text{ pOH} = 11.80, [OH^-] = 1.6 \times 10^{-12} \text{ M}$

- 7. percent ionization = 1.29 %
- 8. pH = 2.87

- \Box . HNO₂+H₂O \rightleftharpoons NO₂⁻(aq)+H₃O⁺(aq) 9. b. $x = [OH^{-}] = 4.0 \times 10^{-3} M$ Test for approximation: $\frac{4.0 \times 10^{-3}}{0.036} \times 100 = 11\%$. Approximation is not valid c. Using quadratic equation $x = [H_3 O^+] = 3.8 x \, 10^{-3} M$ d. pH = 2.4210. O. $NH_3(aq)+H_2O(l) \rightleftharpoons NH_4^+(aq)+OH^-(aq)$ b. $[NH_4^+] = [OH^-] = 2.7 \times 10^{-3} M$ c. Approximation: $\frac{2.7 \times 10^{-3}}{0.40} \times 100 = 0.68$ %, Approximation is valid d. pOH = 2.57pH = 11.43Self-test Exercise 1.3 pH = 4.921. 2. pH = 2.723. a. 4.74 b. 4.74 с. 4.75 d. 4.74 e. i. 10.99 and ii. 3.0
- Self-test Exercise 1.4
- 1. a. carbonic acid and sodium hydroxide
- 2. Carbonate ion(CO_3^{2-})
- 3. Basic. This is because the anions of the salt react with water and produce OH^- as follows:

 $\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(1) \rightleftharpoons \text{HCO}_3^{-}(\text{aq}) + \text{OH}^{-}(\text{aq})$

Self-test Exercise 1.5

- 1. The indicator is a compound that imparts color on gaining or losing electrons in the solution. For example, Methyl orange imparts a red color when the solution is strongly acidic (pH 1-3), an orange color when the solution is weakly acidic (pH 3-5) and a yellow color in the basic solution (pH > 5). However, Phenolphthalein imparts a bright pink color in the basic solution (pH > 8) and gives no color in acidic solutions. Hence, the indicator is selected on the basis of the chemical reaction.
- 2. The molarity of the HCl solution is 0.16 M.
- 3. pH = 2.876
- 4. pOH = 2.18 and pH = 14 2.18 = 11.82
- 5. The reason for the above mentioned changes is the common-ion effect. When CH₃COONa is added to the weak acid CH₃COOH, CH₃COONa dissociates completely. While CH₃COOH being a weak acid does not dissociate completely. The dissociation of CH₃COOH gets even more hindered due to the generation of common acetate ions. The suppressed ionization of the weak acid results in a lesser number of liberated H⁺ ions than there would have been without the addition of CH₃COONa. As a result, the pH of the solution increases. Similarly, the addition of NH₄Cl to NH₄OH suppresses the dissociation of NH₄OH and hence, decreases the pH of the solution.

Self- Assessment Questions for unit 1

Multiple choice Questions

1. A	4. C	7. B	10.A	13.C
2. A	5. B	8. D	11.B	14.A
3. B	6. C	9. B	12.C	15.C



- 1. Color change at the end point is from colorless to pink color.
- The volume of sodium hydroxide added at the end point is obtained by taking the difference between the initial level and the end point level of the burette.
- 3. The normality of hydrochloric acid at the end point is calculated using the relation

$$N_1V_1 = N_2V_2$$

Where N_1 and V_1 refer to the normality and volume of the hydrochloric acid solution, respectively, and N_2 and refer to the normality and volume of the sodium hydroxide solution, respectively. Normality of Sodium hydroxide (N_2) is 0.1 N and its volume (V_2) is determined from the experiment. The volume of hydrochloric acid solution(V_1) is 10 mL. Thus, the normality (N_1) of hydrochloric acid can be determined from the relation

$$N_1 = \frac{N_2 V_2}{V_1}$$

4. The main difference between the equivalence point and the endpoint is that the equivalence point comes in a titration process when the moles of the titrant get equal to the moles of the titrand. But, an endpoint of this process is attained when the reaction takes place and the substance chanes its color. It means that the required amount of a reactant has been mixed in the solution.

The equivalence point can be attained even before the change of color occurs in a chemical reaction. On the other hand, the endpoint is reached when there is a change of color in a chemical reaction. The equivalence point is a theoretical point, and the endpoint is not a conceptual point. It is an actual point that we discover in the laboratory. The equivalence point can take place several times during a chemical

process. But the endpoint only takes place once in a chemical process.

Equivalence point	End point
Equivalence point is the actual point	End point of a titration is the
where the chemical reaction in the	point where a color change
titration mixture ends	occurs
Gives the point where the unknown	Does not always give the point
analyte has completely reacted with	where the unknown analyte
the titrant	has completely reacted with
	the titrant.
Not always indicated by the color	Always indicated by the
change of the reaction mixture	color change of the reaction
	mixture

UNIT ELECTRO CHEMISTRY

Introduction

Dear learner, electrochemistry is the branch of chemistry that deals with the inter-conversion of electrical energy and chemical energy. Electrochemical processes are redox (oxidation-reduction) reactions in which the energy released by a spontaneous reaction is converted to electricity or in which electrical energy is used to cause a non-spontaneous reaction to occur.

In redox reactions, electrons are transferred from one substance to another. The reaction between magnesium metal and hydrochloric acid is an example of a redox reaction:

$$\overset{0}{Mg}(s) + 2\overset{+1}{HCl}(aq) \rightarrow M\overset{+2}{gCl_2}(aq) + \overset{0}{H_2}(g)$$

Recall that the numbers above the elements are the oxidation numbers of the elements. The loss of electrons by an element during oxidation is marked by an increase in the element's oxidation number. In reduction, there is a decrease in oxidation number resulting from a gain of electrons by an element. In the preceding reaction Mg metal is oxidized and H^+ ions are reduced; the Cl_2 ions are spectator ions.

Objectives

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

- describe the fundamental concepts related to oxidation-reduction reaction
- explain the application of redox reactions in production of new substances and energy
- demonstrate an understanding of fundamental concepts related to the inter-conversion of chemical & electrical energy
- distinguish between metallic conduction and electrolytic conduction
- identify & describe the functioning of the components of electrolytic & galvanic cells
- distinguish difference between electrolytic and galvanic cells
- apply Faradays laws to solve problems associated with electrolysis experiment
- measure through experimentation the mass of metal deposited by electroplating (e.g.:- copper from copper(II) sulphate), and apply
 Faraday's law to relate the mass of metal deposited to the amount of charge passed
- predict the spontaneity of redox reactions and overall cell potentials by studying a table of half-cell reduction potentials
- determine the emf of an electrochemical cell experimentally or from given data
- explain the application of electrochemistry in our daily lives and in industry
- explain corrosion as an electrochemical process, and describe corrosion- inhibiting techniques (e.g. painting, galvanizing, cathodic protection)
- describe examples of common galvanic cells and evaluate their environmental and social impact
- Demonstrates scientific enquiry skills along this unit: observing, classifying, comparing & contrasting, communicating, asking question, measuring, relating cause and effect and problem solving.

Unit Content

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6 weeks

If you set an average of one hour per day, you will be able to complete unit two by the end of the assigned week. Try to do all the learning activities. And compare your answers with the ones provided at the end of the Module.

If you do not get a particular exercise right in the first attempt, you should not get discouraged, but instead, go back and attempt it over and over again. If you still do not get it right after several attempts, then you should seek help from your friend or even your tutor.

Unit Learning Strategies

Individual study (self-study) is the advised methodology for this unit, and for individuals with internet access, visual-based learning is also advised. Activities are presented at the start of each unit part. The learners are required to think critically about the activities and the given exercise and validate their findings by contrasting them with the solution provided at the conclusion of the module.

You can recall what you learnt in a prior module or unit thanks to the activity. Please evaluate yourself by completing the self-test exercises and rating the check list that is provided at the end of each segment. See the feedback provided at the module's end for the solution to the self-test exercise. Please visit the module to read the provided notes again and attempt to answer the questions once more if you didn't meet the required minimum standard for the activities and self-test exercise.

Section 2.1: Oxidation-Reduction Reactions

Dear learner, the term oxidation was originally defined in terms of adding oxygen to a compound. However, now days, it has a broader meaning that includes reactions involving not only oxygen. In this case Oxidation is a process in which an atom/element loses an electron and therefore increases its oxidation number.

The term reduction was originally used to describe the production of a metal from an ore. It has been modified through time to include other reactions. Thus, Reduction is a process in which an atom gains an electron and therefore decreases its oxidation number.

Can oxidation occur without reduction and vice versa?

For example for the following reaction

$$\begin{array}{c} 0 & 1 + & 2 + & 0 \\ Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + & H_2(g) \end{array}$$

Mg metal is oxidized and H^+ ions are reduced; the Cl⁻ ions are spectator ions.

Note that oxidation and reduction reactions are always occur in pairs. Since oxidation and reduction reactions cannot occur independently, they as a whole are called 'Redox Reactions'.

After completing this subunit, you will be able to:

- define redox reaction
- define oxidation in terms of electron transfer and change in oxidation number.
- define reduction in terms of electron transfer and change in oxidation number.
- describe the oxidizing and reducing agents
- identify the species that are oxidized and reduced in a given redox reaction and determine the oxidizing and reducing agents.

2.1.1 Balancing Oxidation-Reduction (Redox) Reactions

Because atoms are neither created nor destroyed in an ordinary chemical reaction, chemical equations must have an equal number of atoms of each element on the reactant and product sides. In addition, the net electrical charges in the reactant side must be equal to the net electrical charges in the product side. The methods used to balance redox reactions are the change in oxidation number methods and Half-reaction methods.

1. Balancing Redox Reactions Using Change in Oxidation-Number Method

This method is used to balance redox reactions that do not occur in aqueous solutions, and also reactions that do not involve ions. Steps used to balance the chemical equations using the change in oxidation state method are:

- 1. Write an unbalanced chemical equation
- 2. Assign oxidation numbers to all elements in the reaction
- 3. From the changes in oxidation numbers, identify the oxidized and reduced species
- 4. Compute the number of electrons lost in the oxidation and gained in the reduction from the oxidation numbers changes
- Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients
- 6. Complete the balancing by inspection, adding states of matter

Example 2.1

1. Balance the following chemical equation, using the change in oxidation-number method.

 $PbS(s) + O_2(g) \rightarrow PbO(s) + SO_2(g)$

Solution

Step 1.Write an unbalanced chemical equation

 $PbS(s) + O_2(g) \rightarrow PbO(s) + SO_2(g)$

Step 2 Assign oxidation numbers to all elements

$$Pb^{+2}S(s) + O_2^0(g) \rightarrow Pb^{+2}O(s) + SO_2^0(g)$$

Step 3. Identify oxidized and reduced species

- PbS was oxidized (Oxidation number of S changes from -2 to +4)
- $-O_2$ was reduced (Oxidation number of O changes from 0 to -2)
- Step 4. Compute electron lost and electron gained

- In the oxidation: 6 electrons were lost from S

- In the reduction: 2 electrons were gained by each O
- Step 5. Multiply by factors to make electron lost equal to electron gained, and use the factors as coefficients

S lost 6 electrons, O gained 4 electrons (2 electrons each O).

Thus, put the coefficient $\frac{3}{2}$ before O_2 $PbS(s) + \frac{3}{2}O_2(g) \rightarrow PbO(s) + SO_2(g)$

Step 6. Complete the balancing by inspection

$$PbS(s) + \frac{3}{2}O_2(g) \rightarrow PbO(s) + SO_2(g)$$

The chemical equation is balanced, because the number of atoms in the reactant side is equal to the number of atoms in the product side. It can also be confirmed that the net charge is zero on each side.

2. Balance the following chemical equation by using the change in oxidation-number method		
$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$		
Solution		
Step 1.Write an unbalanced chemical equation		
$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$		
Step 2. Assign oxidation numbers to the elements that change their		
oxidation number		
$^{+0}_{Cu+HNO_3} \xrightarrow{+5}^{+2}_{Cu(NO_3)_2} \xrightarrow{+2}^{+2}_{NO+H_2O}$		
Step 3. Identify oxidized and reduced species		
– Cu was oxidized (Oxidation number of Cu changes from 0 to +2)		
- HNO ₃ was reduced (Oxidation number of N changes from +5 to +2)		
Step 4. Compute electron lost and electron gained		
– In the oxidation: 2 electrons were lost from Cu		
– In the reduction: 3 electrons were gained by each N		
Step 5. Multiply by factors to make electron lost equal to electron gained,		
and use the factors as coefficients		
Cu lost 2 electrons, N gained 3 electrons.		
Thus, put the coefficient 3 before Cu and 2 before NO		
$3Cu + HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + H_2O$		
Step 6. Complete the balancing by inspection In the above equation we		
see that two NO_3^- ions are converted to two NO, but we need six		
NO_3^- to balance the six NO_3^- ions that are present in three $Cu(NO_3)_2$.		
Therefore, the coefficient of HNO_3 becomes 8.Hydrogen atoms can		
be balanced by making the coefficient of water as 4		
$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$		
The chemical equation is balanced, because the number of atoms		
in the reactant side is equal to the number of atoms in the product		
side.		

2. Balancing Redox Reactions using Half-Reaction Method

In half-reaction method, the overall reaction is divided into two halfreactions, one for oxidation and one for reduction. The equations for the two half-reactions are balanced separately and then added together to give the overall balanced equation. Steps used to balance the chemical equations using the Half-Reaction method are:

- 1. Separate the equation into oxidation half-reaction and reduction halfreaction
- 2. Balance the atoms and charges in each half-reaction.
 - Atoms are balanced in this order: atoms other than O and H, then O,

then H.For reactions in an acidic medium, add H_2O to balance the O atoms and H^+ to balance the H atoms.

• Charge is balanced by adding electrons (e^{-}) to the left sides in the reduction half-reaction and to the right side in the oxidation half-reaction.

If necessary, multiply one or both half-reactions by an integer so that the number of e^- gained In reduction is equal to the number of e^- lost in oxidation

- 3. Add the balanced half-reactions, and include states of matter.
- 4. Check that the atoms and charges are balanced.

(B

Example 2.2

1. Use the half-reaction method to balance the following equation:

$$Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$$

Solution

Step 1: Separate the equation into two half-reactions

Oxidation: $Fe^{2+} \rightarrow Fe^{3+}$

Reduction: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

Step 2: Balance each half-reaction for number and type of atoms and

charges. For reactions in an acidic medium, add H_2O to balance the *O* atoms and H^+ to balance the *H* atoms.

Oxidation half-reaction: The atoms are already balanced. To balance the charge, we add an electron to the right-hand side of the arrow:

 $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$

Note: In an oxidation half-reaction, electrons appear as a product; in a reduction half reaction, Electrons appear as a reactant.

Reduction half-reaction: Because the reaction takes place in an acidic medium, we add seven H_2O molecules to the right-hand side of the arrow to balance the O atoms:

 $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

To balance the H atoms, we add 14 H^+ ions on the left-hand side:

 $14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

There are now 12 positive charges on the left-hand side and only six positive charges on the right-hand side. Therefore, we add six electrons on the left

 $14H^{+} + Cr_{2}O_{7}^{2-} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O$

Step 3 : Add the two half-reactions together and balance the final equation by inspection. The electrons on both sides must cancel. If the oxidation and reduction half-reactions contain different numbers of electrons, we need to multiply one or both half-reactions to equalize the number of electrons. Here you have only one electron for the oxidation halfreaction and six electrons for the reduction half-reaction, so we need to multiply the oxidation half-reaction by 6 and write

$$\begin{split} & 6(Fe^{2+} \rightarrow Fe^{3+} + e^{-}) \\ & \frac{14H^{+} + Cr_2O_7^{-2-} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O}{6Fe^{2+} + 14H^{+} + Cr_2O_7^{-2-} + 6e^{-} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + 6e^{-}} \end{split}$$

The electrons on both sides cancel, and we are left with the balanced net ionic equation:

 $6Fe^{^{2+}} + 14H^+ + Cr_2O_7^{^{2-}} \rightarrow 6Fe^{^{3+}} + 2Cr^{^{3+}} + 7H_2O$

- Step 4: Verify that the equation contains the same type and numbers of atoms and the same charges on both sides of the equation. For reactions in a basic medium, we proceed through step 4 as if the reaction were carried out in acidic medium. Then, for every H^+ ion we add an equal number of OH^- ions to both sides of the equation. Where H^+ and OH^- ions appear on the same side of the equation, we combine the ions to give H_2O .
- 2. Write a balanced ionic equation using the half-reaction method to represent the oxidation of iodide ion (I⁻) by permanganate ion (MNO₄⁻) in basic solution to yield molecular iodine (I₂) and manganese(IV) oxide (MnO₄⁻). MNO₄⁻ + I⁻ → MnO₂ + I₂
 Solution
 Step 1: The two half-reactions are Oxidation: I⁻ → I₂
 Reduction: MnO₄⁻ → MnO₂
 Step 2: We belance each half reaction for number and type of atoms

Step 2: We balance each half-reaction for number and type of atoms and charges. Oxidation half-reaction: We first balance the I atoms: $2I^- \rightarrow I_2$

To balance charges, we add two electrons to the right-hand side of the equation:

 $2I^- \rightarrow I_2 + 2e^-$

Reduction half-reaction: To balance the O atoms, we add two H_2O molecules on the right:

 $MnO_A^- \rightarrow MnO_2 + 2H_2O$

To balance the H atoms, we add four H^+ ions on the left:

 $\operatorname{MnO}_{\Delta}^{-} + 4H^{+} \rightarrow MnO_{2} + 2H_{2}O$

There are three net positive charges on the left, so we add three electrons to the same side to balance the charges:

 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$

Step 3: We now add the oxidation and reduction half reactions to give the overall reaction. To equalize the number of electrons, we need to multiply the oxidation half-reaction by 3 and the reduction halfreaction by 2 as follows:

 $3(2I^{-} \rightarrow I_{2}+2e^{-})$ $2(MnO_{4}^{-}+4H^{+}+3e^{-} \rightarrow MnO_{2}+2H_{2}O)$ $\overline{6I^{-}+2MnO_{4}^{-}+8H^{+}+6e^{-} \rightarrow 3I_{2}+2MnO_{2}+4H_{2}O+6e^{-}}$

The electrons on both sides cancel, and we are left with the balanced net ionic equation:

$$6I^- + 2\mathrm{MnO}_4^- + 8H^+ \rightarrow 3I_2 + 2MnO_2 + 4H_2O$$

This is the balanced equation in an acidic medium. However, because the reaction is carried out in a basic medium, for every H^+ ion we need to add an equal number of OH^- ions to both sides of the equation:

 $6I^- + 2MnO_4^- + 8H^+ + 8OH^- \rightarrow 3I_2 + 2MnO_2 + 4H_2O + 8OH^-$

Finally, combining the H^+ and OH^- ions to form water, we obtain

 $6I^- + 2MnO_4^- + 4H_2O \rightarrow 3I_2 + 2MnO_2 + 8OH^-$

Step 4: A final check shows that the equation is balanced in terms of both atoms and charges

Activity 2.1

- 1. Which of the following reactions are redox reactions? Explain your answer for each case.
 - A. $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
 - $\mathsf{B}. \quad H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
 - C. $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
- 2. Use the given chemical equation to answer the following question

 $Mg(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Mg^{2+}(aq)$

Identify the:

- A. oxidized substance c. oxidizing agent.
- B. reduced substance. d. reducing agent.
- 3. Calculate the oxidation number of:

A. C in
$$C_2 O_4^{2-}$$

b. $Crin K_2 CrO_4$

c. Cl in $HClO_4$

Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand I can.....

- describe
- oxidation reaction
- reduction reaction
- identify the two methods used to balance redox reactions
- explain why oxidation and reduction reactions cannot occur independently
- identify the kinds of electrodes on which oxidation and reduction occur
- define the terms such as
- oxidation
- reduction
- oxidizing agent
- reducing agent

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1. Balance the following equation for the reaction in an acidic medium by the half-reaction method:

$$\Box. H_2C_2O_4 + MnO_4^- \rightarrow CO_2 + Mn^{2+}$$

b.
$$Cr_2O_7^{2-} + Fe^{2+} \to Cr^{3+} + Fe^{3+}$$

C.
$$H_5 IO_6 + Cr \to IO_3^- + Cr^{3+}$$

d.
$$NO_3^- + H_2O_2 \rightarrow NO + O_2$$

$$\Rightarrow . BrO_3^{-} + Fe^{2+} \rightarrow Br^{-} + Fe^{3+}$$

2. Use the oxidation number method to balance the following equations and then identify the oxidizing and reducing agents:

a.
$$HNO_3 + H_3AsO_3(aq) \rightarrow NO(g) + H_3AsO_4(aq) + H_2O(l)$$

b.
$$KClO_3 + HBr \rightarrow Br_2 + H_2O + KCl$$

$$CH_2S + HNO_3 \rightarrow S + NO + H_2O$$

Section 2.2: Electrolysis of Aqueous Solutions

Dear learner, before you study the electrolysis of aqueous solutions, let you consider some important concepts about conductivity. Electrical conductivity is the ability of a substance to transmit electricity. The substances, which allow the passage of electric current, are called **conductors**. Conductors of electricity are further classified into two types depending on their mode of transport of electrical charges inside them. These are electronic (metallic) conductors and electrolytic conductors.

Metals and alloys conduct electricity due to the movement (mobility) of delocalized outer shell electrons present inside them and are known as electronic conductors (or) metallic conductors. An electronic conductor allows the flow of electricity without causing any decomposition of the substance. The most common examples of electronic conductors are metals, graphite and minerals. The flow of electricity in such conductors happens due to the flow of electrons within the substance through which the electricity is made to pass. As opposed to metallic conductors, the flow of electricity in electrolytic conduction happens due to the movement of ions in the solution or in their fused state. The process of inducing chemical reactions by the application of an electric energy is termed electrolysis, and the apparatus in which the reaction is carried out are known as electrolytic cells. During electrolysis of aqueous solutions, the substance undergoes decomposition. In this section we will look at the fundamental principles of electrolysis reactions. Brief accounts of some quantitative aspects of the process will also seen.

After completing this subunit, you will be able to:

- explain metallic conductivity, electrolytic conductivity and electrolysis of molten electrolytes
- draw labeled diagrams of an electrolytic cell
- define preferential discharge
- explain factors that affect preferential discharge
- describe the effect of nature of the ions on the electrolysis of aqueous solutions of dil. H₂SO₄ and NaOH
- describe the effect of concentration of the ions on the electrolysis of dilute and concentrated solutions of NaCl
- describe the effects of types of electrodes on the electrolysis of CuSO₄ solution using Ni electrodes and Cu electrodes
- write electrode half reactions and overall reactions for the electrolysis
 of dil. H₂SO₄, NaOH, dil.NaCl, conc. NaCl and CuSO₄ solutions
- distinguish between molten electrolytes and aqueous electrolytic solutions.

Electrolytic conduction: Electrovalent (or) ionic compounds conduct electricity in their dissolved state (in solutions) or in their fused state only. These compounds consist of ions of opposite charges and in aqueous solution they exist as ions. In the presence of applied electrical field, these ions migrate to respective electrodes exhibiting electrical conductivity (Figure 2.1). This mobility of ions is responsible for conduction of electricity through electrolytes and is referred as electrolytic conduction. In the electrolytic conduction:

- Passage of current through electrolytes is accompanied by chemical changes.
- There is actual transfer of matter since ions move towards respective electrodes.
- The conductivity of electrolytes increases with increase in temperature. This is due to increase with ionic mobility.



Figure 2.1 Electrical Conductivity Apparatus

Experiment 2.1

Dear learner, to understand the difference between conductors and insulators, perform the following experiment. To conduct the experiment, visit a nearby high school and request a teacher who is teaching Grade 12 chemistry to help you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory. If you couldn't find a high school in your area, request your tutor to get support and advices.

Title: Electrical Conductivity Test

Objective: To classify substances as electrical conductors and insulators. **Materials and chemicals:** Copper wire, light bulb, power supply (DC) or dry cells, scotch tape, distilled water, 1M *NaCl* solution, 1M H_2SO_4 solution, 1 M *CH*₃*COOH* solution, 1 M sugar solution, magnesium ribbon and an iron nail.



Figure 2.2 (a) Electrical conductivity apparatus(b) Electrical conductivityapparatus for solid materials.for liquids and solutions.

Procedure:

- Polish the strip of copper and connect the two ends of the copper wire as shown in Figure 2.2a. Do the same thing for iron nail and magnesium. Record your observations.
- Rinse the 100 mL beaker thoroughly with distilled water and fill to the 50 mark and insert the two ends of the copper wire as shown in Figure 2.2b. Record your observations.
- 3. Clean the two ends of the copper wire in Figure 2.2b with distilled water and insert them into a beaker containing 50 mL of 1 M *NaCl* solution.

Repeat the same thing for the 1 M H_2SO_4 , 1 M CH_3COOH and 1 M sugar solutions. Record your observation.

Results and Discussion:

- Why is it important to polish the magnesium ribbon and iron nail before use?
- 2. Classify the materials you used as conductors, strong electrolytes, and weak electrolytes and none electrolytes.
- 3. Label the two ends of the wire in Figure 2.2b as cathode and anode.

🗙 🛛 Activity 2.2

Which of the following substances are capable of conducting electricity? Give your reasons.

- B. Iron c. Solid sodium chloride
- C. Sulphur d. Molten calcium chloride

2.2.1 Electrochemical cells

) Can you differentiate the difference of electrochemical and electrolytic cells?

An electrochemical cell is a device that can generate electrical energy from the chemical reactions occurring in it, or use the electrical energy supplied to it to facilitate chemical reactions in it. These devices are capable of converting chemical energy into electrical energy, or vice versa. A common example of an electrochemical cell is a standard 1.5volt cell which is used to power many electrical appliances such as TV remotes and clocks. There are two types of electrochemical cells. These are Electrolytic cells and Galvanic cells (also known as Voltaic cells)

Electrolytic cells



Figure 2.3 Electrolytic cell containing molten sodium chloride.

- a. Indicate the migration of sodium ions and chloride ions.
- b. Label the anode and the cathode.
- c. Write the reduction half-reaction, oxidation-half reaction, and the overall reaction.

An electrolytic cell is an electrochemical cell that utilizes an external source of electrical energy to force a chemical reaction that would otherwise not occur. The external energy source is a voltage applied between the cell's two electrodes; an anode (positively charged electrode) and a cathode (negatively charged electrode), which are immersed in an electrolyte solution. The net reaction taking place in an electrolytic cell is a non-spontaneous reaction. i.e, the Gibbs free energy is positive.

2.2.2 Preferential Discharge

During electrolysis, the cations being positively charged get attracted towards the negatively charged electrode (cathode) and anions being negatively charged get attracted towards the positively charged electrode (anode). If more than one cations or anions reach an electrode, only one of them preferentially gets discharged at one electrode. Thus, there is a choice amongst the ions that will get discharged on an electrode. This is called the preferential discharge of ions during electrolysis. There are different factors that affect preferential discharge of ions during electrolysis. These are:

Position of ions in the electrochemical series

The **reactivity series** is a list of metals in decreasing order of their reactivity. It is used to determine the products of single displacement reactions, whereby metal A will replace another metal B in a solution if A is higher in the series. Activity series of some of the more common metals, listed in descending order of reactivity is given in table 2.1.

Table 2.1 Reactivity series of metals

Activity of Metals	Reactivity	
Li		
K		
Ba	Displaces $\rm H_{\rm 2}$ gas from cold water, steam and	
	acids and forms hydroxides	
Sr		
Са		
Na		
Mg		
Al		
Zn	Displaces H_2 gas from steam and acids an	
Cr	forms hydroxides but do not displace hydrogen	
Fe	from cold water.	
Cd		
Со		
Ni		
Sn	Displaces H_2 gas from acids only and forms hydroxides	
Pb		
H ₂	Included for comparison	
Cu		
Hg		
Ag	Unreactive with water or acids.	
Pt		
Au		

When a metal in elemental form is placed in a solution of another metal salt it may be more energetically feasible for this "elemental metal" to exist as an ion and the "ionic metal" to exist as the element. Therefore the elemental metal will "displace" the ionic metal and the two swap places. A metal can displace metal ions listed **below** it in the activity series, but not above. For example, zinc is more active than copper and is able to displace copper ions from solution

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

However, silver **cannot** displace copper ions from solution. This is because silver is found below copper in the activity series. It is important to distinguish between the displacement of hydrogen from an acid and hydrogen from water. Sodium is highly active and is able to displace hydrogen from water:

 $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

Less active metals like iron or zinc cannot displace hydrogen from water but do readily react with acids:

$$Zn(s) + 2H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

Those metals that can displace H⁺ ions from acids are easily recognized by their position above H in the activity series. The boundary between the metals that react with water and those that don't is harder to mark. For example, calcium is quite reactive with water, whereas magnesium does not react with cold water but does displace hydrogen from steam. A more sophisticated calculation involving electrode potentials is required to make accurate predictions in this area. The activity series of common cations and anions are given in table 2.2.



Table 2.2 The ease of discharge of some common cations and anions.

The ions that are lower in the electrochemical series get discharged in preference to those above them. For example, if a solution has potassium ions and copper ions, the copper ions will accept electrons, and get discharged as copper atoms first. The potassium ions will not be affected. In general, if two or more positive ions migrate to the cathode, the ion lower in the series is discharged preferentially. Similarly, if two or more negative ions migrate to the anode, the ions lower in the series are discharged preferentially.

The concentration of ion

Higher the concentration of anions in the electrolytic solution, greater is its probability of being discharged at the anode. For example, a solution of sodium chloride in water contains two types of anions i.e., the chloride (Cl^-) ions and the hydroxide (OH^-) ions. The hydroxide ions are lower in the electrochemical series than the chloride ions. But if the concentration of chloride ions is much higher than that of the hydroxide ions, then the chloride ions get discharged first.

The nature of electrode

If the electrode used is inert i.e. made of less reactive material such as graphite, platinum etc, the electrode does not play any role in deciding the preferential discharge of ion at it. But when the electrode used is active i,e made of active material such as Cu, Ag, Ni etc it takes part in the electrode reaction and plays an important role in deciding the ions which will preferentially be discharged. In such a case, anions migrate to the anode but do not get discharged; instead the active anode itself loses electrons and forms ions. For example, in the electrolysis of copper sulphate solutions, using graphite electrodes, oxygen gas is liberated at the anode and copper metal is deposited at the cathode, as shown below.

 $\text{CuSO}_4(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Anode: $4OH^{-}(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^{-}$

Cathode: $Cu^{2+}(aq)+2e^{-} \rightarrow Cu(s)$

However, if the electrolysis of copper sulphate solutions is performed using copper electrodes, the copper electrode at the anode dissolves and copper metal will be deposited at the cathode, as indicated below.

Anode: $Cu(s) \rightarrow Cu^{2+}(aq)+2e^{-}$

Cathode: $Cu^{2+}(aq)+2e^{-} \rightarrow Cu(s)$

2.2.3 Electrolysis of Some Selected Aqueous Solutions

Activity 2.4

Reflect each of the following questions.

- 1. Prior to electrolysis, why sodium chloride must be in molten state?
- 2. For the electrolysis of molten KCI , write a balanced equation for the:
 - a. anode reaction b. cathode reaction c. overall reaction
- 3. Why are H ⁺ and Cl⁻ ions discharged in preference to Na⁺ and OH ⁻ ions in concentrated sodium chloride solution?

Electrolysis is defined as a process of decomposing ionic compounds into their elements by passing a direct electric current through the compound in an aqueous solution. In the process of electrolysis, there is an interchange of ions and atoms due to the addition or removal of electrons from the external circuit. Basically, on passing current, cations move to the cathode, take electrons from the cathode (given by the supply source-battery), and is discharged into the neutral atom. The neutral atom, if solid, is deposited on the cathode and if gas, move upwards. This is a reduction process and the cation is, reduced at the cathode.

At the same time anions, give up their extra electrons to the anode and is oxidized to neutral atoms at the anode. Electrons released by the anions travel across the electrical circuit and reach the cathode completing the circuit. Electrolysis involves a simultaneous oxidation reaction at anode and a reduction reaction at the cathode. During electrolysis, the free ions furnished by the electrolyte are migrated towards oppositely charged electrodes and are discharged under electric potential. i.e. Cations migrate towards the cathode and are reduced. Anions migrate towards the anode and are oxidized.

Electrolysis of concentrated Sodium Chloride solution (brine solution)

Sodium chloride is dissociated and exists as sodium and chloride ions in aqueous solution. Electrolysis of sodium chloride is easier in aqueous solution. But, water itself can undergo reduction and oxidation reactions at different potentials. So, the substance that is oxidized or reduced is not sodium and chloride ions alone but it may involve the water molecule also. That is in the concentrated sodium chloride solution there are Na⁺, Cl^- , H^+ and OH^- ions that compute for preferential discharge. When a potential difference is established across the two electrodes, Na⁺ and H^+ ions move towards the cathode, and Cl^- and OH^- ions move towards the anode. The reduction reaction that occurs at the cathode does not produce sodium metal, instead, the H^+ is reduced as shown in Figure 2.4. This is because the reduction potential for water is only – 0.83 V compared to –2.71 V for the reduction of sodium ions. This makes the reduction of H^+ preferable because its reduction potential is less negative.

On the other hand you might expect H_2O to be oxidized in preference to Cl^- under standard-state conditions, However, the potentials are close and over voltages at the electrodes could alter this conclusion. It is possible, nevertheless, to give a general statement about the product expected at the anode. Electrode potentials, as you have seen, depend on concentrations. It turns out that when the solution is concentrated enough

in Cl^- , Cl_2 is the product, but in dilute solution, O_2 is the product.

Chlorine gas is still produced at the anode.

Cathode (Reduction): $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Anode (oxidation): $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$

Over all reaction: $2H^+(aq) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g)$

As the overall reaction shows, the concentration of the Cl^- ions decreases during electrolysis and that of the OH^- ions increases. Therefore, in addition to H_2 and Cl_2 , the useful by-product *NaOH* can be obtained by evaporating the aqueous solution at the end of the electrolysis.



Figure 2.4 Electrolysis of brine solution.

Electrolysis of Dilute Sodium Chloride Solution



c. Write the electrode half-reactions and overall reaction

Experiment 2.2

Dear learner, to understand about the electrolysis of electrolytes, perform the following experiment. To conduct the experiment, visit a nearby high school and request a teacher who is teaching Grade 12 chemistry to help you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory. If you couldn't find a high school in your area, request your tutor to get support and advices.

Title: Investigating electrolysis of sodium chloride solution

Objective: To electrolyze sodium chloride solution and observe the reaction occurring at the electrodes.

Apparatus and Chemicals: Water, sodium chloride, beakers, measuring cylinder, graphite electrodes, batteries and connecting wires.



Figure 2.5 Electrolysis of sodium chloride solution

Procedure:

- 1. Prepare 0.1 M sodium chloride solution.
- 2. Transfer the solution to the beaker.
- 3. Immerse the graphite electrodes in the sodium chloride solution.
- 4. Arrange the setup as shown in the Figure 2.5

Results and Discussion:

- 1. What do you observe at the surface of the electrodes?
- 2. Identify the cathode and anode in the Figure 2.5.
- 3. Name the gases evolved at the cathode and anode.
- 4. Write the equations for anode and cathode reactions.

Sodium chloride is dissociated and exists as sodium and chloride ions in aqueous solution. Electrolysis of sodium chloride is easier in aqueous solution. But, water itself can undergo reduction and oxidation reactions at different potentials. So, the substance that is oxidized or reduced is not sodium and chloride ions alone but it may involve the water molecule also. For very dilute aqueous sodium chloride solution, the small amount of ionic sodium chloride helps the ionic conductivity of the solution. In small concentration, the electrolysis of water becomes more predominant yielding hydrogen at cathode and oxygen at the anode.

 $\begin{array}{ll} Anode \ reaction(oxidation): 2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- & E^o = +1.4 \ V \\ Cathode \ reaction(\operatorname{Re} \ duction): 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- & E^o = -1.0 \ V \\ Overall \ reaction: 2H_2O \rightarrow H_2(g) + O_2(g) & E^o = -2.4 \ V \\ \end{array}$

Electrolysis of Dilute Sulphuric Acid Solution

Dilute sulfuric acid contains water. The ions present in this mixture are H^+ and OH^- ions (from water) and H^+ and SO_4^{2-} ions from the sulfuric acid. When a potential difference is applied across the two electrodes (anode and cathode), the H^+ ions are attracted to the cathode and the two negative ions (OH^- and SO_4^{2-}) are attracted to the anode. At the cathode H^+ is discharged and at the anode OH^- ions are preferentially discharged because the OH^- ion is below the SO_4^{2-} ion in the electrochemical series. The electrode reactions are:

Anode (oxidation): $4OH^{-}(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^{-}$

Cathode (reduction): $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

Overall reaction: $2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$

Note that the electrolysis of dilute NaCl and dilute H_2SO_4 solutions results in the decomposition of water to oxygen and hydrogen gases.

Electrolysis of Copper (II) Sulphate Using Inert Electrodes

Electrolyte $CuSO_4$ dissociates in to Cu^{2+} and SO_4^{2-} ions along with H^+ and OH^- ions in the aqueous solution. Cu^{2+} ion preferentially discharged because it

has higher reduction potential than H^+ . On the other hand OH^- has higher oxidation potential than SO_4^{2-} , so it gets preferentially oxidized.

Electrode reactions are:

Cathode(Reduction): $2Cu^{2+}(aq) + 4e^{-} \rightarrow 2Cu(s)$

Anode (oxidation): $4OH^{-}(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^{-}$

Overall reaction: $2Cu^{2+}(aq) + 4OH^{-}(aq) \rightarrow 2Cu(s) + 2H_2O(l) + O_2(g)$

Hence, C_u at cathode and O_2 at anode are produced by electrolysis of aqueous $CuSO_4$ with inert electrodes. Since copper ions are deposited at the cathode, and hydroxide ions at the anode, the solution becomes acidic due to the formation of H_2SO_4 using H^+ and SO_4^{2-}

Electrolysis of Copper (II) Sulphate Solution Using Copper Electrodes

) Activity 2.6

Reflect each of the following questions.

- Are the copper electrodes reactive or inert in the electrolysis of CuSO₄ solution?
- Write the reactions occurring at the anode and at the cathode during the electrolysis of CuSO₄ solution, using copper electrodes.
- 3. What is the net result of the electrolysis of CuSO₄ solution, using copper electrodes?

The use of copper electrodes illustrates how copper is refined industrially. Replacing the inert Electrodes with clean copper plates produces a different anode reaction. At the anode, no oxygen is produced, rather the copper anode dissolves. On the other side of the half reaction a deposit of copper forms on the cathode. The half-cell reactions are:

Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$

Cathode reaction: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

During this electrolysis, the mass gained of copper at the cathode is equal to the mass lost at the anode.
) CHECKLIST-2.2

Put ($\sqrt{}$) in the box for the tasks you can perform or the concepts you understand I can.....

- describe the process of
 - electronic conduction
 - electrolytic conduction
 - Electrolysis of some selected aqueous solutions
- distinguish between the two types of electrical conduction
- explain why a given material conducts electricity in the way it does
- identify the kinds of electrodes on which oxidation and reduction occur
- State Faraday's laws of electrolysis
- define the terms such as
 - Electrolysis
 - Electrolyte
 - preferential discharge
 - inert electrode
 - Reactive or active electrode.

Self-teat Exercise 2.2

- 1. For the electrolysis of dilute NaOH solution,
 - a. write the balanced chemical equations for the reduction halfreaction and oxidation half reactions.
 - b. write the balanced overall cell reaction.
- 2. What happens to the concentration of the dilute H_2SO_4 solution after electrolysis?
- 3. Does the concentration of $CuSO_4$ increase, decrease or remain the same after the electrolysis of $CuSO_4$, using inert electrodes? Explain.
- 4. What gases are liberated at the cathode and anode if concentrated hydrochloric acid is electrolyzed? Write the reduction half-reaction, oxidation half-reaction and the overall reaction.

Section 2.3: Quantitative Aspects of Electrolysis

Dear learner, the quantitative treatment of electrolysis was developed primarily by Michael Faraday in the year 1834. His early research on electrolysis led him to propose a relationship between the amount of current passed through a solution and the amount of substance decomposed or produced by the current.

Objective

After completing this subunit, you will be able to:

- state Faraday's first law of electrolysis;
- write the mathematical expressions for the Faraday's first law of electrolysis;
- do calculations related to Faraday's first law of electrolysis;
- state Faraday's second law of electrolysis;
- write the mathematical expressions for Faraday's second law of electrolysis; and
- do calculations related to Faraday's second law of electrolysis.

2.3.1 Faraday's First Law of Electrolysis

Faraday's first Law of electrolysis states that when an electrolyte, either in molten state or solution state is electrolyzed, the mass of a substance (m) deposited or dissolved at electrodes is directly proportional to the quantity of electricity (coulombs, Q) passed through the electrolyte.

Mathematically,

 $m \propto Q \text{ or }$

m = z*Q*

where, z is a proportionality constant called electrochemical equivalent

Since
$$z = \frac{E}{F} \& Q = It$$

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We can also rewrite the equation as: $m = \frac{EIt}{F}$ Where:

- E = equivalent weight of substance
- F = Faraday Constant (96,500 Coulombs)
- m = mass of substance
- I = current in amperes
- t = time required

equivalent weight of a substance $E = \frac{Molecular mass(M)}{Valence(n)}$

Thus, $m = \frac{MIt}{nF}$

For example, in the electrolysis of molten NaCl, the cathode reaction tells us that one Na atom is produced when one Na^+ ion accepts an electron from the cathode. To reduce 1 mole of Na^+ ions, we must supply one mole of electrons (6.02 x10²³ electrons) to the cathode.

Example 2.3

 How many moles of chlorine, magnesium and aluminum are formed when 2, 2 and 3 moles of charge are passed through three different solution containing chloride, magnesium and aluminum ions respectively? Solution:

The stoichiometry of the anode reaction shows that oxidation of two Cl^- ions yields one chlorine molecule and releases two electrons. Therefore, the formation of 1 mole of chlorine results in 2 moles of electrons supplied by the

 $\mathit{Cl}^{\scriptscriptstyle-}$ ions to the anode. Similarly, it takes 2 moles of electrons to reduce 1 mole

of Mg^{2+} ions and 3 moles of electrons to reduce 1 mole of Al^{3+} ions:

 $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$

 $Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$

 $Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$

Example 2.4

2

1. Calculate the mass of calcium metal and chlorine gas that can be produced when a current of 0.452 A is passed through molten CaCl, for 1.5 h.

Solution: In solving electrolysis problems of this type, the first step is to determine which species will be oxidized at the anode and which species will be reduced at the cathode. Here the choice is straight

forward because we only have Ca^{2+} and Cl^{-} ions in molten $CaCl_{2}$. Thus, we write the half and overall reactions as:

Anode (Oxidation): $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$

Cathode (Reduction): $Ca^{2+}(aq) + 2e^{-} \rightarrow Ca(s)$

Over all Reaction: $Ca^{2+}(aq) + 2Cl^{-}(aq) \rightarrow Ca(s) \rightarrow Cl_{2}(g)$

The quantities of calcium metal and chlorine gas formed depend on the number of electrons that pass through the electrolytic cell, which in turn depends on current x time or charge.

Charge (Q) = current (I) in A x time (t) in s

$$Q = l xt = (0.452 \text{ A}) \times (1.5 \times 60 \times 60 \text{ s})$$

$$= 2.44 \times 10^3 \text{ A s}$$

$$= 2.44 \times 10^3 \text{ C}$$

$$l \text{ mol } e^- = 96,500 \text{ C}$$

$$x = 2.44 \times 10^3 \text{ C}$$

$$\Rightarrow x = \frac{2.44 \times 10^3 \text{ C} x \text{ 1 mol } e^-}{96,500 \text{ C}} = 0.0253 \text{ mol } e^-$$

$$2 \text{ moles of electrons are required to produce 1 mole, or 40 g, of calcium metal at the cathode. Hence, the mass of calcium formed is$$

$$2 \text{ mol } e^- = 1 \text{ mole } \text{ Ca} = 40.08 \text{ g } Ca$$

$$0.0253 \text{ mol } e^- = x$$

$$\Rightarrow x = \frac{0.0253 \text{ mol } e^- x \ 40.08 \text{ g } Ca}{2 \text{ mol } e^-} = 0.507 \text{ g } Ca$$

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The anode reaction indicates that 1 mole, or 71 g, of chlorine is produced by giving 2 moles of electrons to the anode. Hence, the mass of chlorine gas formed is

2 mol e⁻ = 71 g Cl₂ = 1 mole Cl₂
0.0253 mol e⁻ = x

$$\Rightarrow x = \frac{0.0253 \text{ mol } e^{-} x \text{ 71 g } Cl_{2}}{2 \text{ mol } e^{-}} = 0.898 \text{ g } Cl_{2}$$

2.3.2 Faraday's Second Law of Electrolysis

Faraday's second law of electrolysis states that the masses of different substances, liberated or dissolved by the same amount of electricity, are proportional to their equivalent masses." When the same quantity of electricity is passed through several electrolytic solutions connected in series, then the masses of the different materials liberated or dissolved (m_1 , m_2 , m_3 ...) at the respective electrodes are in the ratio of their equivalent masses (E_1 , E_2 , E_3 ...).

Mathematically, $m \alpha E_{OT} m_1 \alpha E_1$, $m_2 \alpha E_2$, and $m_3 \alpha E_3$ etc Replacing the proportionality by the proportionality constant, the equation become

$$\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3} = k \frac{m_1}{E_1} = \frac{m_2}{E_2}$$

The law can be illustrated by passing the same quantity of electric current through three solutions containing H_2SO_4 , $CuSO_4$ and $AgNO_3$, connected in series, as shown in Figure 2.6.



Figure 2.6: Solutions connected in series to a battery.

In the first solution, hydrogen and oxygen are liberated. In the second solution copper is deposited and in the third, silver is deposited.

 $\frac{mass of hydrogen}{equivalent mass of Hydrogen} = \frac{mass of copper}{equivalent mass of copper} = \frac{mass of silver}{equivalent mass of silver}$

Example 2.5

1. Calculate the mass of copper deposited by the electrolysis of $CuSO_4$

solution placed in series with a silver nitrate solution, when 0.108 g of Ag is being deposited.

Solution:

The equivalent mass of silver and copper can be obtained from their reduction half-reaction:

$$Ag^{+}(aq) + 1e^{-} \rightarrow Ag(s), \quad E_{Ag} = \frac{108 \ g / mol}{1} = 108 \ g / eq$$
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s), \quad E_{Cu} = \frac{63.5 \ g / mol}{2} = 31.75 \ g / eq$$

The mass of Ag is 0.108 g, and you are asked to find the mass of copper.

$$\frac{m_{Ag}}{E_{Ag}} = \frac{m_{Cu}}{E_{Cu}} \implies m_{Cu} = \frac{E_{Cu}m_{Ag}}{E_{Ag}}$$
$$= \frac{31.75 \text{ g/eq x } 0.108 \text{ g}}{108 \text{ g/eq}} = 0.032 \text{ g of Cu is deposited}$$

CHECKLIST -2.3

Put (\checkmark) in the box for the tasks you can perform or the concepts you understand

l can.....

- state Faraday's first law of electrolysis
- use the mathematical expressions of the Faraday's first law of electrolysis to solve problems.
- state Faraday's second law of electrolysis
- use the mathematical expressions of Faraday's second law to solve problems.

Self-Test Exercise 2.3

- 1. Calculate the volume of H_2 and O_2 gases at 25°C and 1.00 atm that will be collected at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 2 hours with 10 ampere current.
- 2. Calculate the mass of copper and volume of oxygen (at 25°C and 760 mmHg) that would be produced by passing a current of 0.5 A through a

 $CuSO_4$ solution between Pt electrodes for 3 hours.

- 3. What mass of aluminum is deposited electrolytically in 30 minutes by a current of 40 A?
- 4. Two cells are connected in series. One contains *AlCl*₃, and the other contains *AgNO*₃ as the electrolytes. What mass of Ag is deposited when 18 g of Al is deposited at cathode?
- 5. 0.2 moles of electrons are passed through three electrolytic cells in series that contain silver ions, zinc ions and iron (III) ions. How many grams of each metal will be deposited at cathode?

Section 2.4: INDUSTRIAL APPLICATION OF ELECTROLYSIS

Dear learner, electrolysis is a process of chemical decomposition produced by passing an electric current through a liquid or solution containing ions. In this process, we generally pass a direct electrical current through an ionic substance which is either present in its molten form or is dissolved in any appropriate solvent, producing chemical reactions at the electrodes and causing material decomposition. The key process of electrolysis is the exchange of atoms and ions from the external circuit by removing or adding electrons. Often the desired electrolysis products are in a different physical state from the electrolyte and some physical processes can remove them. The main components needed for electrolysis are an electrolyte, electrical supply and two electrodes. Electrolysis is applied in various fields such as in the extraction of metals, production of nonmetals, metal refining, production of chemicals, electroplating etc.

Unit Outcomes

After completing this subunit, you will be able to:

- mention the industrial applications of electrochemistry;
- explain electroplating and electro refining;
- demonstrate copper refining; and
- explain how electrolysis is used in the production of some metals, nonmetals and compounds

The production of chemicals

) Can you mention list of chemicals that can be produced by the electrolysis?

Electro synthesis of metals

Electro synthesis is the method of producing substances through electrolysis reactions.

2.4.1 Extraction of Metals



Reflect on each of the following questions.

- 1. List active metals that can be extracted from their compounds by electrolysis.
- 2. Explain why electrolytic reduction rather than chemical reduction is often used to obtain active metals from their compounds.
- 3. Why are molten metal chlorides used as electrolytes rather than using other molten salts?

Metals and their alloys are extensively used in our day-to-day life. They are used for making machines, railways, motor vehicles, bridges, buildings, agricultural tools, aircrafts, ships etc. Therefore, production of a variety of metals in large quantities is necessary for the economic growth of a country. Only a few metals such as gold, silver, mercury etc. occur in Free State in nature. Most of the other metals, however, occur in the earth's crust in the combined form, i.e., as compounds with different anions such as oxides, sulphides, halides etc.

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(B

Do you know the term minerals before?

A naturally occurring material in which a metal or its compound occurs is called a mineral. A mineral from which a metal can be extracted economically is called an ore. An ore is that mineral in which a metal is present in appreciable quantities and from which the metal can be extracted economically

If a metal is less reactive than carbon, it can be extracted by reacting it with carbon in a displacement reaction. In a displacement reaction, the more reactive metal is able to take the place of a less reactive metal in a compound, since the more reactive metal forms stronger bonds. Carbon replaces the less reactive metal in a redox reaction, where the carbon is oxidized and the metal is reduced. We therefore refer to this method as reduction using carbon. But metals more reactive than carbon are extracted using electrolysis. Electrolysis is a process that uses electricity to separate the elements in a compound. Aluminum, for example, is a reactive and the most abundant metal on Earth, but it is most commonly found as its ore, aluminum oxide (Al_2O_3) . We can extract aluminum from its ore, with the industrial set up of the electrolytic cell .Electrolysis is used to remove the oxygen and extract aluminum, which means that reduction takes place. The electrolyte is molten aluminum oxide, and the electrodes are graphite. The aluminum (Al^{3+}) cations are attracted to the cathode, where they are reduced to form molten aluminum.

Reduction reaction: $4Al^{3+} + 12e^{-} \rightarrow 4Al$

The aluminum is deposited on the bottom of the cell and drains away. The oxygen (O²⁻) anions are attracted to the anode, where they are oxidized to release oxygen gas.

Oxidation reaction: $6O^{2-} \rightarrow 3O_2 + 12e^-$

Overall reaction: $4Al^{3+} + 6O^{2-} \rightarrow 4Al + 3O_2$

2.4.2 Electrolytic refining of Metals

Activity 2.8

Answer each of the following questions.

- 1. Define electro refining.
- 2. What are the purposes of electro refining?
- 3. Describe the electro refining of copper. Include the appropriate chemical equations.

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Except in the electrolytic reduction method, metals produced by any other method are generally impure. The impurities may be in the form of

- i. other metals
- ii. unreduced oxide of the metal
- iii. non-metals like carbon, silicon, phosphorus, sulphur etc. and
- iv. flux or slag. A large number of crude metals like copper, silver; zinc, tin etc. are refined by electrolysis.

A block of impure metal is made the anode and a thin sheet of pure metal forms the cathode of the electrolytic cell containing an acidified solution of copper sulphate which acts as an electrolyte (Figure 2. 7). On passing an electric current of low voltage through the solution copper (II) ions obtained from copper sulphate solution go to the cathode where they are reduced to the free copper metal and get deposited while more electropositive impurities are left in solution. Less electropositive metals do not dissolve and fall away from the anode to settle below it as anode mud.

 $Cu^{2+} + 2e^{-} \rightarrow Cu$ (at cathode)

An equivalent amount of the metal from the anode dissolves into the electrolyte as Cu^{2+} ions: $Cu \rightarrow Cu^{2+} + 2e^{-}(at anode)$

As the process goes on, anode becomes thinner while the cathode becomes thicker. The impurities like silver, gold settle down at the bottom of the cell as 'anode mud'.



Figure 2.7 Purification of Copper by Electrolysis

2.4.3 Electroplating of Metals

What is an electroplating? Can you define it?

Electroplating is the process of plating one metal onto another by electrolysis, most commonly for decorative purposes or to prevent corrosion of a metal. There are also specific types of electroplating such as copper plating, silver plating, and chromium plating. Electroplating allows manufacturers to use inexpensive metals such as steel or zinc for the majority of the product and then apply different metals on the outside to account for appearance, protection, and other properties desired for the product. In the process of electroplating, an external source of electric current is usually applied. This takes place in an electrolytic cell. The metal on which electroplating takes place is made the cathode (negative terminal) while the metal which is going to be plated as a layer on the metal is made the anode (positive terminal). The object that is to be plated is connected to the negative terminal of the power supply. A piece of silver is connected to the positive terminal. The electrolyte is a silver nitrate solution. This process can also be used to purify silver. We can take an impure block at the positive terminal and a strip of pure silver to the negative. The pure silver is deposited via electrolysis at the negative terminal, leaving behind the impurities.

Experiment 2.3

Dear learner, to have a clear understanding of Electroplating, perform the following ex-periment. To conduct the experiment, visit a nearby high school and request a teacher who is teaching Grade 12 chemistry to help you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory. If you couldn't find a high school in your area, request your tutor to get support and advices.

Title: Electroplating of an iron key with copper metal

Objective: To conduct Electroplating of an iron key with copper metal

Apparatus and chemicals: Beaker, sand paper, copper wire, power supply (DC) or dry cells, distilled water, 1M copper sulphate solution, 1 M H_2SO_4 solution, copper rode and an iron switch



Procedure:

- 1. Dissolve two teaspoonful of $CuSO_4$ in 250 mL of distilled H_2O in a clean and dry beaker. To increase conduction, add a few drops of dilute H_2SO_4 to $CuSO_4$ solution. Take a copper plate of 10 cm x 4cm size and a door key made of iron. Use sandpaper to clean the copper plate and iron key. Rinse the copper plate and iron key with water and dry them.
- 2. Place the cleaned copper plate in the $CuSO_4$ solution and connect it to the positive terminal of a battery as shown in Figure 2.8. This copper plate becomes the anode or positive electrode.
- 3. Place the clean iron key in the $CuSO_4$ solution at a small distance from the copper plate and connect the negative terminal of a battery to the iron key. This iron key becomes the cathode or negative electrode.
- 4. Switch on the electric current by closing the switch. Allows the current to pass for about 15 minutes.
- 5. Remove the copper plate and iron key from the $CuSO_4$ solution.

Observations and analysis:

- 1. What are the purposes of electroplating?
- 2. Why is it important to polish the copper plate and iron key before use?
- 3. What do you observe from the surface of the iron key?
- 4. What will happen to the free copper ions in the CuSO₄ solution?
- 5. What will happen to the copper plate connected to the positive terminal of the battery?

2.4.4 Electro synthesis of Nonmetals and compounds

Activity 2.9

Think critically and reflect on the following questions.

- 1. Explore nonmetals and compounds that are prepared by electrolysis.
- 2. Write the cathode and anode reactions during the electrolysis of molten mixture of potassium fluoride and hydrogen fluoride.
- 3. Why is a small amount of electrolyte solute added in the electrolysis of water?

) Why is a small amount of electrolyte solute added in the electrolysis of water?

Many Nonmetals and compounds can be produced using electrolysis. For example, the chlorine-alkali industry is an important part of the chemical industry, which produces **chlorine** (nonmetal) and **sodium hydroxide** (compound) through the electrolysis of the raw material **brine**. The reactions that take place at the electrodes (when graphite electrodes are used) are as follows:

Anode reaction: $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$

Cathode reaction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ Overall cell reaction is:

 $2NaCl(aq) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + Cl_2(g) + H_2(g)$

Put (\checkmark) in the box for the tasks you can perform or the concepts you understand

l can.....

- define
- Electrolytic cell
- Anode
- Cathode
- Faraday
- describe the industrial application of Electrolysis
- explain how electrolysis is used in the production of some metals, nonmetals and compounds
- assemble, diagrammatically, the basic components of an electrolysis cell into a complete cell
- define the terms such as
- extraction
- refining
- electroplating



Section 2.5: VOLTAIC CELLS

Dear learner, an electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell. The device used to convert the chemical energy produced on a red-ox reaction into electrical energy is called an electrochemical cell or simply a chemical cell. These are also called galvanic cells or voltaic cell after the names of Luigi Galvanic and Alessandro Volta who were first to perform experiments on the conversion of chemical energy into electrical energy. In electrochemical cell, a spontaneous redox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy. An indirect red-ox reaction is such that reduction and oxidation processes are carried out in two separate vessels called half-cells.



What makes a Galvanic cell different from an electrolytic cell?

After completing this subunit, you will be able to:

- define Voltaic cell and salt bridge;
- define electrode potential and cell potential;
- explain how standard electrode potential is measured;
- describe the reactivity of metal from its position in the activity series or electromotive series
- decide whether a given redox reaction is spontaneous or not
- explain the effect of concentration on cell potential
- mention the different types of Voltaic cells
- give examples of each type of Galvanic cell
- describe how a hydrogen-oxygen fuel cell operates
- distinguish between primary and secondary cells
- identify the cathode, anode and electrolyte of a given Galvanic cell
- compare and contrast electrolytic and Galvanic cells
- explain metallic corrosion in terms of redox reactions
- explain the negative effects of corrosion; and
- Explain the different methods of the prevention of corrosion.

2.5.1 Construction of Voltaic Cells (Zn-Cu voltaic Cell)



Answer each of the following questions.

- 1. Describe the basic features of an electrochemical cell. Why are the two components of the cell separated from each other?
- 2. Given the following chemical reaction as:

 $Mg(s)+2H^+(aq) \rightarrow Mg^{2+}(aq)+H_2(g)$ write equations for the oxidation and reduction half-reactions.

When a piece of zinc metal is placed in a $CuSO_4$ solution, Zn is oxidized to

 Zn^{2+} ions while Cu^{2+} ions are reduced to metallic copper.

 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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The electrons are transferred directly from the reducing agent (Zn) to the oxidizing agent (Cu^{2+}) in solution. However, if we physically separate the oxidizing agent from the reducing agent, the transfer of electrons can take place via an external conducting medium (a metal wire). As the reaction progresses, it sets up a constant flow of electrons and hence generates electricity (that is, it produces electrical work such as driving an electric motor).

The experimental apparatus for generating electricity through the use of a spontaneous reaction is called a galvanic cell or voltaic cell. (Figure 2.9) shows the essential components of a galvanic cell. A zinc bar is immersed in a $ZnSO_4$ solution, and a copper bar is immersed in a $CuSO_4$ solution. The cell operates on the principle that the oxidation of Zn to Zn^{2+} and the reduction of Cu^{2+} to Cu can be made to take place simultaneously in separate locations with the transfer of electrons between them occurring through an external wire. The zinc and copper bars are called electrodes. This particular

arrangement of electrodes (Z_n and C_u) and solutions (Z_nSO_4 and $CuSO_4$) is called the Daniell cell. By definition, the **anode** in a galvanic cell is the electrode at which oxidation occurs and the **cathode** is the electrode at which reduction occurs. For the Daniell cell, the **half-cell reactions**, that is, the oxidation and reduction reactions at the electrodes are

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ Reduction: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Overall Reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions in that half-cell to deposit copper metal atoms. The net result is that zinc metal reacts with copper ions to produce zinc ions and copper metal, and electric current flows through the external circuit. Note that unless the two solutions are separated from each other, the Cu^{2+} ions will react directly with the zinc bar and no useful electrical work will be obtained.

To complete the electrical circuit, the solutions must be connected by a conducting medium through which the cations and anions can move from one electrode compartment to the other. This requirement is satisfied by a salt bridge, which, in its simplest form, is an inverted U tube containing an

inert electrolyte solution, such as KCl, KNO_3 or NH_4NO_3 , whose ions will not react with other ions in solution or with the electrodes.

During the course of the overall redox reaction, electrons flow externally from the anode (Z_n electrode) through the wire and light bulb to the cathode (C_u electrode).

In the solution, the cations $(Zn^{2+}, Cu^{2+}, \text{ and } K^+)$ move toward the cathode, while the anions $(SO_4^{2-} \text{ and } Cl^-)$ move toward the anode. Without the salt bridge connecting the two solutions, the buildup of positive charge in the anode compartment (due to the formation of Zn^{2+} ions) and negative charge in the cathode compartment (created when some of the Cu^{2+} ions are reduced to Cu) would quickly prevent the cell from operating.



Figure 2.9 Daniell cell.

Cell diagram (Cell Notation)

The conventional notation for representing the components of a voltaic cells or galvanic cells is the cell diagram. For example cell notation for the Daniell cell shown in Figure 2.9 is given by:

$$Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s)$$

You will use the following generally accepted conventions in writing cell notation.

- The components of the anode compartment (oxidation half-cell) are written to the left of the components of the cathode compartment (reduction half-cell).
- > A boundary between different phases (an electrode and a solution) is represented by a single vertical line. For example, $Zn(s)|Zn^{2+}(aq)$ indicates that solid Zn is in a different phase with aqueous Zn^{2+}
- The boundary between half-cell compartments, commonly a salt bridge, is represented by a double vertical line. Species in aqueous solution are placed on either side of the double vertical line.
- Different species within the same solution are separated from each other by a comma.

For example, the notation for the voltaic cell shown in the following reaction is:

Oxidation half reaction: $2I^{-}(aq) \rightarrow I_{2}(s) + 2e^{-}$

Reduction half reaction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ Over all (Cell) reaction:

 $MnO_4^{-}(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

graphite
$$|I^{-}(aq)|I_{2}(s)||MnO_{4}^{-}(aq), H^{+}(aq), Mn^{2+}(aq)|$$
 graphite

That is, in the cathode compartment, MnO_4^- , H^+ and Mn^{2+} ions are in an aqueous solution with Solid graphite (inert electrode) immersed in it. If needed, the concentrations of dissolved components are given in parentheses; for example, if the concentrations of Zn^{2+} and Cu^{2+} are 1M, we write $Zn(s) | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s) \text{ or}$ $Zn(s) | Zn^{2+}(aq, 1M) || Cu^{2+}(aq, 1M) | Cu(s)$

anod $\rightarrow Zn \mid Zn^{2+} (aq, 1.00M) \underset{\text{solt bridge}}{\text{II}} CU^{2+} (aq, 1.00M) \mid Cu(s) \leftarrow \text{cathod}$

- Half-cell components usually appear in the same order as in the halfreaction, and electrodes appear at the far left (anode) and far right (cathode) of the notation.
- Ions in the salt bridge are not part of the reaction so they are not in the notation.

The notation for any Galvanic cell has the following form: anode | anode electrolyte (M) | | cathode electrolyte (M) | cathode

Every redox reaction is the sum of an oxidation half-reaction and a reduction half reaction written in such a way as to cancel out the electrons by suitably multiplying the half-reactions by the minimum integers.

Example 2.6

1. Write the cell notation for a Galvanic cell, for the cell reaction:

 $Cr(s) + 3Ag^+(aq) \rightarrow Cr^{3+}(aq) + 3Ag(s)$

Assume that the solution concentrations are 0.20 M

Solution:

Write the oxidation half-reaction and the reduction half-reaction separately.

Oxidation half-reaction (anode): $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$

Reduction half-reaction (cathode): $Ag^+(aq) + e^- \rightarrow Ag(s)$

The cell notation is $Cr(s) | Cr^{3+}(0.20M) || (0.020M) Ag^+ | Ag(s)$

2.5.2 Measuring Standard electrode Potentials

A cell potential is a measure of the driving force of the cell reaction. This reaction occurs in the cell as separate half-reactions: an oxidation halfreaction and a reduction half-reaction. The general forms of these halfreactions are

Anode (Oxidation): Reduction Species \rightarrow Oxidized Species + ne⁻

Cathode (Reduction): Oxidized Species + $ne^- \rightarrow \text{Re}$ duction Species Just as the overall cell reaction can be thought of as the sum of two half-cell reactions, the measured electrode potential of the cell can be treated as the sum of the electrical potentials at the Zn and Cu electrodes. Knowing one of these electrode potentials, we could obtain the other by subtraction. It is impossible to measure the potential of just a single electrode, but if we arbitrarily set the potential value of a particular electrode at zero, we can use it to determine the relative potentials of other electrodes. The hydrogen electrode, shown in Figure 2.10, serves as the reference for this purpose. In the hydrogen electrode, hydrogen gas is bubbled into a hydrochloric acid solution at 25°C. The platinum electrode has two functions.

First, it provides a surface on which the dissociation of hydrogen molecules can take place:

$H_2 \rightarrow 2H^+ + 2e^-$

Second, it serves as an electrical conductor to the external circuit.

Under standard-state conditions (when the pressure of H_2 is 1 atm and the concentration of the *HCl* solution is 1*M*), the potential for the reduction of H^+ at 25°C is taken to be exactly zero:

 $2H^+(1M) + 2e^- \rightarrow H_2(1 \text{ atm}), \quad E^0 = 0V$

The superscript "O" denotes standard-state conditions, and E° is the standard reduction potential, or the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm. Thus, the standard reduction potential of the hydrogen electrode is defined as zero. The hydrogen electrode is called the standard hydrogen

electrode (SHE).

The standard hydrogen electrode (SHE) consists of a platinum electrode that has H_2 gas at 1 atm bubbling through it and is immersed in 1 M strong acid, $H^+(aq)$ or $H_3O^+(aq)$ (Figure 2.10). Thus, the reference half-reaction is $2H^+(aq; 1M) + 2e^- \rightarrow H_2(g; 1 atm), \quad E_{reference}^0 = 0.00V$



Figure 2.10. The Standard Hydrogen Electrode (SHE)

We can use the SHE to measure the potentials of other kinds of electrodes. To find an unknown standard electrode potential ($E^0_{unknown}$), we construct a voltaic cell consisting of this reference half-cell and the unknown halfcell. Since $E^0_{reference}$ is zero, the overall E^0_{cell} gives $E^0_{unknown}$.

Depending on the unknown half-cell, the reference half-cell can be the anode or the cathode:

• When H_2 is oxidized, the reference half-cell is the anode, and so reduction occurs at the unknown half-cell:

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$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$$
$$= E^{0}_{unknown} - E^{0}_{reference}$$
$$= E^{0}_{unknown} - 0.00V$$
$$= E^{0}_{unknown}$$

When H_2 is reduced, the reference half-cell is the cathode, and so oxidation occurs at the unknown half-cell:

$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$$
$$= E^{0}_{reference} - E^{0}_{unknown}$$
$$= 0.00V - E^{0}_{unknown}$$
$$= -E^{0}_{unknown}$$

Figure 2.11 shows a voltaic cell that has the $Zn(s)|Zn^{2+}$ half-reaction in one compartment and the $H^+|H_2$ (or $H_3O^+|H_2$) half-reaction in the other. The zinc electrode is negative relative to the hydrogen electrode, so we know that the zinc is being oxidized and is the anode and the SHE is the cathode.

The cell notation is

 $Zn(s) | Zn^{2+}(1M) || H^{+}(1M) | H_{2}(1 atm) | Pt(s)$



Figure 2.11A cell consisting of a zinc electrode and a hydrogen electrode.

As mentioned earlier, the Pt electrode provides the surface on which the reduction takes place. When all the reactants are in their standard states

(that is, H_2 at 1 atm, H^+ and Zn^{2+} ions at 1 **M**), the electromotive force (EMF) of the cell is 0.76 V at 25°C. We use this value to find the unknown standard electrode potential, E_{zinc}^0 :

We can write the half-cell reactions as follows:

Anode (Oxidation): $Zn(s) \rightarrow Zn^{2+}(1M) + 2e^{-1}$

Cathode (Reduction) : $2H^+(1M) + 2e^- \rightarrow H_2(1M)$

Overall reaction: $Zn(s) + 2H^+(1M) \rightarrow Zn^{2+}(1M) + H_2(1M)$

By convention, the standard EMF of the cell, E^0_{cell} which is composed of a contribution from the anode and a contribution from the cathode, is given by

 $E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$

Where both $E^{\circ}_{cathode}$ and E°_{anode} are the standard reduction potentials of the electrodes. For the Zn-SHE cell, we write

$$E^{0}_{cell} = E^{0}_{H^{+}/H_{2}} - E^{0}_{Zn^{2+}/Zn}$$

0.76 V = 0 - $E^{0}_{Zn^{2+}/Zn}$

where the subscript H^+/H_2 means $2H^+ + 2e^- \rightarrow H_2$ and the subscript Zn^{2+}/Zn means $Zn^{2+} + 2e^- \rightarrow Zn$. Thus, the standard reduction potential of zinc, $E^0_{Zn^{2+}/Zn}$, is $-0.76 \vee$

Note that we write the reaction as a reduction, even though it occurs in reverse as oxidation. Whenever we assign a potential to a half-reaction, we write the reaction as a reduction.

The standard electrode potential of copper can be obtained in a similar fashion, by using a cell with a copper electrode and a SHE (Figure 2.12). In this case, the copper electrode is the cathode because its mass increases during the operation of the cell, as it is consistent with the reduction reaction:

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The cell notation is: $Pt(s) | H_2(1 \text{ atm}) | H^+(1M) || Cu^{2+}(1M) | Cu(s)$ and the halfcell reactions are:

Anode (Oxidation): $H_2(1 \text{ atm}) \rightarrow 2H^+(1M) + 2e^-$

Cathode (Reduction): $Cu^{2+}(1M) + 2e^{-} \rightarrow Cu(s)$

Overall Reaction: $H_2(1 \text{ atm}) + Cu^{2+}(1M) \rightarrow 2H^+(1M) + Cu(s)$

Under standard-state conditions and, the EMF of the cell is 0.34 V, so we write

$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$$

$$0.34 V = E^{0}_{Cu^{2+}/Cu} - E^{0}_{H^{+}/H_{2}}$$

$$0.34 V = E^{0}_{Cu^{2+}/Cu} - 0$$

$$E^{0}_{Cu^{2+}/Cu} = 0.34 V$$

In this case, the standard reduction potential of copper, $E^{o}_{Cu^{2^+}/Cu}$, is 0.34 V, where the subscript means: $Cu^{2^+} + 2e^- \rightarrow Cu$

For the Daniell cell shown in Figure 2.9, we can now write

Anode (Oxidation):
$$Zn(s) \rightarrow Zn^{2+}(1M) + 2e^{-}$$

Cathode (Reduction):
$$Cu^{2+}(1M) + 2e^{-} \rightarrow Cu(s)$$

Overall Reaction: $Zn(s) + Cu^{2+}(1M) \rightarrow Zn^{2+}(1M) + Cu(s)$

The EMF of the cell is

$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$$
$$V = E^{o}_{cu^{2+}/Cu} - E^{o}_{Zn^{2+}/Zn}$$
$$= 0.34 \lor - (-0.76 \lor)$$
$$= 1.10 \lor$$

You can use the sign of E° to predict the extent of a redox reaction.

A positive **E**° means the redox reaction will favor the formation of products at equilibrium.

A negative **E**° means that more reactants than products will be formed at equilibrium.

The standard reduction potentials for other half-reactions are established in the way that we did for the Cu^{2+}/Cu half-reaction. The standard reduction potentials of some of the half-reactions are given in Table 2.3

Table 2.3 Standard Reduction Potential in Aqueous Solution at 25°C.

]	Half-Reaction	$E^{\circ}(\mathrm{V})$
Increasing Strength as oxidizing agent	Half-Reaction $F_{2}(g) + 2e^{-} \longrightarrow 2F'(aq)$ $O_{3}(g) + 2H^{+}(aq) + 2e^{-} \longrightarrow O_{2}(g) + H_{2}O$ $Co^{3*}(aq) + 2e^{-} \longrightarrow Co^{2*}(aq)$ $H_{2}O_{2}(aq) + 2H^{+}(aq) + SO_{4}^{-2*}(aq) + 2e^{-} \longrightarrow PbsO_{4}(s) + 2e^{-}$ $Ce^{3*}(aq) + e^{-} \longrightarrow Ce^{3*}(aq)$ $MnO_{4}^{-}(aq) + 8H^{+}(aq) + Se^{-} \longrightarrow Mn^{2*}(aq) + 4H_{2}O$ $Au^{3*}(aq) + 3e^{-} \longrightarrow Au(s)$ $Cl(g) + 2e^{-} \longrightarrow 2Cl^{-}(aq)$ $Cr_{2}O_{7}(aq) + 14H^{+}(aq) + 6e^{-} \longrightarrow 2Cr^{3*}(aq) + 7H_{2}O$ $MnO_{2}(s) + 4H^{+}(aq) + 4e^{-} \longrightarrow 2H_{2}O$ $Br_{2}(I) + 2e^{-} \longrightarrow 2Br(aq)$ $NO_{3}^{-}(s) + 4H^{+}(aq) + 3e^{-} \longrightarrow NO(aq) + 2H_{2}O$ $2Hg^{2*}(aq) + 2e^{-} \longrightarrow Hg^{2*}(aq)$ $Hg_{2}^{2*}(aq) + 2e^{-} \longrightarrow 2Hg(I)$ $Ag^{*}(aq) + e^{-} \longrightarrow Ag(s)$ $Fe^{3*}(aq) + e^{-} \longrightarrow Fe^{2*}(aq)$ $O_{2}(g) + 2H^{+}(aq) + 2e^{-} \longrightarrow MnO_{2}(s)$ $I_{2}(s) + 2e^{-} \longrightarrow 2Ir(aq)$ $O_{2}(g) + 2H^{+}(aq) + 2e^{-} \longrightarrow MnO_{2}(s)$ $I_{2}(s) + 2e^{-} \longrightarrow 2Ir(aq)$ $O_{2}(g) + 2H_{2}O + 4e^{-} \longrightarrow 4OH^{+}(aq)$ $Cu^{2*}(aq) + 2e^{-} \longrightarrow Ag(s) + Cl^{-}(aq)$ $SO_{4}^{-*}(aq) + 2e^{-} \longrightarrow Ag(s) + Cl^{-}(aq)$ $SO_{4}^{-*}(aq) + 2e^{-} \longrightarrow Ag(s) + Cl^{-}(aq)$ $SO_{4}^{-*}(aq) + 2e^{-} \longrightarrow Bg(s) + Cl^{-}(aq)$ $SO_{4}^{-*}(aq) + 2e^{-} \longrightarrow Cu^{+}(aq)$ $SD_{4}^{-*}(aq) + 2e^{-} \longrightarrow Bg(s) + Cl^{-}(aq)$ $SD_{4}^{-*}(aq) + 2e^{-} \longrightarrow Bg(s) + SD_{4}^{-*}(aq)$ $Cu^{2*}(aq) + 2e^{-} \longrightarrow Bg(s) + SO_{4}^{-*}(aq)$ $Cu^{2*}(aq) + 2e^{-} \longrightarrow Cu(s)$ $PbSO_{4}(s) + 2e^{-} \longrightarrow Bg(s) + SO_{4}^{-*}(aq)$ $Cu^{2*}(aq) + 2e^{-} \longrightarrow Bg(s) + SO_{4}^{-*}(aq)$ $Cu^{2*}(aq) + 2e^{-} \longrightarrow Cu(s)$ $PbSO_{4}(s) + 2e^{-} \longrightarrow Cu(s$	$E^{\circ}(\mathbf{V})$ +2.87 +2.07 +1.82 +1.77 +1.82 +1.77 2H ₂ O +1.61 +1.51 +1.50 +1.36 +1.33 +1.23 +1.23 +1.23 +1.07 +0.96 +0.92 +0.85 +0.80 +0.77 +0.68 +0.59 +0.53 +0.40 +0.59 +0.53 +0.40 +0.59 +0.53 +0.40 +0.53 +0.40 +0.59 +0.53 +0.40 +0.53 +0.40 +0.53 +0.40 +0.53 +0.40 +0.55 +0.13 0.00 -0.13 -0.14 -0.25 -0.28 -0.31 -0.40 -0.44 -0.74 -0.76 -0.83 -1.18 -1.66
	$Cd^{2+}(aq) + 2e^{-} \longrightarrow Cd(s)$ $Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$ $Cr^{3+}(aq) + 3e^{-} \longrightarrow Cr(s)$ $Zn^{2+}(aq) + 2e^{-} \longrightarrow H_{2}(g) + 2OH^{-}(aq)$ $Mn^{2+}(aq) + 2e^{-} \longrightarrow Mn(s)$ $Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$ $Be^{2+}(aq) + 2e^{-} \longrightarrow Be(s)$ $Mg^{2+}(aq) + 2e^{-} \longrightarrow Mg(s)$ $Na^{+}(aq) + e^{-} \longrightarrow Na(s)$ $Ca^{2+}(aq) + 2e^{-} \longrightarrow Sr(s)$ $Ba^{2+}(aq) + 2e^{-} \longrightarrow Ba(s)$ $K^{+}(aq) + e^{-} \longrightarrow K(s)$	-0.40 -0.44 -0.74 -0.76 -0.83 -1.18 -1.66 -1.85 -2.37 -2.71 -2.87 -2.89 -2.90 -2.93 -3.05

For all half-reactions the concentration is 1 **M** for dissolved species and the pressure is 1 atm for gases. These are the standard-state values

- The E° values apply to the half-cell reactions as read in the forward (left to right) direction.
- ➤ The more positive **E**° is, the greater the tendency for the substance to be reduced. For example, The half-cell reaction: $F_2(1 \text{ atm}) + 2e^- \rightarrow 2F^-(1M)$, $E^0 = 2.87 \text{ V}$ has the highest positive **E**° value among all the half-cell reactions. Thus, F_2 is the strongest oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction

$Li^{+}(1M) + 2e^{-} \rightarrow Li(s), \qquad E^{0} = -3.05 V$

which has the most negative \mathbf{E}° value. Thus, Li^{+} is the weakest oxidizing agent because it is the most difficult species to reduce. Conversely, we say that F_2 is the weakest reducing agent and Li metal is the strongest reducing agent. Under standard-state conditions, the oxidizing agents (the species on the left-hand side of the half-reactions in Table 2.1 increase in strength from bottom to top and the reducing agents (the species on the left-hand side of the half-reactions) increase in strength from top to bottom.

- > The half-cell reactions are reversible. Depending on the conditions, any electrode can act either as an anode or as a cathode. Earlier we saw that the SHE is the cathode (H^+ is reduced to H_2) when coupled with zinc in a cell and that it becomes the anode (H_2 is oxidized to H^+) when used in a cell with copper.
- Under standard-state conditions, any species on the left of a given halfcell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located below it in Table 2.2.This principle is sometimes called the diagonal rule. In the case of the Daniell cell,

(S

(g

$$Cu^{2+}(1M) + 2e^{-} \rightarrow Cu(s), \quad E^{0} = 0.34 V$$

 $Zn^{2+}(1M) + 2e^{-} \rightarrow Zn(s), \quad E^{0} = -0.76 V$

We see that the substance on the left of the first half-cell reaction is Cu^{2+} and the substance on the right in the second half-cell reaction is Zn. Therefore, as we saw earlier, Zn spontaneously reduces Cu^{2+} to form Zn^{2+} and Cu. The diagonal line shows that Cu^{2+} is the oxidizing agent and Zn is the reducing agent.

⁷ Changing the stoichometric coefficients of a half-cell reaction does not affect the value of E_{red}° , because electrode potentials are intensive properties. This means that the value of E_{red}° is unaffected by the size of the electrodes or the amount of solutions present but is dependent on the concentration of the solutions and the pressure of a gas. For example:

$$I_2(s) + 2e^- \rightarrow 2I^-(1M), \quad E^0_{red} = +0.53 V$$

but $E^{\scriptscriptstyle 0}$ does not change if we multiply the half-reaction by 2

$$2I_2(s) + 4e^- \rightarrow 4I^-(1M), \quad E^0_{red} = +0.53 V$$

The sign of E^{o}_{red} changes, but its magnitude remains the same when we reverse a reaction.

Example 2.7

1. A galvanic cell consists of a Mg electrode in a 1.0 M $Mg(NO_3)_2$ solution

and a Ag electrode in a 1.0 M $AgNO_3$ solution. Calculate the standard emf of this cell at 25°C. Is this reaction spontaneous?

Solution:

At first it may not be clear how to assign the electrodes in the galvanic cell. From Table

2.1we write the standard reduction potentials of Ag and Mg and apply the diagonal rule to determine which is the anode and which is the cathode.

The standard reduction potentials are

 $Ag^{+}(1.0M) + e^{-} \rightarrow Ag(s), \quad E^{0} = 0.80 V$

 $Mg^{2+}(1.0M) + 2e^{-} \rightarrow Mg(s), \quad E^{0} = -2.37 V$

Applying the diagonal rule, we see that Ag^+ will oxidize Mg:

Anode (oxidation): $Mg(s) \rightarrow Mg^{2+}(1.0M) + 2e^{-}$

Cathode (reduction): $2Ag^+(1.0M) + 2e^- \rightarrow 2Ag(s)$

Overall Reaction: $Mg(s) + 2Ag^+(1.0M) \rightarrow Mg^{2+}(1.0M) + 2Ag(s)$

Note that in order to balance the overall equation we multiplied the

reduction of Ag^+ by 2. We can do because, as an intensive property, **E**° is not affected by this procedure. We find the EMF of the cell by using Table 2.1

$$E_{cell}^{0} = E_{cathode}^{0} - E_{anod}^{0}$$

= $E_{Ag^{+}/Ag}^{0} - E_{Mg^{2+}/Mg}^{0}$
= 0.80 V - (-2.37 V)
= 3.17 V

The positive value of E°_{cell} shows that the forward reaction is favored.

Experiment 2.4

Dear learner, to understand about the Determination of Cell Potential of Daniell Cell, perform the following experiment. To conduct the experiment, visit a nearby high school and request a teacher who is teaching Grade 12 chemistry to help you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory. If you couldn't find a high school in your area, request your tutor to get support and advices.

Title: Determination of Cell Potential of Daniell Cell

Objective:

- > To determine cell potential of Daniell cell and
- > To identify the cathode and anode.

Apparatus and chemicals : Voltmeter, copper strip, zinc strip, 1 M ZnSO4

, 1 M $CuSO_4$, saturated KCl solution, two 100 mL beakers, U-tube, a fine sandpaper or file and cotton.





Procedure:

- Fill each U-tube with saturated KCl and plug each end with cotton. Be sure not to rap of any air bubbles in the tube. The cotton also helps to prevent the leakage of KCl solution.
- 2. Clean the metal strips (Zn and Cu) with a fine sandpaper or file, if needed. These strips are to be used as electrodes.
- 3. Assemble a Zn half-cell as shown in Figure 2.13a.

- > Dip one end of the Zn metal strip in a 50 mL of 1 M $ZnSO_4$ in a 100 mL beaker. Then, attach one end of the copper wire with the strip of zinc and the other to terminal of a voltmeter.
- Do the same thing to construct the copper half-cell shown in Figure 2.13b. Connect the two half-cells using a salt bridge as shown in Figure 2.13c.

Read the voltage, Record your observations and give explanations for those observations.

Results and discussion:

- 1. What happens to the needle in the voltmeter when current flows in the external circuit?
- 2. Label the cathode and anode.
- 3. Write the half-reactions at each half cell.
- 4. Is there any color change in the intensity of copper sulphate solution?

2.5.3 Electromotive Force (EMF)

Activity 2.11

Reflect on the following questions.

- 1. Why does water in a river flow downhill rather than uphill?
- 2. How do you relate this concept to the movement of electrons in a wire?

Every Galvanic or Voltaic cell is made up of two half-cells, the oxidation half- cell (anode) and the reduction half-cell (cathode). One of the electrodes must have a higher electrode potential (higher tendency to lose electrons) than the other electrode. As a result of this potential difference, the electrons flow from an electrode at a higher potential to the electrode at a lower potential. The force which causes the flow of electrons from one electrode to another electrode and thus results in the flow of current from electrode at higher potential to electrode at lower potential to the force (EMF).

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The EMF of the cell or cell potential can be calculated from the values of electrode potential of the two half cells constituting the cell. When oxidation potential of anode and cathode are taken into account

$$E^0_{\ cell} = E^0_{\ anode} - E^0_{\ cathode}$$

When reduction potential of cathode and anode are taken into account

$$E^{0}_{\ cell} = E^{0}_{\ cathode} - E^{0}_{\ anode}$$

Dependence of Cell Potential EMF on Concentration

The cell potential depends on the concentrations of ions and on gas pressures. For that reason, cell potentials provide a way to measure ion concentrations. The pH meter, for example, depends on the variation of cell potential with hydrogen-ion concentration. You can relate cell potentials to the standard electrode potentials by using the Nernst. equation

Nernst Equation

The standard electrode potentials are measured in their standard states when the concentration of the electrolyte solutions are fixed as 1 M and temperature is 298 K. In actual practice electrochemical cells do not have always fixed concentration of the electrolyte solutions. The electrode potentials depend on the concentration of the electrolyte solutions. A change in concentration affects the change of cell potential which is a result of free energy change. According to chemical thermodynamics

$$\Delta G = \Delta G^0 + RT \ln Q$$

Where, Q is the reaction quotient, and Q was used to calculate the effect of concentration on ΔG

You can apply this equation to a voltaic cell. In that case, the concentrations and gas pressures are those that exist in the cell at a particular instant.

Since $\Delta G = -nFE_{cell}$ and $\Delta G^0 = -nFE_{cell}^0$ the equation becomes $-nFE_{cell} = -nFE_{cell}^0 + RT \ln Q$

This result rearranges to give the **Nernst equation** that gives a relation between electrode potentials and the concentration of electrolyte solution

$$E_{cell} = E_{cell}^{0} - \frac{RT}{nF} \ln Q \text{ or } E_{cell} = E_{cell}^{0} - \frac{2.303RT}{nF} \log Q \text{ : Nernst equation}$$

If you substitute 298 K (25 °C) for the temperature in the Nernst equation and put in values for RandF, you get (using common logarithms)

$$E_{cell} = E_{cell}^{o} - \frac{0.0592}{n} \log Q \text{ (Value in volts at 25 °C)}$$

You can show from the Nernst equation that the cell potential, E_{cell} , decreases as the cell reaction proceeds. As the reaction occurs in the voltaic cell, the concentrations of products increase and the concentrations of reactants decrease. Therefore, Q and $\log Q$ increase. The second term

in the Nernst equation, $(\frac{0.0592}{n}\log Q)$, increases, so that the difference $E_{cell}^o - \frac{0.0592}{n}\log Q$ decreases. Thus, the cell potential, E_{cell} , becomes smaller. Eventually the cell potential goes to zero, and the cell reaction comes to equilibrium.

As an example of the computation of the equilibrium constant, consider the cell notation of the following voltaic cell:

 $Cd(s) | Cd^{2+}(0.010M) || H^{+}(1.00M) | H_{2}(1.00 atm) | Pt$

The cell reaction is: $Cd(s)+2H^+(aq) \rightleftharpoons Cd^{2+}(aq)+H_2(g)$ The expression for the equilibrium constant is given by

$$K = \frac{\left[Cd^{2+}\right]p_{H_2}}{\left[H^+\right]^2}$$

Note that the hydrogen-gas concentration is given here in terms of the pressure (in atmospheres). To have consistent units, we convert the given pressure to molarity with the ideal gas law:

$$PV = nRT$$
$$\frac{P}{RT} = \frac{n}{V}$$
$$\frac{1 \ atm}{0.0821 \frac{L \ atm}{K \ mol}} \times 298.15 = 0.041M$$

Then we substitute into the above equation gives as:

$$K = \frac{0.010 \ x \ 0.041}{(1.00)^2} = 0.00041 = 4.1 \ x \ 10^{-4}$$
Example 2.8

Calculate the equilibrium constant for the following reaction at 25°C $Sn(s) + 2Cu^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + 2Cu^{+}(aq)$

Solution:

The equilibrium constant (K) can be calculated, using the equation,

$$\ln K = \frac{nE_{cell}^0}{0.0257 V}$$
$$K = e^{\left(\frac{nE_{cell}^0}{0.0257 V}\right)}$$

The half-reactions are:

Anode (oxidation): $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^{-}$

Cathode (reduction):
$$2Cu^{2+}(aq) + 2e^{-} \rightarrow 2Cu^{+}(aq)$$

From the above reaction and using Table 2.2, we can calculate the cell potential,

$$E^{0}_{cell} = E^{0}_{red} (cathode) - E^{0}_{red} (anode)$$

= $E^{0}_{red} (Cu^{2+} / Cu^{+}) - E^{0}_{red} (Sn^{2+} / Sn)$
= 0.15 V - (-0.14 V) = + 0.29 V

 E^{0}_{cell} is 0.29 V, and n = 2 (because 2 mol of electrons are consumed in the reaction), then,

$$\ln k = \frac{nE_{cell}^{0}}{0.0257 V} = \frac{2 \times 0.29 V}{0.0257 V} = 22.6$$
$$\implies K = e^{22.6} = 6.532 \times 10^{9}$$

The reaction favors the formation of products.

Example 2.9

 Calculate the standard free-energy changes for the following reaction when it is at 25 °C

 $2Au(s) + 3Ca^{2+}(1.0M) \rightarrow 2Au^{3+}(1.0M) + 3Ca(s)$

Solution: The relationship between the standard free energy change and the standard cell potential is given by $\Delta G^0 = -nFE^0_{cell}$.

The half-reactions are:

Anode (oxidation) : $2Au(s) \rightarrow 2Au^{3+}(1.0M) + 6e^{-}$ Cathode (reduction) : $3Ca^{2+}(1.0M) + 6e^{-} \rightarrow 3Ca(s)$

$$E^{0}_{cell} = E^{0}_{red} (cathode) - E^{0}_{red} (anode)$$

= $E^{0}_{red} (Ca^{2+} / Ca) - E^{0}_{red} (Au^{2+} / Au)$
= -2.87 V - 1.5 V = - 4.37 V

The overall reaction shows that n = 6 (6 moles of electrons are involved).

Now we can calculate
$$\Delta G^{\circ}$$
, using the following equation:

$$\Delta G^{0} = - nFE^{0}_{cell}$$

= - 6 × (96500 J/V mol) × (- 4.37 V)
= 2.53 × 10⁶ J/mol = 2.53 × 10³ kJ/mol

Therefore, the large positive value of ΔG^0 tells us that the reaction favors the reactants at equilibrium. The forward reaction is non-spontaneous, that is, gold cannot reduce calcium.

Example 2.10

1. Write the half cell and net cell reactions for the following cell,

 $Zn | ZnSO_4(aq) || CuSO_4(aq) | Cu$

Calculate the standard EMF of the given cell

$$E^{0}_{Zn^{2+}/Zn} = -0.76 V \text{ and } E^{0}_{Cu^{2+}/Cu} = +0.34 V$$

Solution: Half-cell reactions

Anode Reaction: $Zn \rightarrow Zn^{2+} + 2e^{-}$ Cathode Reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu$ Over all Reaction: $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$ $E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$ $= E^{0}_{Cu^{2+}/Cu} - E^{0}_{Zn^{2+}/Zn}$ = 0.34 V - (-0.76 V) = 1.1 V

Example 2.11

1. What is the cell potential of the following voltaic cell at 25°C?

 $Zn(s) | Zn^{2+}(1.0 \times 10^{-5}M) || Cu^{2+}(0.100M) | Cu(s)$. The standard cell potential of this cell is 1.10 V.

Solution The cell reaction is

 $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

The number of moles of electrons transferred is two; hence, n = 2. The equilibrium constant is

$$K = \frac{\left[Zn^{2^+}\right]}{\left[Cu^{2^+}\right]} = \frac{1.0 \ x \ 10^{-5}}{0.100} = 1.0 \ x \ 10^{-4}$$

The standard cell potential is 1.10 V, so the Nernst equation becomes

$$E_{cell} = E_{cell}^{0} - \frac{0.0592}{n} \log K$$

= 1.10 - $\frac{0.0592}{2} \log (1.0 \times 10^{-4})$
= 1.10 - (-0.12) = 1.22 V

Concentration Cells

Because electrode potential depends on ion concentrations, it is possible to construct a galvanic cell from two half-cells composed of the same material but differing in ion concentrations. Such a cell is called a concentration cell. The two solutions are in separate half-cells, so they do not mix, but their concentrations become equal as the cell operates.

Finding E_{cell} for a Concentration Cell

Suppose a voltaic cell has the Cu/Cu^{2+} half reaction in both compartments. The cell reaction is the sum of identical half-reactions, written in opposite

directions. The standard cell potential, E^0_{cell} , is zero because the standard electrode potentials are both based on 1 MCu^{2+} , so they cancel. In a concentration cell, however, the concentrations are different. Thus, even

though E^{0}_{cell} is still zero, the nonstandard cell potential, E_{cell} , depends on the ratio of concentrations, so it is not zero.

For the final concentration to be equal, a concentration cell must have the dilute solution in the anode compartment and the concentrated solution in the cathode compartment. For example, let's use 0.10 M Cu^{2+} in the anode half-cell and $1.0MCu^{2+}$ in the cathode half-cell (Figure 2.14):

Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq; 0.1 M) + 2e^{-}$





Figure 2.14. A concentration cell based on the Cu/Cu^{2+} half-reaction; $E_{cell} > 0$ as long as the half-cell concentrations are different.

The overall cell reaction is the sum of the half-reactions:

$$Cu^{2+}(aq; 1.0 M) \rightarrow Cu^{2+}(aq; 0.1 M) E_{cell} = ?$$

The cell potential at the initial concentrations of 0.10 M(dilute) and 1.0M (concentrated), with n = 2, is obtained from the Nernst equation:

$$E_{cell} = E_{cell}^{0} - \frac{0.0592 \ V}{2} \log \frac{\left[Cu^{2+}\right] dilute}{\left[Cu^{2+}\right] conc.}$$

= 0 V - $\left(\frac{0.0592 \ V}{2} \log \frac{0.10M}{1.0M}\right)$
= 0 V - $\left(\frac{0.0592 \ V}{2}(-1.00)\right)$
= 0.0296 V

Since E_{cell}^{0} is zero, E_{cell} depends entirely on the $\left[\left(\frac{0.0592 V}{n}\right)\log K\right]$ term

How a Concentration Cell Works?

- > In the anode (dilute) half-cell, Cu atoms in the electrode give up electrons and the resulting Cu^{2+} ions enter the solution and make it more concentrated.
- > In the cathode (concentrated) half-cell, Cu^{2+} ions gain the electrons and the resulting Cu atoms plate out on the electrode, which makes that solution less concentrated. As in any voltaic cell, E_{cell} decreases until equilibrium is attained, which happens when $[Cu^{2+}]$ is the same in both half-cells. The same final concentration would result if we mixed the two solutions, but no electrical work would be done.

Determination of pH

The pH of a solution can be obtained very accurately from cell potential measurements, using the Nernst equation. To see how this is done, suppose you have a test solution whose pH you would like to determine.

You set up a voltaic cell as follows: You use the test solution as the electrolyte for a hydrogen electrode and bubble in hydrogen gas at 1 atm. Now connect this hydrogen electrode to a standard zinc electrode to give the following cell:

 $Zn(s) | Zn^{2+}(1M) || H^{+}(test \ solution) | H_{2}(1 \ atm) | Pt$

The cell reaction is: $Zn(s) + 2H^+(test \ solution) \rightarrow Zn^{2+}(1M) + H_2(1 \ atm)$

The cell potential depends on the hydrogen-ion concentration of the test solution, according to the Nernst equation. The standard cell potential of the cell equals 0.76 V, and

$$K = \frac{\left[Zn^{2+}\right]p_{H_2}}{\left[H^+\right]^2} = \frac{1}{\left[H^+\right]^2}$$

Substituting into the Nernst equation, you obtain

$$E_{cell} = 0.76 - \frac{0.0592}{2} \log \frac{1}{\left[H^+\right]^2} = 0.76 + 0.0592 \log\left[H^+\right]$$

where $[H^+]$ is the hydrogen-ion concentration of the test solution. To obtain the relationship between the cell potential (E_{cell}) and pH, you substitute the following into the preceding equation: $pH = -\log[H^+]$ The result is

$$E_{cell} = 0.76 - 0.0592 \, pH$$

Which one you rearrange to give the pH directly in terms of the cell potential?:

$$pH = \frac{0.76 - E_{cell}}{0.0592}$$

In this way, measurement of the cell potential gives you the pH of the solution. The main difference between electrolytic and voltaic cell is summarized in table 2.4

Chemistry Grade 12

Table 2.4 comparison of Galvanic Cell / Voltaic and Cell Electrolytic Cell

Galvanic Cell / Voltaic Cell	Electrolytic Cell			
Energy released by spontaneous	Electrical energy is used to derive			
redox reaction is converted to	non-spontaneous redox reaction.			
Electrical energy				
In these electrochemical cells, the	These cells feature a positively			
anode is negatively charged and the	charged anode and a negatively			
cathode is positively charged.	charged cathode.			
Oxidation half reaction	Oxidation half reaction			
$Y \to Y^+ + e^-$	$Z^- \rightarrow Z + e^-$			
Reduction half reaction	Reduction half reaction			
$Z^+ + e^- \to Z$	$Y^+ + e^- \to Y$			
Overall reaction	Overall reaction			
$Y + Z^+ \to Y^+ + Z \qquad (\Delta G < 0)$	$Y^+ + Z^- \to Y + Z (\Delta G > 0)$			





It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are called **electrolytic cells.** Electrolytic cells, like galvanic cells, are composed of two half-cellsone is a reduction half-cell, the other is an oxidation half-cell (Figure 2.15b). The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells (Figure 2.15a), but the definition of both cathode and anode remain the same, where reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

 \square

 \square

Put (\checkmark) in the box for the tasks you can perform or the concepts you understand

I can.....

- Define
- galvanic cell cell
- salt bridge
- cell potential
- cell diagram
- reduction potential
- illustrate the possibilities of displacement reactions between two metals
- distinguish between the half cells for reduction and oxidation in a galvanic cell
- assemble, diagrammatically, the basic components of an electrolysis cell into a complete cell
- deduce the half-reaction and the overall reaction when the cell diagram is known
- explain why a potential difference can develop in a galvanic cell
- calculate
- E^{o}_{cell} from E^{o}_{cell} values of the half-cells
- E^{o}_{cell} from E^{o}_{cell} for a given cell when the E of the other half-cell is known

Self-test Exercise 2.5

- Write the cell notation for a Galvanic cell consisting of an Al electrode placed in 1M Al(NO₃)₃ solution and a Ag electrode placed in a 1 M AgNO₃ solution.
- 2. Explain the use of a salt bridge.
- 3. Can Sn reduce $Zn^{2+}(aq)$ under standard-state conditions?
- 4. What is the standard emf of a galvanic cell made of a Cd electrode in a 1.0

 $MCd(NO_3)_2$ solution and a Cr electrode in a 1.0 $MCr(NO_3)_3$ solution at 25°C?

5. The following overall reaction is given:

 $Cu^{2+}(1.0M) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(1.0M)$

- a. Sketch the Galvanic cell based on the reaction.
- b. Identify the cathode and anode.
- c. Show the direction of electron flow through the external circuit.
- 6. In a test of a new reference electrode, a chemist constructs a voltaic

cell consisting of a Zn / Zn^{2+} half-cell and an H_2 / H^+ half-cell under

the following conditions: $[Zn^{2+}] = 0.010M$, $[H^+] = 2.5M$, $pH_2 = 0.30 atm$. Calculate E_{cell} at 298.15 K.

- 7. A concentration cell consists of two Ag/Ag^+ half-cells. In half-cell A, the electrolyte is 0.010 M $AgNO_3$; in half-cell B, it is 4.0 x 10⁻⁴ M $AgNO_3$. What is the cell potential at 298.15 K?
- 8. What is the cell potential of the following voltaic cell at 25 0C?

 $Zn(s) | Zn^{2+}(0.200 M) || Ag^{2+}(0.002M) | Ag(s)$

9. Predict whether the following reaction would proceed spontaneously as written at 298 K:

$$Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$$
 given that
 $\begin{bmatrix} Co^{2+} \end{bmatrix} = 0.25M \text{ and } \begin{bmatrix} Fe^{2+} \end{bmatrix} = 0.94M$

10. A voltaic cell houses the reaction between aqueous bromine and zinc metal: $Br_2(s) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Br^-(aq)$ $E^0_{cell} = 1.83 V$ Calculate $E^0_{bromine}$, given $E^0_{Zn} = 0.76 V$.

2.5.4 Batteries

A **battery** is a galvanic cell, or a series of combined galvanic cells, that can be used as a source of direct electric current at a constant voltage. Although the operation of a battery is similar in principle to that of the galvanic cells, a battery has the advantage of being completely selfcontained and requiring no auxiliary components such as salt bridges. Here you will discuss types of batteries that are in widespread use.



Activity 2.12

Based on your knowledge of grade 10 chemistry answer the following questions.

- 1. Collect some used and disposed dry cell batteries in your area. Identify the parts of the batteries, which you have collected, the type of electrodes as well as physical and chemical nature of the electrolyte present in the battery.
- 2. Write the anode, cathode and cell reaction for the battery you have collected.

2.5.5 Fuel cells

A **fuel cell** is essentially a battery, but it differs in operating with a continuous supply of energetic reactants, or fuel. Figure 2.16 shows a proton-exchange membrane (PEM) fuel cell that uses hydrogen and oxygen. In its simplest form, a hydrogen-oxygen fuel cell consists of an electrolyte solution, such as potassium hydroxide solution, and two inert electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments



Figure 2.16 A hydrogen – oxygen fuel cell.

On one side of the cell, the anode, hydrogen passes through a porous material containing a platinum catalyst, the electrolyte solution here is phosphoric acid, H_3PO_4 . The electrode equations for acid hydrogen-oxygen fuel cell are:

Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

The $2H^+(aq)$ ions then migrate through a proton-exchange membrane to the other side of the cell to participate in the cathode reaction with $O_2(g)$

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(g)$

You can also run a hydrogen-oxygen fuel cell with an alkaline electrolyte: for example potassium hydroxide solution, KOH(aq). In the case of the alkaline hydrogen-oxygen fuel cell the different electrode equations are:

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

 $Cathode: O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$



The sum of the half-reactions for an acid and an alkaline electrolyte hydrogen-oxygen fuel cell is

 $Overall: 2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$, which is the net reaction in the fuel cell.

The applications of fuel cells are power for lighting, emergency power generators, communications equipment, automobiles, and buses. Other types of cells using other materials and fuels such as hydrocarbons or methanol are either in commercial production or under development.

2.5.6 Corrosion of Metals

Corrosion is the term usually applied to the deterioration of metals by an electrochemical process. Corrosion causes tens of billions of dollars of damage to cars, ships, buildings, and bridges each year. This natural process, which oxidizes metals to their oxides and sulfides, shares similarities with the operation of a voltaic cell. We focus on the corrosion of iron, but many other metals, such as copper and silver, also corrode.

The Corrosion of Iron

The most common and economically destructive form of corrosion is the rusting of iron. Iron rust is *not* a direct product of the reaction between iron and oxygen but arises through a complex electrochemical process. The important facts about iron corrosion are:

- > Iron does not rust in dry air; moisture must be present.
- > Iron does not rust in air-free water; oxygen must be present.
- > Iron loss and rust formation occur at different places on the same object.
- > Iron rusts more quickly at low pH (high $[H^+]$).
- > Iron rusts more quickly in ionic solutions
- > Iron rusts more quickly in contact with a less active metal (such as Cu) and more slowly in contact with a more active metal (such as Zn)

Two separate Redox processes occur during corrosion:

1. The loss of iron. A strain or dent in contact with water is usually the site of iron loss. This site is called an anodic region because of the following half-reaction (Figure 2.17):

Anodic region; Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$



Figure 2.17 A small area of the surface, showing the steps in the corrosion process.

Once the iron atoms lose electrons, the damage to the object has been done, and a pit (depression or hollow) forms where the iron is lost. The electrons given up by iron reduce atmospheric oxygen to water at the cathode, which is another region of the same metal's surface:

Cathodic region; $r \in duction : O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

This portion of the corrosion process (the sum of these two half-reactions) occurs without any rust forming:

Overall reaction: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

2. The rusting process. Rust forms in another redox reaction. The Fe^{2+} ions formed at the anodic region disperse through the water and react with

 O_2 , often away from the pit, to form the Fe^{3+} in rust. The overall reaction for this step is:

$$2Fe^{2+}(aq) + \frac{1}{2}O_2(g) + (2+n)H_2O(l) \rightarrow Fe_2O_3.nH_2O(s) + 4H^+(aq)$$

[The coefficient n for H_2O appears because of rust, $Fe_2O_3.nH_2O$, has a variable number of waters of hydration.] The rust deposit is incidental to the real damage, which is the loss of iron that weakens the strength of the object. Adding the two previous equations gives the overall equation for the loss and rusting of iron:

$$Fe(s) + \frac{3}{2}O_2(g) + nH_2O(l) \rightarrow Fe_2O_3.nH_2O(s)$$

Other species ($2Fe^{2+}$ and $2H_2O$) also cancel, but we showed the canceled

 $[H^+]$ ions to emphasize that they act as a catalyst: they speed the process as they are used up in one step and created in another. For this reason, rusting is faster at low pH (high $[H^+]$).

lonic solutions speed rusting by improving the conductivity of the aqueous medium near the anodic and cathodic regions. The effect of ions is especially evident on ocean going vessels and on the underbodies and around the wheel wells of cars driven in cold climates, where salts are used to melt ice on slippery roads. Thus, in some key ways, corrosion resembles the operation of a voltaic cell:

- > Anodic and cathodic regions are physically separated.
- The regions are connected via an external circuit through which the electrons travel.
- In the anodic region, iron behaves like an active electrode, whereas in the cathodic region, it is inactive.
- The moisture surrounding the pit functions somewhat like an electrolyte and salt bridge.

Metallic corrosion is not limited to iron. Consider aluminum, a metal used to make many useful things, including airplanes and beverage cans. Aluminum has a much greater tendency to oxidize than iron does; in Table 2.2 we see that *Al* has a more negative standard reduction potential

than Fe. Based on this fact alone, we might expect to see airplanes slowly corrode away in rainstorms, and soda cans transformed into piles of corroded aluminum. These processes do not occur because the layer of

insoluble aluminum oxide (Al_2O_3) that forms on its surface when the metal is exposed to air serves to protect the aluminum underneath from further corrosion. The rust that forms on the surface of iron, however, is too porous to protect the underlying metal. Coinage metals such as copper and silver also corrode, but much more slowly.

 $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $Ag(s) \rightarrow Ag^{+}(aq) + 2e^{-}$

In normal atmospheric exposure, copper forms a layer of copper carbonate

 $(CuCO_3)$, a green substance also called patina, that protects the metal underneath from further corrosion. Likewise, silverware that comes into contact with foodstuffs develops a layer of silver sulfide (Ag_2S) .

Protecting Against the Corrosion of Iron

ζ) Activity 2.13

Reflect your understandings on the following questions.

- 1. How do we prevent iron from rusting?
- 2. What is common in all methods of preventing the rusting of iron?

A number of methods have been devised to protect metals from corrosion. Most of these methods are aimed at preventing rust formation. The most obvious approach is to coat the metal surface with paint. However, if the paint is scratched, pitted, or dented to expose even the smallest area of bare metal, rust will form under the paint layer.

The tendency for iron to oxidize is greatly reduced when it is alloyed with certain other metals. For example, in stainless steel, an alloy of iron and chromium, a layer of chromium oxide forms that protects the iron from corrosion. An iron container can be covered with a layer of another metal such as tin or zinc. The point regarding corrosion concerns the relative activity of other metals in contact with iron. The essential idea is that iron functions as both anode and cathode in the rusting process, but it is lost only at the anode. Thus

Corrosion increases when iron behaves more like the anode. When iron is in contact with a less active metal (weaker reducing agent), such as copper, it loses electrons more readily (its anodic function is enhanced; Figure 2.18). Non conducting rubber or plastic spacers are placed between the metals to avoid this problem.



Figure 2.18 A small area of the surface, showing the steps in the corrosion process.

Corrosion decreases when iron behaves more like the cathode. In cathodic protection, the most effective way to prevent corrosion, iron makes contact with a more active metal (stronger reducing agent), such as zinc. The iron becomes the cathode and remains intact, while the zinc acts as the anode and loses electrons (Figure 2.19). Coating iron with a "sacrificial" layer of zinc is called galvanizing. In addition to blocking physical contact with H_2O and O_2 , the zinc (or other active metal) is "sacrificed" (oxidized) instead of the iron. Sacrificial anodes are used underwater and underground to



protect iron and steel pipes, tanks, oil rigs, and so on.

Figure 2.19 The effect of Metal-metal contact on the corrosion of iron; Fe in contact with Zn does not corrode. This method of preventing corrosion is known as cathodic protection.

) CHECKLIST-2.6

Put (\checkmark) in the box for the tasks you can perform or the concepts you understand

I can.....

- define
 - A battery
 - A fuel cell
 - Corrosion
- describe corrosion of metals
- write the anidic and cathodic reactions of
- explain how corrosion resembles the operation of voltaic cell
- describe the different methods of protecting corrosion of iron
- explain how corrosion increases or decreases when iron behaves like the anode and the cathode

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Self-test Exercise 2.6

Attempt the following questions.

- 1. Explain the difference between a dry cell and a lead storage battery.
- 2. Write the reactions that occur at the cathode and anode during the charging of a lead storage battery.
- 3. What is the electrolyte in a dry cell?
- 4. Define corrosion.
- 5. Explain the negative effects of corrosion.
- 6. Aluminum does not rust as iron does. Why?

Unit Summary

- An oxidation-reduction (redox) reaction involves the transfer of electrons from a reducing agent to an oxidizing agent.
- The half-reaction method of balancing divides the overall reaction into half reactions that are balanced separately and then recombined.
- There are two types of electrochemical cells: voltaic and electrolytic cell. In a voltaic cell, a spontaneous reaction generates electricity and does work on the surroundings. In an electrolytic cell, the surroundings supply electricity that does work to drive a non-spontaneous reaction.
- In both types of cell, two electrodes dip into electrolyte solutions; oxidation occurs at the anode, and reduction occurs at the cathode.
- A voltaic cell consists of oxidation (anode) and reduction (cathode) halfcells, connected by a wire to conduct electrons and a salt bridge to maintain charge neutrality.
- Electrons move from the anode (left) to the cathode (right), while cations move from the salt bridge into the cathode half-cell and anions move from the salt bridge into the anode half-cell.
- The cell notation shows the species and their phases in each half-cell, as well as the direction of current flow.
- The output of a cell is the cell potential (E_{cell}), measured in volts (1V = 1J/C).
- With all substances in their standard states, the output is the standard cell potential (E^0_{cell}).
- $E^{0}_{cell} > 0$ for a spontaneous reaction at standard-state conditions.

- By convention, a standard electrode potential ($E^0_{half-cell}$) refers to the reduction half reaction.
- E^{0}_{cell} equals $E^{0}_{half-cell}$ of the cathode minus $E^{0}_{half-cell}$ of the anode.
- Using a standard hydrogen (reference) electrode ($E^{0}_{half-cell} = 0V$), $E^{0}_{half-cell}$ values can be measured and used to rank oxidizing (or reducing) agents.
- Spontaneous redox reactions combine stronger oxidizing and reducing agents to form weaker reducing and oxidizing agents, respectively.
- A metal can reduce another species (H^+ , H_2O , or an ion of another metal)
 - if E^0_{cell} for the overall reaction is positive.
- A spontaneous process has a negative ΔG and a positive E_{cell} , $\Delta G = -nFE$. . The ΔG of the cell reaction represents the maximum electrical work the cell can do.
- The standard free energy change, ΔG^0 , is related to E^0_{cell} and to K.
- For nonstandard conditions, the Nernst equation shows that E_{cell} depends on E^0_{cell} and a correction term based on Q. E_{cell} is high when Q is small (high [reactant]), and it decreases as the cell operates. At equilibrium, ΔG

and E_{cell} are zero, which means that Q = K

- Concentration cells have identical half-reactions, but solutions of differing concentration. They generate electrical energy as the concentrations become equal.
- Ion-specific electrodes, such as the pH electrode, measure the concentration of one species.
- Batteries are voltaic cells arranged in series and are classified as primary (e.g., alkaline, mercury, and silver), secondary (e.g., lead-acid, nickel metal hydride, and lithium-ion), or fuel cells.
- Supplying electricity to a rechargeable (secondary) battery reverses the redox reaction, re-forming reactant.
- Fuel cells are not self-contained and generate a current through the controlled oxidation of a fuel such as H_2 .
- Corrosion damages metal structures through a natural electrochemical process.

- Iron corrosion occurs in the presence of oxygen and moisture and is increased by $high[H^+]$, high[ion], or contact with a less active metal, such as Cu.
- *Fe* is oxidized and O_2 is reduced in one redox reaction, while Fe^{2+} is oxidized and O_2 is reduced to form rust (hydrated form of Fe_2O_3) in another redox reaction that often takes place at a different location.
- Because Fe functions as both anode and cathode in the corrosion process, an iron object can be protected by physically covering it or by joining it to a more active metal (such as Zn, Mg, or Al), which acts as the anode in place of the Fe.
- An electrolytic cell uses electrical energy to drive a non-spontaneous reaction.
- Oxidation occurs at the anode and reduction at the cathode, but the direction of electron flow and the charges of the electrodes are opposite those in voltaic cells.
- In electrolysis of a pure molten salt, the metal cation is reduced at the cathode, and the nonmetal anion is oxidized at the anode.
- The reduction or oxidation of water takes place at nonstandard conditions.
- Overvoltage causes the actual voltage required to be unexpectedly high

(especially for gases, such as H_2 and O_2) and can affect the product that forms at each electrode

 The amount of product that forms depend on the quantity of charge flowing through the cell, which is related to the time the charge flows and the current. Self-Assessment Questions for Unit 2

Multiple Choice Questions

1. What is the oxidation number of chromium in the ionic compound ammonium dichromate, $(NH_4)_2Cr_2O_7$?

Α.	+ 3	C.	+ 5
Β.	+ 4	D.	+ 6

2. What are the oxidation numbers for nickel, sulfur, and oxygen in Ni₂(SO₄)₃?

Α.	Ni +3;S +6; O -2	C.	Ni +3; S +4; O -2
Β.	Ni +2; S +4; O -2	D.	Ni +2; S +2; O -2

3. What is the coefficient for hydroxide, and how many electrons are transferred after balancing the reaction?

 $Pb(OH)_4^{2-} + ClO^- \rightarrow PbO_2 + Cl^- + OH^- + H_2O$

- A. 2 OH⁻ and 2 electrons
- B. 3 OH-and 4 electrons
- C. 1 OH⁻ and 2 electrons
- D. 2 OH⁻ and 4 electrons
- 4. What was oxidized and what was reduced in the following reaction?

 $2Hg^{2+} + N_2H_4 \rightarrow 2Hg + N_2 + 4H^+$

- A. Hg^{2+} was oxidized; N_2H_4 was reduced
- B. Hg^{2+} was reduced; N_2H_4 was oxidized
- C. Hg^{2+} was oxidized; N_2H_4 was oxidized
- D. Hg^{2+} was reduced; N_2H_4 was reduced
- 5. Which of the following statements is true about electrochemical cells?
 - A. Reduction occurs at the anode
 - B. An element with a high affinity for electrons is likely to be easily oxidized
 - C. Oxidation occurs at the anode
 - D. Only oxidation half-reactions are useful

- 6. Which statement is **not correct** about voltaic cells?
 - A. Reduction occurs at the cathode.
 - B. Anions move through the barrier/bridge toward the electrode where oxidation is occurring.
 - C. The electrode where reduction is occurring is represented by a positive sign.
 - D. Electrons flow in the external circuit from the cathode to the anode.
- 7. The electrochemical reaction shown below is given, if the standard reduction potential of $Zn^{2+} \rightarrow Zn$ is 0.76 V, what is the standard reduction potential of $Mg^{2+} \rightarrow Mg$?

 $Mg | Mg^{2+}(aq) || Zn^{2+}(aq) | Zn E^{\circ} = + 1.61 V$ A. -0.85 V B. +0.85 V C. +2.37 V D. -2.37 V

- Use the Table of Standard Reduction Potential table, which species would react with Al³⁺?
 - A. Pb only C. Fe and Pb
 - B. Au³⁺ only D. Both Mg and K

 The oxidation of hydrogen by oxygen is one of the most-used reactions in fuel-cell technology. The overall reaction, which is given below, has a ΔG° value of – 474 k J/mol. What is the standard cell potential for this fuel

се	$\ \stackrel{?}{:} 2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$	$\Delta G^{\circ} = -4/4 \text{ kJ/mol}$
Α.	2.46 V	C. 1.23 V
Β.	4.91 V	D. 2.46 V

- 10. Which one of the following equations shows the relationship between standard Gibbs free energy and equilibrium constant?
 - A. $K = \Delta G^0$ C. $\Delta G^0 = -RT \ln K$
 - B. $K = RT \ln \Delta G^{\circ}$ D. $\Delta G^{\circ} = RT \ln K$

11. What is ΔG° for the following balanced reaction, if $E^{\circ} = +2.431 \text{ V}$?

	$Al(s) + Fe^{2+}(aq) \rightarrow Al^{3+} + Fe(l)$	E° = + 2.431		
Α.	-704 kJ/mol	C.	-235 kJ/mol	
Β.	+704 kJ/mol	D.	-469 kJ/mol	

12. The value of E° for the following reaction is 1.10 V. What is the value of E_{cell} when the concentration of Cu^{2+} is 1.0 M and the concentration of Zn^{2+} is 0.025 M?

 $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq) E^{\circ} = 1.10 V, \qquad [Cu^{2+}] = 1.0M$ and $[Zn^{2+}] = 0.025M$ A. 1.40 V C. 1.15 V B. 0.95 V D. 0.80 V

- 13. One of the basic differences between a fuel cell and a battery is:
 - A. fuel cell is rechargeable, while battery is not.
 - B. fuel cell does not store chemical energy, but a battery can store chemical energy.
 - C. both a fuel cell and a battery are rechargeable.
 - D. a and c.
- 14. A battery is ''dead'' if:
 - A. reactants and products reach their equilibrium concentrations.
 - B. E_{cell} is equal to zero.
 - C. ΔG is equal to zero.
 - D. all of the above.
- 15. A metal corrodes if:
 - A. it serves as cathode in the corrosion process.
 - B. it serves as anode in the corrosion process.
 - C. it does not react with oxygen.
 - D. all of the above.

Written assignment for unit 2

Short Answer Questions

- 1. Define each of the following terms:
 - A. oxidation
 - B. reduction

- D. electrolytic cell
- E. corrosion

- C. Galvanic cell
- 2. Balance each of the following chemical equations, using oxidation state change method.
 - A. $2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

$$\mathsf{B}. \quad Cu + HNO_3 \to Cu(NO_3)_2 + NO_2 + H_2O$$

3. Balance each of the following chemical equations in basic and acidic medium, using ion-electron method.

a.
$$ClO_3^- + SO_2 \rightarrow SO_4^{2-} + Cl^-$$

b.
$$H_2S + NO_3^- \rightarrow S_8 + NO$$

 $\mathsf{C}.\,H_2S + HNO_3 \rightarrow NO + S + H_2O$

d. $Cu + SO_4^{2-} \rightarrow Cu^{2+} + SO_2$

- 4. When an aqueous solution of copper(II)sulfate, $CuSO_4$, is electrolyzed, copper metal is deposited. $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (The other electrode reaction gives oxygen: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). If a constant current was passed for 5.00 h and 404 mg of copper metal was deposited, what was the current?
- 5. When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are: $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}$ and $2H_{2}O(l) + 2e^{-} \rightarrow H_{2}(aq) + 2OH^{-}(aq)$. How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?
- 6. Predict whether the following reaction would proceed spontaneously as written at 298 K: $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$, given that $[Co^{2+}] = 0.25$ M and $[Fe^{2+}] = 0.94$ M.
- 7. What is ΔG^{0} at 1000°C for the following reaction? $CaCO_{3}(s) \rightleftharpoons CaO(s) + CO_{2}(g)$. Is this reaction spontaneous at 1000°C and 1 atm?

- 8. Using standard electrode potentials, calculate the standard free-energy change at 25°C for the reaction $Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$
- 9. The standard cell potential for the following voltaic cell is 1.10 V: $Zn(s) |Zn^{2+}(aq)| Cu^{2+}(aq) |Cu(s)$. Calculate the equilibrium constant K_c for the reaction: $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$
- 10. Explain
 - A. How corrosion occurs?
 - B. How can corrosion be prevented?

ਤ) Answer key to Activities of Unit 2

Activity 2.1

1. The reaction in (a) is redox reaction. In this reaction, Ca is oxidized and hydrogen is reduced.

However, the reaction in (b) and (c) are non-redox reactions because there is no change in oxidation state.

- 2. a. Mg b Zn^{2+} c. Zn^{2+} d. Mg
- 3. a. +3 b.+6 c.+7

E Activity 2.2

Which of the following substances are capable of conducting electricity? Give the reason of your answer for yourself.

- a. Iron conducts electricity because iron metal has delocalized electrons
- b. Sulfur do not conduct electricity because sulfur is a nonmetal so that it has no delocalized electrons and freely mobile ions.
- c. Solid sodium chloride do not conduct electricity because ionic compounds do not conduct electric current in solid state because cations and anions are not free to move.
- d. Molten calcium chloride conducts electricity because it has free cations and anions.

E Activity 2.3

- a. Ions usually migrate towards oppositely charged electrodes. Hence, Na+ migrate towards the cathode and CI- to the anode.
- b. The anode is the electrode that is attached to the positive terminal of the battery while the cathode is attached to the negative terminal of the battery.



c. Cathode (reduction): $2Na^+(l) + 2e^- \rightarrow 2Na(l)$

Anode (oxidation): $2 \operatorname{Cl}^{-}(l) \rightarrow \operatorname{Cl}_{2}(g) + 2 e^{-}$

Overall reaction: $2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$



- Solid sodium chloride does not conduct electricity, because there are no free ions in solid sodium chloride. However, in molten state, there are free ions to conduct electricity.
 - a. Anode (oxidation): $2Cl^{-}(l) \rightarrow Cl_{2}(g) + 2e^{-}$
 - b. Cathode (reduction): $2K^+(aq) + 2e^- \rightarrow 2K(s)$
 - c. Overall reaction: $2Cl^{-}(l) + 2K^{+}(aq) \rightarrow Cl_{2}(g) + 2K(s)$
- 2. H^+ is discharged in preference to Na^+ because its reduction potential is less negative. For concentrated solutions Cl^- is discharged in preference to OH^- . That is when the solution is concentrated enough in Cl^- , Cl_2 is the product, but in dilute solution, O_2 is the product.

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Chemistry Grade 12 Distance Module -I

Activity 2.5

- 1. a. Dilute sodium chloride solution contains Na^+ , Cl^- , H^+ and OH^- ions.
 - b. Na^+ and H^+ ions migrate towards the cathode, and Cl^- and OH^- ions migrate towards the anode.
 - c. At the cathode, the H^+ ions are discharged in preference to the Na^+ ions. Since the concentration of the Cl^- ions is very small in dilute sodium chloride solution, the OH^- ions are discharged in preference to the Cl^- ions.

Cathode reaction: $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

Anode reaction: $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

Overall reaction: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$



- 1. Reactive electrodes.
- 2. Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$

Cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

3. If copper slab attached to anode contains more reactive impurities such as iron or zinc, the concentration of copper (II) sulphate decreases because the more reactive metals are oxidized at the anode, equal moles of copper metal are deposited at the anode. However, if the impurities are less reactive metals like gold and silver, after electrolysis the concentration of copper (II) sulphate solution is almost constant because copper electrode is oxidized at the anode and an equal amount of copper (II) ions are reduced at the cathode.

Crivity 2.7

- 1. Alkali metals, alkaline earth metals and aluminum are extracted by electrolysis.
- 2. Since active metals are highly reactive, they cannot be reduced from their compounds using the common reducing agents like carbon.
- 3. This is due to the fact that molten metal chlorides have lower melting points than other readily available salts.



- 1. Electrolytic refining is a process of refining a metal (mainly copper) by the process of electrolysis.
- 2. The main purpose of electro-refining is to purify the metals.
- In electro-refining the pure metal acts as cathode and impure metal acts as the anode whereas the electrolyte is soluble salt of the same metal. By passing the electricity the pre metal from anode is deposited over the cathode. The impurities are settled as anode mud.

Anode: $Cu \rightarrow Cu^{2+} + 2e^{-}$ Cathode: $Cu^{2+} + 2e^{-} \rightarrow Cu$

E Activity 2.9

- Non-metals such as fluorine, chlorine, hydrogen and oxygen are prepared by electrolysis. Electrolysis is also used in the preparation of compounds such as sodium hydroxide.
- 2. Anode(oxidation): $2F^{-}(aq) \rightarrow F_{2}(g)$

Cathode (reduction): $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Overall reaction: $2H^+(aq) + 2F^-(aq) \rightarrow H_2(g) + F_2(g)$

3. Pure water is a poor conductor of electricity, so a small amount of ionic solute is added to increase its electrical conductivity.

E Activity 2.10

An electrochemical cell contains two electrodes immersed in their 1. corresponding electrolyte solutions which are connected by a salt bridge. In order to do useful work, the two components of the cell should be separated and connected by a

salt bridge.

2. a. Oxidation half-reaction: $Mg(s) \rightarrow Mg^{2+}(aq)$ Anode reaction

Reduction half-reaction: $2H^+(aq) \rightarrow H_2(g)$ Cathode reaction



- 1. As it is observed in our daily life, water flows from uphill (high potential energy) to downhill (low potential energy). But when there is an external force, water flows from downhill (low potential energy) to uphill (high potential energy). Example tape water.
- 2. Similarly, electrons flow in a wire from negative (high electrical potential energy) to positive (low electrical potential energy).

Crivity 2.12

- 1. The electrolyte consists of ammonium chloride and zinc chloride in water. A carbon rod serves as the cathode and zinc as anode.
- 2. The cell reactions are

Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Cathode: $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ **Overall Reaction:**

$$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + 2NH_3(aq) + H_2O(l) + Mn_2O_3(s)$$

E Activity 2.13

- 1. Painting, galvanizing with zinc, electroplating with less active metals like chromium.
- 2. All methods prevent the direct contact of iron with oxygen and water.



- Self-test Exercise 2.1
- 1. Balance the following equation for the reaction in an acidic medium by the half-reaction method:

A.
$$5H_2C_2O_4 + 6H^+ + 2MnO_4^- \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

- B. $14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$
- C. $3H^+ + 3H_5IO_6 + 2Cr \rightarrow 2Cr^{3+} + 3IO_3^- + 9H_2O$
- D. $2HNO_3 + 3H_2O_2 \rightarrow 2NO + 4H_2O + 3O_2$
- E. $6H^+ + BrO_3^- + 6Fe^{2+} \rightarrow 6Fe^{3+} + Br^- + 3H_2O$
- 2. Use the oxidation number method to balance the following equations and then identify the oxidizing and reducing agents:
 - A. $2HNO_3 + 3H_3AsO_3(aq) \rightarrow 2NO(g) + 3H_3AsO_4(aq) + H_2O(l)$
 - B. $KClO_3 + 6HBr \rightarrow 3Br_2 + 3H_2O + KCl$
 - C. $3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O$

Self-test Exercise 2.2

- 1. a Anode reaction: $4O H^{-}(aq) \rightarrow 2 H_2 O(l) + O_2(g) + 4e^{-}$
 - b. Cathode reaction: $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$ Overall reaction: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
- 2. The concentration of H_2SO_4 increases because water is electrolyzed and its amount decreases.
- 3. The copper (II) sulfate solution is decreased. Because copper (II) ion from

sulfuric acid discharged at the cathode to form copper metal.

4. Chlorine gas is liberated at the anode and Hydrogen gas is liberated at the cathode

Anode Reaction: $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$

Cathode Reaction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Overall Reaction: $2 \operatorname{H}^{+}(aq) + 2Cl^{-}(aq) \rightarrow \operatorname{H}_{2}(g) + \operatorname{Cl}_{2}(g)$

Self-test Exercise 2.3

- 1. Volume of hydrogen is 9.05 L and that of oxygen is 4.52 L. Note that the volume of oxygen is half of hydrogen.
- 2. Mass of copper deposited at the cathode is 1.78 g and the volume of oxygen gas liberated at the anode is 0. 345 L.
- 3. Mass of Al is 0.672 g.
- 4. The mass of silver is 216 g.
- 5. Mass of Ag = 21.6 g, mass of Zn = 6.5 g and mass of Fe = 3.73 g

Self-test Exercise 2.4

- 1. c
- 2. b
- 3. a

Self-test exercise 2.5

- 1. $Al | Al(NO_3)_3 (l M) || AgNO_3 (l M) || Ag$
- 2. A salt bridge is used to complete a circuit or to maintain the electroneutrality of the solution.
- 3. No, because Sn is the weakest reducing agent
- 4. + 0. 34 V

5. a.



- b. $Mg \mid Mg^{2+}(1M)$ is anode, and $Cu^{2+}(1M) \mid Cu$ is cathode
- c. Electrons flow from anode (magnesium) to cathode (copper) in the external circuit.
- 6. $E_{cell} = 0.90 V$
- 7. $E_{cell} = 0.0828 V$
- $E_{cell} = 1.53 V$
- 9. $E_{cell} = 20.14 V$ Because E_{cell} is negative, the reaction is not spontaneous in the direction written.
- 10. $E^0_{bromine} = 1.07V$

Self-test Exercise 2.6

- A dry cell is a primary cell which is used only once and then discarded but lead storage battery is a secondary cell and can be used more than once by recharging it.
- 2. Cathode: $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

Anode: $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$

Overall Reaction: $2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$

- 3. Ammonium chloride and zinc chloride in water
- 4. Corrosion is a deterioration of a metal by redox process, which converts a metal to unwanted compound.
- 5. Corrosion destroys metals and returns them to their natural ores. As a result, it has negative economic impact.
- 6. Aluminum can form a thin layer of oxide which prevents further oxidation of Aluminum. Because of this thin layer of oxide, aluminum cannot be corrode

Self- Assessment Questions for unit 2					
Multiple choice Questions					
1. D	4. B	7. D	10.C	13.D	
2. A	5. C	8. D	11.A	14.D	
3. A	6. D	9. C	12.C	15.B	
Answer key to observations of Experiments					

Experiment 2.1

- 1. It is important to polish the surfaces of magnesium ribbon and iron nail because their surfaces are covered with oxide layer. As a result, the oxide layer precludes electrical conductivity. If a material is plugged to complete the circuit of Figure 2.2 (a) and the bulb gives light, the material is conductor. Otherwise it is non-conductor or insulator.
- 2. To distinguish strong electrolytes, weak electrolytes and non-electrolytes, you need to have two dry cells (here higher potential difference is required to see observable changes). This is because the resistance of an electrolyte solution is higher than a solid conductor. Students should immerse the open ends of the circuit in each solution. you can classify these solutions as strong electrolytes, weak electrolytes and non-electrolytes based on the brightness of the bulb. The brighter the bulb, the stronger the electrolyte, and the dimmer the bulb, the weaker the electrolyte. The bulb does not give light at all for non-electrolytes. Thus 1 M sodium chloride solution is strong electrolyte
 - 1 M sugar solution is non electrolyte
 - 1 M acetic acid solution is weak electrolyte
 - 1 M sulphuric acid solution is strong electrolyte.
- 3. The anode is the terminal that is attached to the positive terminal of the battery and the cathode is the one attached to the negative terminal of the battery. Students usually have difficulties in identifying cathodes and anodes practically. This is a great opportunity for the students to internalize the concepts.

Experiment 2.2

- 1. Bubbling of gases will be observed on the surfaces of the electrodes.
- 2. The graphite electrode attached to the positive terminal of the battery becomes anode and the other connected to the negative terminal becomes cathode.
- 3. Hydrogen gas discharges at the cathode and oxygen gas discharges at the anode. However, in concentrated sodium chloride solution, hydrogen gas discharges at the cathode and chlorine gas discharges at the anode

Anode: $4OH^{-}(aq) + 4e^{\downarrow} \rightarrow O_{2}(g) + H_{2}O(l)$ Cathode: $4H^{+}(aq) + 4e^{\downarrow} \rightarrow 2H_{2}(g)$

Experiment 2.3

- 1. Electroplating is widely used in various industries for coating metal objects with a thin layer of a different metal. The layer of metal deposited has some desired property, which the metal of the object lacks. For example, chromium plating is done on many objects such as car parts, bath taps, kitchen gas burners, wheel rims and many others for the fact that chromium is very corrosion-resistant, and thus prolongs the life of the parts. It is also used in making expensive jeweler.
- It is important to polish the surfaces of copper plate and iron spoon before use because their surfaces are covered with oxide layer. As a result, the oxide layer precludes electrical conductivity.
- 3. The iron key has got reddish layer of copper metal all over its surface
- 4. The dissolved copper metal present in the copper sulphate solution as positively copper ions gets attracted to the negatively charged electrode iron key. The positively charged copper ions lose their positive charge on coming in contact with the negatively charged iron key and form copper atoms. These copper atoms deposit on the iron key to form a thin layer of copper metal all over the surface of iron key. In this way, copper metal in the electrolyte comes out of the solution and forms a thin layer on the iron key

5. The copper metal of positively charged copper plate electrode dissolves by forming positively charged copper ions. The copper ions thus formed go in to the copper sulphate solution.

Experiment 2.4

- 1. The pointer of the ammeter deflects from zinc to copper half cells. This indicates electron flows from zinc to copper half cells.
- 2. Copper serves as cathode and Zinc serves as anode.
- 3. (-) Anode (oxidation): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$
 - (+) cathode (reduction): $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
- 4. As time passes the intensity of copper sulphate solution decreases or it becomes light blue because the copper ions are consumed in the half-cell.

References

- 1. D. D. Ebbing and E. S. D. Gammon, general chemistry, Ninth edition.
- 2. C. Raymond and O. Jason, General Chemistry: The Essential Concepts, Sixth Edition.
- 3. M. S. Silberberg, Principles of general chemistry, third edition.
- 4. R.H. Petrucci, F.G. Herring, J.D. Madura and C. Bissonnette, General Chemistry: Principles and Modern Applications, Eleventh edition.