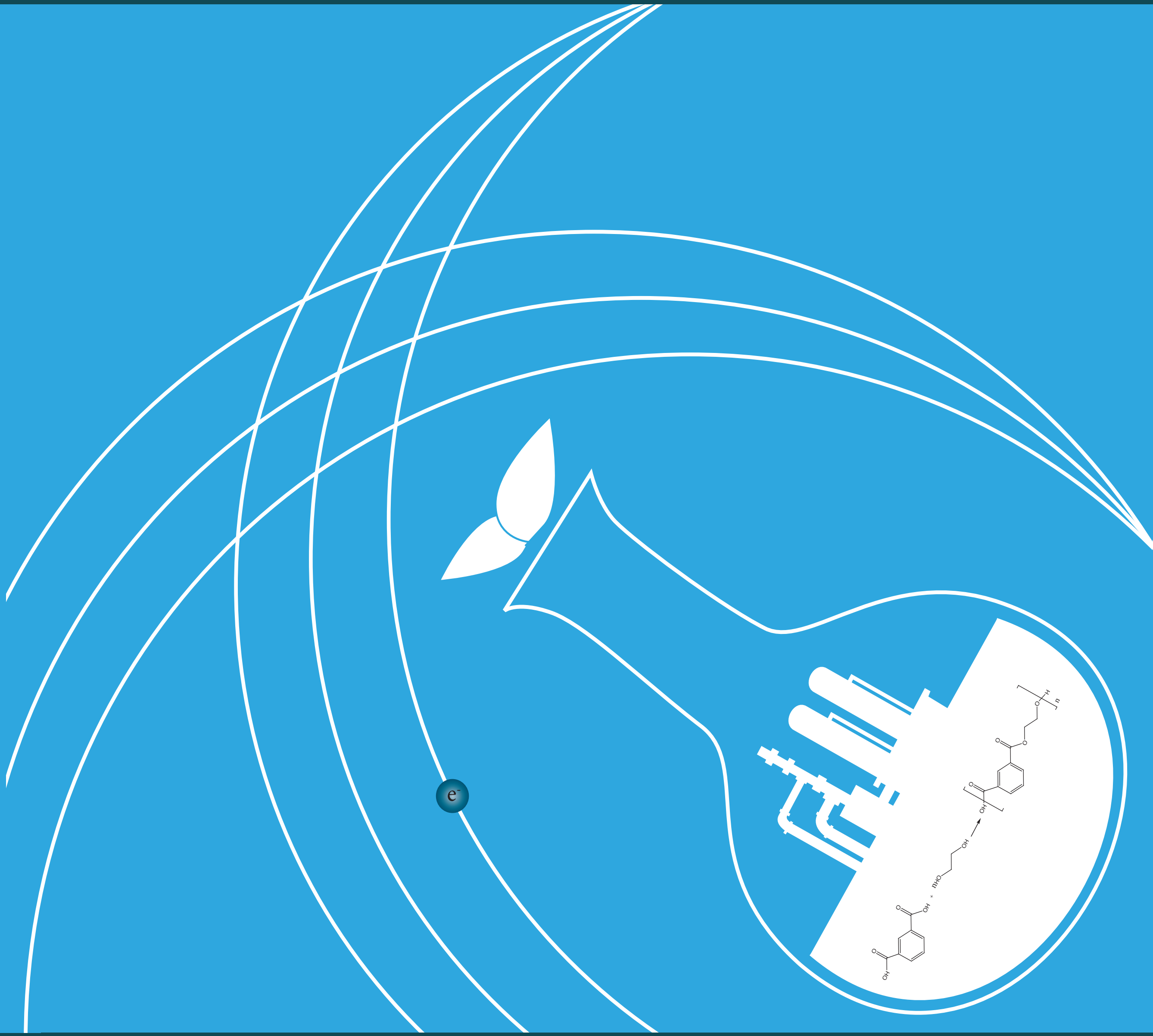
CHEMISTRY

STUDENT TEXTBOOK

Grade 12



FEDERAL DEMOCRATIC REPUBLIC OF ETHIOPIA MINSTRY OF EDUCATION

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UNIT 1 ACID-BASE EQUILIBRIA

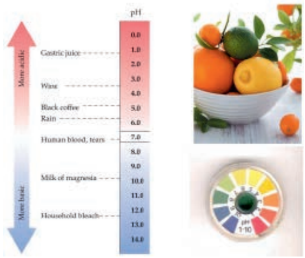
UNIT 2 ELECTROCHEMISTRY

UNIT 3 INDUSTRIAL CHEMISTRY

UNIT 4 POLYMERS

UNIT 5 INTRODUCTION TO ENVIRONMENTAL CHEMISTRY

UNIT 1



ACID-BASE EQUILIBRIA

Unit outcomes

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, P^H *and* P^{OH}
- *discuss the common ion effect, buffer solution, hydrolysis of salts, acid-base 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.*

Start-up Activity

You have learnt the acid-base concepts and properties. Remember this and discuss the following questions in group. After discussion write a report and present to the class:

1. Explain the properties of acids and bases
2. What do you observe when the following indicators added in the solutions listed in the table?

Soluion	Color of indicator			
	Red litmus paper	Blue litmus paper	Phenolphthalein	Methyl Orange
Acetic acid solution				
Hydrochloric acid solution				
Sodium chloride solution				
Ammonia solution				
Lemon juice				

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, we will learn some ways of expressing concentrations of hydronium ions and of hydroxide ions in solutions of weak acids and weak bases. Then you will examine equilibria involving these weak electrolytes. You will also see that the indicators, used in titration, such as phenolphthalein, are weak acids or weak bases. Finally, you will learn how to use these properties to select an appropriate indicator for a titration.

1.1 Acid-Base Concepts

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* $[H^+]$ *and* $[H^+]$ *from pH*
- *calculate pOH from* $[OH^-]$ *and* $[OH^-]$ *from pOH.*

1.1.1 Arrhenius Concept of Acids and Bases

Activity 1.1

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

1. Explain Arrhenius acid and base concepts using suitable 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.

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. $HBr(aq) + H_2O(l) \rightarrow H_3O^+(aq) + 2Br^-(aq)$
   b. $NaCl(s) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq)$
   c. $NaOH(aq) + H_2O(l) \rightarrow Na^+(aq) + 2OH^-(aq)$

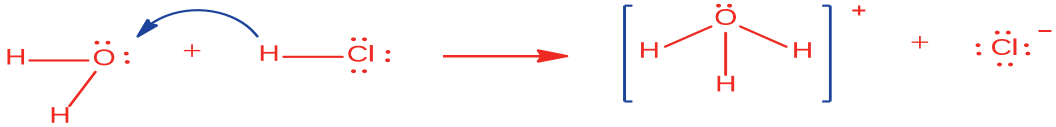
1.1.2 Brønsted-Lowry Concept of Acids and Bases

Activity 1.2

From what you have learnt in Grade 10 chemistry, discuss the following questions and present it for your classmate..

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?

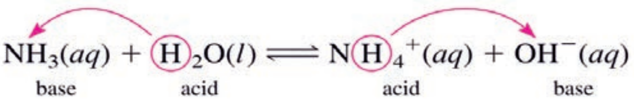
Consider the ionization of hydrochloric acid in water:



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 ammoniain aqueous solution

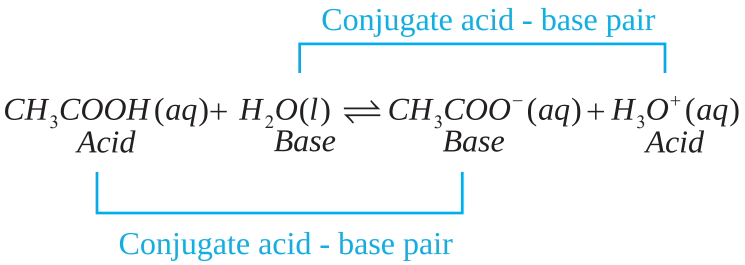


$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

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.

1.1.2.1 Conjugate Acid-Base Pairs

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

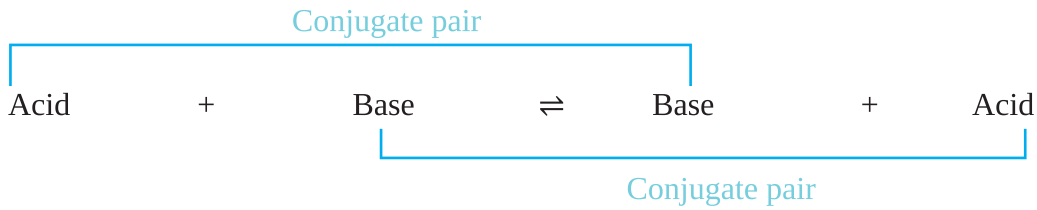


$$\underset{Acid}{CH_3COOH(aq)} + \underset{Base}{H_2O(l)} \rightleftharpoons \underset{Base}{CH_3COO^-(aq)} + \underset{Acid}{H_3O^+(aq)}$$

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.

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



HF	+	H_2O	F^-	+	H_3O^+
HCOOH	+	CN^-	$HCOO^-$	+	HCN
NH_4^+	+	CO_3^{2-}	NH_3	+	HCO_3^-
$H_2PO_4^-$	+	OH^-	HPO_4^{2-}	+	H_2O
H_2SO_4	+	$N_2H_5^+$	HSO_4^-	+	$N_2H_6^{2+}$
HPO_4^{2-}	+	SO_3^{2-}	PO_4^{3-}	+	HSO_3^-

Example 1.1

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.

$$\underset{Base}{NH_3} + \underset{Acid}{H_2PO_4^-} \rightleftharpoons \underset{Acid}{NH_4^+} + \underset{Base}{HPO_4^{2-}}$$

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.

$$\underset{Acid}{HCl} + \underset{Base}{H_2PO_4^-} \rightleftharpoons \underset{Base}{Cl^-} + \underset{Acid}{H_3PO_4}$$

Exercise 1.2

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

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

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

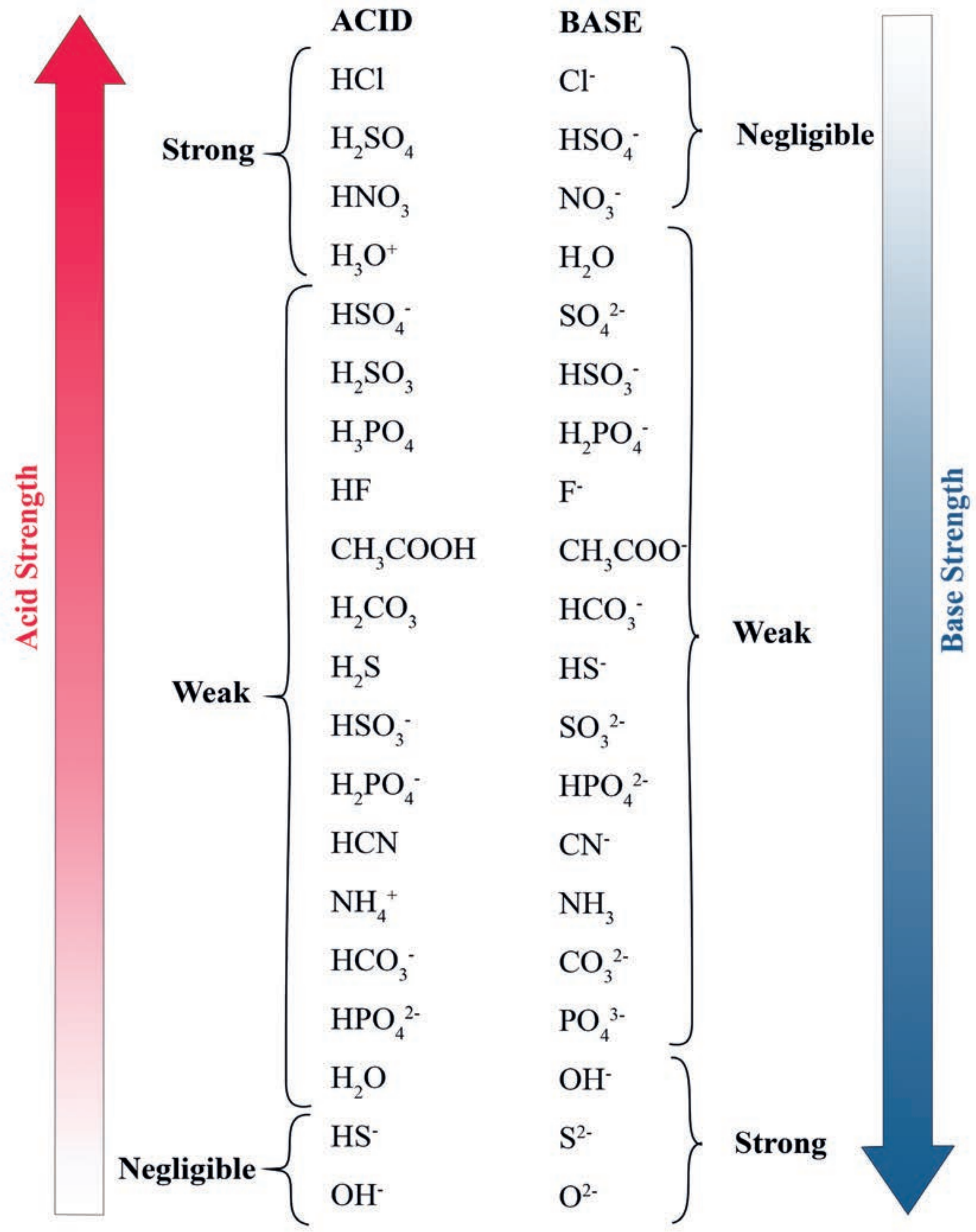
   c. $H_2O + SO_3^{2-} \rightleftharpoons OH^- + HSO_3^-$

Strengths of Conjugate Acid-Base Pairs

How do you know the 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.



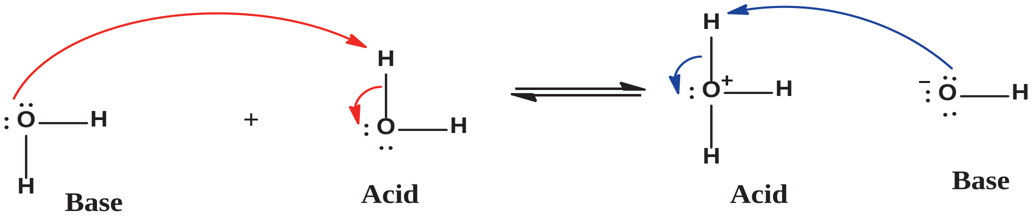
	ACID	BASE	
Strong	HCl	Cl^-	Negligible
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	Weak
Weak	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HF	F^-	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HSO_3^-	SO_3^{2-}	
	$H_2PO_4^-$	HPO_4^{2-}	
	HCN	CN^-	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	Strong
Negligible	HS^-	S^{2-}	
	OH^-	O^{2-}	

Chart 1.1: Strengths of Conjugate Acid-Base Pairs.

1.1.2.2 Auto Ionization of Substances

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

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 we 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 HCl 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: $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

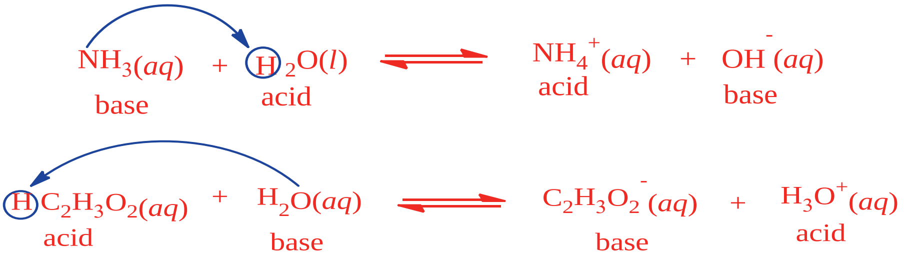


This reaction is sometimes called the ***autoionization*** of water. Note that, in this reaction, some water molecules behave as acids, donating protons, while the other water molecules behave as bases, accepting protons.

1.1.2.3 Amphiprotic Species

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

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)



$$\underset{\text{base}}{NH_{3}(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^{+}(aq)} + \underset{\text{base}}{OH^{-}(aq)}$$

$$\underset{\text{acid}}{HC_2H_3O_2(aq)} + \underset{\text{base}}{H_2O(aq)} \rightleftharpoons \underset{\text{base}}{C_2H_3O_2^{-}(aq)} + \underset{\text{acid}}{H_3O^{+}(aq)}$$

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.

Exercise 1.3

1. Define each of the following terms
   a. autoionization b. amphiprotic species
2. Write equations to show the amphiprotic behavior of
   a $H_2PO_4^-$ b. H_2O
3. Predict the relative strengths of each of the following groups:
   a. OH^-, Cl^-, NO_3^-, CH_3COO^-, and NH_3
   b. $HClO_4$, CH_3COOH, HNO_3 and HCl
4. What is the weakness of the Brønsted-Lowry acids and bases theory?
5. Write the self-ionization of ammonia.

1.1.3 Lewis Concept of Acids and Bases

Activity 1.3

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

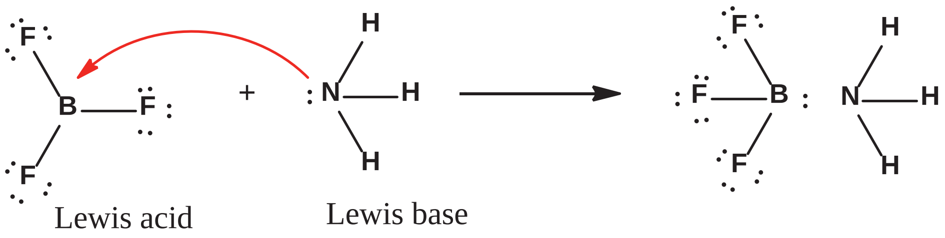
1. What is the main difference between Lewis acid -base and Brønsted-Lowry acid - base concepts?
2. Are all Brønsted-Lowry acids and bases are also acids and bases according to Lewis concept?
3. Is there any limitation to the Brønsted-Lowry definition of acids and bases? Explain if any

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, we 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

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. $BH_3 + (CH_3)_2S \rightarrow H_3BS(CH_3)_2$

   b. $CaO + CO_2 \rightarrow CaCO_3$

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

Solution:

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.

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.

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.

   a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O : BF_3$

   b. $H_2O + SO_3 \rightarrow H_2SO_4$

Solution

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

b. Lewis base: H_2O ; Lewis acid: SO_3

Exercise 1.4

1. Identify Lewis acids and Lewis bases in each of the following reactions.
   a. $H^+ + OH^- \rightleftharpoons H_2O$
   b. $Cl^- + BCl_3 \rightleftharpoons BCl_4^-$
   c. $K^+ + 6H_2O \rightleftharpoons K(H_2O)_6^+$
   d. $OH^- + Al(OH)_3 \rightleftharpoons Al(OH)_4^-$
   e. $CO_2 + H_2O \rightleftharpoons H_2CO_3$
   f. $Ni + 4CO \rightleftharpoons Ni(CO)_4$

1.2 Ionic Equlibria of Weak Acids and Bases

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

☞ *describe the ionization of water*

☞ *derive the expression of ion product for water, K_w*

☞ *explain why water is a weak electrolyte*

☞ *use K_w to calculate $[H_3O^+]$ or $[OH^-]$ 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 it's 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*

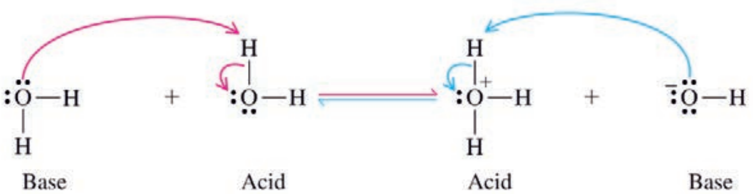
☞ *calculate the $[OH^-]$ and pOH of a basic solution from a given value of K_b and the initial concentration of the solution.*

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 from **self-ionization** (or **autoionization**) 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 ***autoionization*** 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 an equilibrium constant:

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

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 $\left[H_2O\right]^2$ 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 $\left[H_3O^+\right]\left[OH^-\right]$, the ion-product constant for water, K_w. At 25 °C, the value of K_w is 1.0×10^{-14}. Like any equilibrium constant, K_w varies with temperature. At body temperature (37°C), K_w equals 2.5×10^{-14}.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\ ^oC$$

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

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 $x^2 = [H_3O^+][OH^-]$. Then, substituting into the equation for the ion-product constant, $K_w = [H_3O^+][OH^-]$ you get at 25 ºC, $1.0 \times 10^{-14} = \boldsymbol{x^2}$ hence x equals 1.0×10^{-7}. Thus, the concentrations of H_3O^+ and $[OH^-]$ are both 1.0×10^{-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 $\left[H^+\right]$ and $\left[OH^-\right]$ 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 $[OH^-]>[H_3O^+]$.

Activity 1.4

Form a group and discuss the following. Write a report on the discussion and present to the class. Many substances undergo auto-ionization in analogous to water. For example, the auto-ionization of liquid ammonia is:–

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

a. Write K_c expression for auto-ionization of ammonia that is analogous to the K_w expression for water.

b. Name the strongest acids and strongest bases that can exist in liquid ammonia?

c. For water, a solution with $\left[OH^-\right] < \left[H_3O^+\right]$ is acidic. What are the analogous relationships in liquid ammonia?

Example 1.3

A chemistry researcher adds a measured amount of HCl gas to pure water at 25 ^{0}C and obtains a solution with $\left[H_3O^+\right] = 3.0 \text{ x } 10^{-4}$ M. Calculate $\left[OH^-\right]$. Is the solution neutral, acidic, or basic?

Solution:

We use the known value of K_w at 25 ^{0}C ($1.0 \text{ x } 10^{-14}$) and the given $\left[H_3O^+\right]$ ($3.0\text{x}10^{-4}$ M) to solve for $\left[OH^-\right]$. Then we compare $\left[H_3O^+\right]$ with $\left[OH^-\right]$ to determine whether the solution is acidic, basic, or neutral

Calculate for the $\left[OH^-\right] = \dfrac{K_w}{\left[H_3O^+\right]} = \dfrac{1.0 \text{ x } 10^{-14}}{3.0\ x\ 10^{-4}} = 3.3\ x\ 10^{-11} M$

Because $\left[H_3O^+\right] > \left[OH^-\right]$, the solution is acidic

Exercise 1.5

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

   a. $\left[H^{+}\right]=1.0 \text{ x } 10^{-7} M$ b. $\left[OH^{-}\right]=1.0 \text{ x } 10^{-4} M$

   c . $\left[OH^{-}\right]=1.0 \text{ x } 10^{-8} M$

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

   a. $\left[H_3O^{+}\right]=2.0 \text{ x } 10^{-5} M$ b. $\left[H_3O^{+}\right]=\left[OH^{-}\right]$

   c. $\left[H_3O^{+}\right]=10^{2}\ x \left[OH^{-}\right]$

3. Calculate $\left[H_3O^{+}\right]$ in a solution that is at 25 °C and has $\left[OH^{-}\right]=6.7 \text{ x } 10^{-2} M$. Is the solution neutral, acidic, or basic?

4. Why water is a weak electrolyte?

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 $\left[H_3O^{+}\right]$.

$$pH = -\log\left[H_3O^{+}\right] \quad or \quad pH = -\log\ \left[H^{+}\right]$$

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

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

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 $\left[H_3O^{+}\right]$, that corresponds to a particular pH value, we do an inverse calculation. In a solution with $pH = 4.5$,

$\log\left[H_3O^+\right] = -4.50$ and $\left[H_3O^+\right] = 10^{-4.50} = 3.2 \text{ x } 10^{-5} M$

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 a neutral solution, $pH = 7$

Acidic solutions have $pH < 7$

Basic solutions have $pH > 7$

Activity 1.5

In your group, check the color change of the following substances, using a litmus paper. Write your observation in the following table. Compare your results with those of other groups.

Substance	pH	Acidic, Basic or Neutral
Beer		
Milk of Magnsia (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, we define pOH as:

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

If we 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. $K_w = \left[H_3O^+\right]\left[OH^-\right] = 1.0 \text{ x } 10^{-14}$ Taking the negative logarithm of both sides, we obtain

$$-(\log[H_3O^+] + \log[OH^-]) = -\log(1.0 \text{ x } 10^{-14})$$

$$-\log[H_3O^+] + \log[OH^-] = 14$$

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 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

1. Calculate:

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

   b. the $\left[H_3O^+\right]$ and $\left[OH^-\right]$ of human blood at $pH = 7.40$

Solution:

a. $\left[H_3O^+\right] = 5.0 \text{ x } 10^{-3} M$

$pH = ?$ and $pOH = ?$

$pH = -\log\left[H_3O^+\right] = -\log(5.0 \text{ x } 10^{-3})$

$= 3 - \log 5.0 = 2.3$

$pH + pOH = 14$

$pOH = 14 - pH$

$pOH = 14 - 2.3$

$= 11.7$

b. $pH = 7.40, \quad pOH = 14 - 7.40 = 6.6$

$\left[H_3O^+\right] = ? \quad \left[OH^-\right] = ?$

$pH = -\log\left[H_3O^+\right] \quad and \quad pOH = -\log[OH^-]$

$\log\left[H_3O^+\right] = -7.40 \quad and \quad \log[OH^-] = -6.6$

$\left[H_3O^+\right] = 10^{-7.40} = 4.0 \; x \; 10^{-8} M \quad and \quad [OH^-] = 10^{-6.6} = 2.51 \; x \; 10^{-7} M$

Exercise 1.6

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

1.2.2 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.

1.2.2.1 Concentration of Hydrogen and Hydroxide ions

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

By definition 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 ionize 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.

Activity 1.6

By referring to this text book and other chemistry books, list strong acids, strong bases, weak acids and weak bases. Then discuss what you have written with the rest of the class. What is the reason of your classification of acids and bases as strong and weak?

1.2.2.2 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.

1.2.2.3 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:

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

The strength of an acid depends on the percentage of the acid molecules that dissociate in water solution. as with acides, the measure of the strength of a base is its percent ionization, which is defined as the proportion of ionized molecules on a percentage bases. Mathematically:

$$percent\ ionization = \frac{ionized\ base\ concentartion\ at\ equilibrium}{initial\ concentration\ of\ base} \times 100\%$$

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.

1.2.2.4 Dissociation (Ionization) Constants

Acid ionization Constant, K_a

What is the relationship between strength of acids with their acid-dissociation 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:

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

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

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

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:

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

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

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

Name of the Acid	Formula	K_a
Acetic acid	CH_3COOH	1.8×10^{-5}
Ascorbic acid	$C_6H_8O_6$	8.0×10^{-5}
Benzoic Acid	C_6H_5COOH	6.5×10^{-5}
Formic acid	$HCOOH$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hypobromous acid	$HOBr$	2.5×10^{-9}
Hypochlorous acid	$HOCl$	3.0×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}

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:

$$CH_3(CH_2)_2COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3(CH_2)_2COO^-(aq)$$

	$CH_3(CH_2)_2COOH$	H_3O^+	$CH_3(CH_2)_2COO^-$
Initial conc.	0.250 M	-------	-------
Changes	– x	+x	+x
equilib. conc.	0.250 M – x	x	x

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

$$\log\left[H_3O^+\right] = -pH = -2.72$$

$$\left[H_3O^+\right] = 10^{-2.72} = 1.9\ x\ 10^{-3}\,M$$

Now we can solve the following expression for K_a by substituting in the value x = 1.9 x 10 $^{-3}$ M

$$K_a = \frac{(1.9\ x\ 10^{-3})(1.9\ x\ 10^{-3})}{0.250 - 1.9\ x\ 10^{-3}} = 1.5\ x\ 10^{-5}$$

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 F^-, 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	$-x$	+x	+x
Equil. conc.	$0.50-x$	x	x

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

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:

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

This is a quadratic equation that can be solved, using the quadratic formula, or youcan 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

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

$$\left[F^-\right] = \left[H_3O^+\right] = 0.018\ M$$

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%.

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

3. What is the percent ionization of acetic acid in a 0.100M solution of acetic acid, CH_3COOH ?

Solution:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq),\ K_a = 1.8\ x\ 10^{-5}$$

	CH_3COOH	H_3O^+	CH_3COO^-
Initial conc.	$0.100\ M$	-----	-----
Changes	$-x$	$+x$	$+x$
Equilib conc.	$0.100\ M - x$	x	x

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

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{[CH_3COOH]}$$

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

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

$$1.8 \text{ x } 10^{-5} = \frac{x^2}{0.100-x}$$

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 $(1.8 \text{ x } 10^{-5})(0.100) = x^2$

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

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

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.

Exercise 1.7

1. Calculate the percent ionization of a 0.10M solution of acetic acid with a pH of 2.89.
2. Calculate the pH of a 0.10 M solution of acetic acid. $K_a = 1.8 \times 10^{-5}$
3. For a 0.036 M HNO_2 solution.
   - a. Write a chemical equation that shows the ionization of nitrous acid in water.
   - b. Calculate the equilibrium concentration of hydrogen ions and nitrous acid at 25°C, using the approximation method. Then check whether the approximation is valid or not.
   - c. If the approximation is invalid, use the quadratic formula to calculate the concentration of hydrogenions.
   - d. Calculate the pH of the solution.

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:

$$K_c = \frac{\left[NH_4^+\right]\left[OH^-\right]}{[NH_3][H_2O]}$$

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

$$K_b = K_c[H_2O] = \frac{\left[NH_4^+\right]\left[OH^-\right]}{[NH_3]}$$

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:

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

Note that 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_2OH	1.1×10^{-6}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	C_5H_5N	1.7×10^{-9}

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

Example 1.6

1. What is the hydronium-ion concentration of a 0.20 *M* solution of ammonia in water? $K_b = 1.8 \times 10^{-5}$

Solution:

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

	NH_3	NH_4^+	OH^-
initial conc.	0.20 M	-----	-----
changes	– x	+x	+x
equlib.conc.	0.20M-x	x	x

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

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

Exercise 1.8

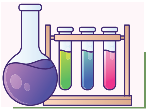
1. For a 0.040 M ammonia **solution:**
   a. Write a chemical equation that shows the ionization of ammonia in water.
   b. Calculate the equilibrium concentration of ammonia, ammonium ions and hydroxide ions, using the approximation method. Check whether the approximation is valid or not.
   c. If the approximation is invalid, use the quadratic formula to calculate the concentration of ammonia.
   d. Calculate the pOH and pH of the solution.

1.3 Common Ion Effect and Buffer Solution

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

- *define the common-ion effect*
- *explain the importance of the common-ion effect*
- *define buffer solution*
- *give some common examples of buffer systems*
- *explain the action of buffer solutions and its importance in chemical processes*
- *calculate the* pH *of a given buffer solution*
- *demonstrate the buffer action of* CH_3COOH / CH_3COONa .

1.3.1 The Common Ion Effect



Activity 1.7

In Grade 11 Chemistry, you learned Le Chatelier's principle. Make a group and discuss the following and present your report to the class. Industrially, ammonia is produced by the Haber process.

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?

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:

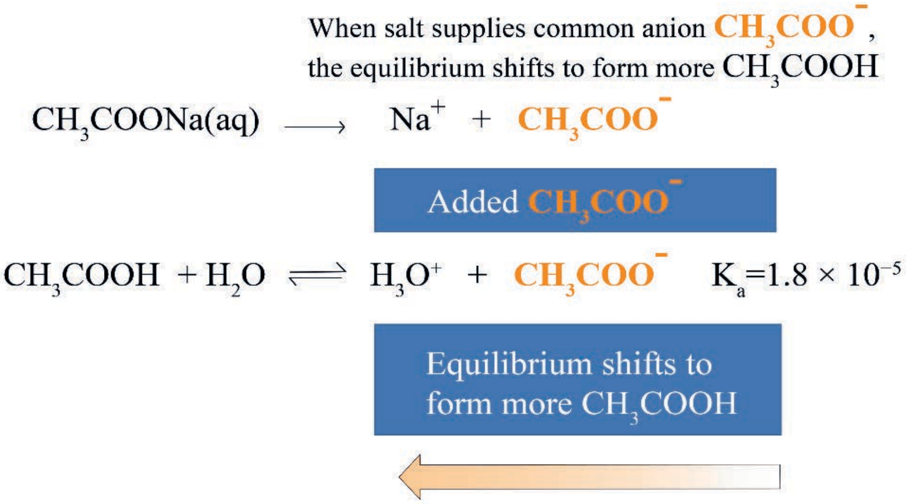
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Suppose you add HCl (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

$$CH_3COOH(aq) + H_2O(l) \leftarrow CH_3COO^-(aq) + \underset{added}{H_3O^+}(aq)$$

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:



When salt supplies common anion CH_3COO^-, the equilibrium shifts to form more CH_3COOH

$$CH_3COONa(aq) \longrightarrow Na^+ + CH_3COO^-$$

Added CH_3COO^-

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \quad K_a = 1.8 \times 10^{-5}$$

Equilibrium shifts to form more CH_3COOH

Example 1.7

1. Determine the $\left[H_3O^+\right]$ and $\left[CH_3COO^-\right]$ in a solution that is 0.10 M in both CH_3COOH and HCl.

Solution:

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

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

	$CH_3COOH(aq)$	$CH_3COO^-(aq)$	$H_3O^+(aq)$
initial conc.	0.10 M	-----	0.10 M
changes	$-x$	$+x$	$+x$
equlib.conc.	$0.10\ M - x$	x	$0.10\ M + x$

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]} = \frac{(0.1+x)(x)}{(0.1-x)}$$

$$1.8\ x\ 10^{-5} = \frac{(0.10+x)(x)}{(0.10-x)}$$

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

$$1.8\ x\ 10^{-5} = \frac{(0.10)(x)}{(0.10)}$$

$$x = \left[CH_3COO^-\right] = 1.8\ x\ 10^{-5}\,M$$

$$[\mathrm{H_3O^+}] = 0.10 + 1.8\times10^{-5} = 0.100018$$

Exercise 1.9

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?

1.3.2 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 un buffered solutions are given in table 1.4

Table1.4: Comparison of buffered and un buffered solutions.

	Initial pH of 1.0 L sample	pH after addition of 0.010 mol NaOH	pH after addition of 0.010 mol HCl
Un buffered **solution:** 1.28×10^{-5} M HCl	4.8	12.0	2.0
Buffered **solution:** 0.099 M CH_3OOH 0.097 M CH_3COONa	4.8	4.8	4.7

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

1. CH_3COOH is a weak acid and the extent of hydrolysis of the CH_3COO^- ion is very small and
2. the presence of CH_3COO^- ions suppress 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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

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

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

Taking the negative logarithm of both sides gives

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

from which definitions gives

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

Rearranging the equation gives

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

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

1. What is the pH of a buffer solution consisting of 0.035M NH_3 and 0.050M NH_4^+ (K_a for NH_4^+ 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:

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

$$pH = 9.23 + \log\left(\frac{0.035}{0.050}\right)$$

$$pH = 9.095$$

2. A buffer is made by mixing 0.060 M NH_3 with 0.040 M 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:

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

$$pOH = pK_b + \log\left(\frac{NH_4^+}{NH_3}\right)$$

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

$$pOH = 4.745 - 0.1761$$

$$= 4.5689$$

$$pH = 14 - pOH$$

$$= 14 - 4.5689$$

$$= 9.4311$$

Exercise 1.10

1. Calculate the pH :
   a. of a buffer solution containing 0.1 M CH_3COOH and a 0.1 M solution of CH_3COONa .
   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 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.

1.4 Hydrolysis of Salts

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

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

What does salt hydrolysis mean?

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 serves as an acid, base or neutral.

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 $NaOH(aq)+HCl(aq)\rightarrow NaCl(aq)+H\ O(l)$ 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).

Can you give more examples?

1.4.2 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.

Activity 1.8

1. Consider Na_2CO_3 and discuss the following:
   a. What are the 'parents' (acid and base) of this salt?
   b. Which ions of the salt can be hydrolyzed?
   c. What will be the nature of Na_2CO_3 solution? Will it be acidic, basic or neutral?

1.4.3 Hydrolysis of Salts of Strong Acids and Weak Bases

When we 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:

$$NH_4^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NH_3(aq)$$

1.4.4 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^+ (5.6×10^{-10}) is somewhat larger than the K_b for formate ion, CHO_2^- (5.9×10^{-11}).

Activity 1.9

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

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

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

1.5 Acid–Base Indicators and Titrations

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

- *define acid-base indicators*
- *write some examples of acid-base indicators*
- *suggest a suitable indicator for a given acid-base titration*
- *explain the equivalents of acids and bases*
- *calculate the normality of a given acidic or basic solution*
- *define acid-base titration*
- *distinguish between end point and equivalent point*
- *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 $\left[H_3O^+\right]$ in the solution

$$\underset{\text{Acid colour}}{HIn} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{Base colour}}{In^-}$$

If the indicator is in a sufficiently acidic medium [increasing $\left[H_3O^+\right]$], 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 $\left[H_3O^+\right]$] 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.

Table 1.5: Some common indicators.

Indicator Change	Acid Color	Base Color	pH Range of 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 1.10

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?

$$\left[H_3O^+\right] = K_a \ x \ \frac{\left[CH_3COOH\right]}{\left[CH_3COO^-\right]} \ = \ 1.8 \ x \ 10^{-5} M \ x \ \frac{0.40}{0.20}$$

Solution:

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

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

The pH value indicates that the solution is acidic

1.5.2 Equivalents of Acids and Bases

Activity 1.10

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

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.

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 ($Ba(OH)_2$)eqsuivalents 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, we 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:

$$N_1V_1 = N_2V_2$$

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

Example 1.10

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

Solution:

$$N_1V_1 = N_2V_2$$

$$V_2 = \frac{N_1V_1}{N_2}$$

$$V_2\ NaOH = \frac{(2.7N\ H_2SO_4)(25.0\ mL\ H_2SO_4)}{2.0N\ NaOH}$$

$$= 33.8\ mL$$

1.5.3 Acid–Base Titrations

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. 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

$$\text{volume of base} \times \text{concentration of base} = \text{volume of acid} \times \text{unknown concentration of acid}$$

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

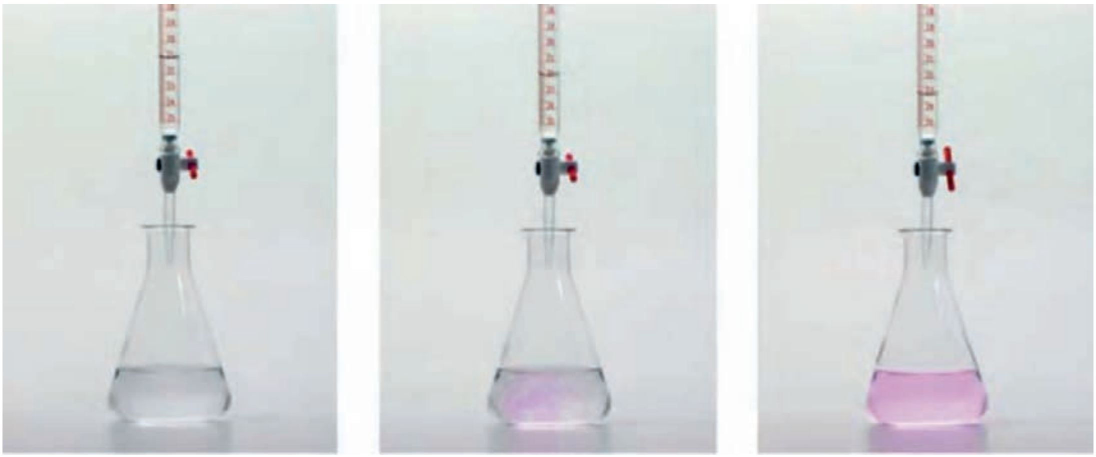


Figure 1.2: The Techniques of Titration.

An acid–base titration curve is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid). Such curves are used to gain insight into the titration process.

Experiment 1.1

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 0.1N sodium hydroxide solution; and fix the burette on the burette clamp in vertical position (**Figure 1.3**).
2. Using a funnel, introduce 0.1N 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.

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 similarity and difference between equivalence point and end point level after reaching the end point?

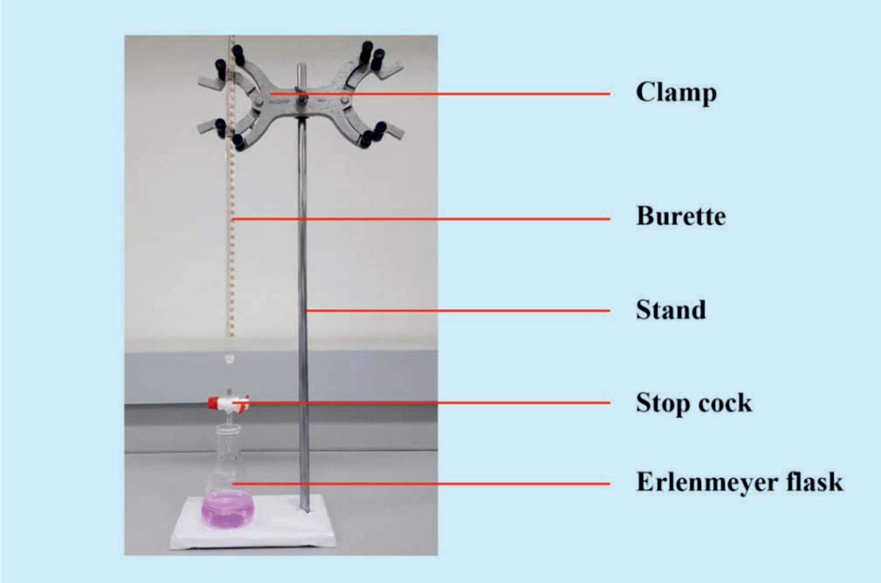


Figure 1.3: Titration Setup.

Unit Summarys

- 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 $\left[H_3O^+\right] < \left[OH^-\right]$

- 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's 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's 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 ^{0}C). $\left[H_3O^+\right]$ and $\left[OH^-\right]$ are inversely related: in acidic solution, $\left[H_3O^+\right]$ is greater than $\left[OH^-\right]$; the reverse is true in basic solution; and the two are equal in neutral solution. To express small values of $\left[H_3O^+\right]$, we use the pH scale ($pH = -\log\left[H_3O^+\right]$). Similarly, $pOH = -\log\left[OH^-\right]$ and. $pK = -\log K$

- A high pH represents a low $\left[H_3O^+\right]$. 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 ^{0}C).
- Acid strength depends on $\left[H_3O^+\right]$ 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^{-2} to 10^{-10}.
- The pH of a buffered solution changes much less than the pH of an unbuffered solution when $\left[H_3O^+\right]$ or OH^- is added.
- An acid-base reaction proceeds to the greater extentin 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 $\left[H_3O^+\right]$ or OH^- added.
- The buffer-component concentration ratio determines the pH ;the ratio and the pH are related by the Henderson-Hasselbalch equation.
- When $\left[H_3O^+\right]$ or OH^- is added to abuffer, one component reacts to form the other; thus $\left[H_3O^+\right]$ (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.

CHECK LIST

KEY TERMS

- *Arrhenius acid-base concept*
- *Bronsted-Lowry concept of acid and bases*
- *Conjugate acid and Conjugate base*
- *Lewis's concept of acids and bases*
- *Autoionization*
- *Amphiprotic species*
- *pH scale*
- *percent ionization*
- *Hydrolysis of salts*
- *Buffer solution*
- *Common ion effect*
- *Equivalents of acids and bases*
- *Acid-base titration*

REVIEW EXERCISE FOR UNIT 1

Part I: Multiple Choice

1. Which of the following is a Brønsted-Lowry base but an Arrhenius base?
   a. NH_3
   b. NaOH
   c. $Ca\,(OH)_2$
   d. KOH
2. Use the following acid ionization constants to identify the correct decreasing order of base strength.

HF	HNO_2	HCN
$Ka = 7.2 \times 10^{-4}$	$Ka = 4.5 \times 10^{-4}$	$Ka = 6.2 \times 10^{-10}$

   a. $CN^- > NO_2^- > F^-$
   b. $F^- > NO_2^- > CN^-$
   c. $NO_2^- > F^- > CN^-$
   d. $NO_2^- > CN^- > F^-$
3. In the Brønsted–Lowry definition of acids and bases, an acid ___________
   a. is a proton donor.
   b. breaks stable hydrogen bonds.
   c. is a proton acceptor.
   d. corrodes metals.
4. Which of the following is the conjugate acid of the hydrogen phosphate ion, HPO_4^{2-}?
   a. H_3PO_4
   b. PO_4^{3-}
   c. $H_2PO_4^-$
   d. H_3O^+
5. Which one of the following is not a conjugate acid–base pair?
   a. NH_3 and NH_4^+
   b. HS^- and H_2S
   c. NH_3 and NH_2^-
   d. H_3O^+ and OH^-
6. Which one of the following is not a conjugate acid–base pair?
   a. NH_3 and NH_2^-
   b. $H_2PO_4^-$ and HPO_4^{2-}
   c. HNO_3 and HNO_2
   d. H_2O and OH^-
7. Which one of the following is not a strong acid?
   a. nitric acid, HNO_3
   b. carbonic acid, H_2CO_3
   c. sulfuric acid, H_2SO_4
   d. perchloric acid, $HClO_4$
8. Each of the following pairs contains one strong acid and one weak acid EXCEPT:
   a. H_2SO_4 and H_2CO_3
   b. HNO_3 and HNO_2
   c. HBr and H_3PO_2
   d. HSO_4^- and HCN

9. When $[H^+] = 4.0 \times 10^{-9}$ M in water at 25°C, then __________

a. pH = 9.40.

b. pH = 8.40.

c. pH = 7.00.

d. pH = 6.40

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

b. 7.08 and 6.92

c. 1.00 and 13.00

d. 5.94 and 8.06

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.

a. 2.5×10^{-5}

b. 1.9×10^{-5}

c. 5.0×10^{-5}

d. 7.4×10^{-3}

12. A cup of coffee has a hydroxide ion concentration of 1.0×10^{-10} M. What is the pH of this coffee?

a. 6

b. 7

c. 4

d. 2

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

a. 3.6×10^{-6} M

b. 1.8×10^{-5} M

c. 1.9×10^{-3} 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 pKa 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 forms aqueous solutions with pH = 7?

a. Na_2S

b. $NaNO_2$

c. NaBr

d. Na_2CO_3

Part II: Short Answer Questions

1. 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. $HBr(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$
   b. $\mathrm{CN^-(aq)} + H_2O(l) \rightleftharpoons \mathrm{HCN(aq)} + \mathrm{OH^-(aq)}$
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
   b. $(CH_3)_2CHCOOH$
   c. H_2SeO_4
   d. $(CH_3)_2CHNH_2$
6. Which of the following are amphiprotic?
   a. OH^-
   b. NH_3
   c. H_2O
   d. H_2S
   e. NO_3^-
   f. HCO_3^-
   g. CH_3COO^-
   h. HNO_3
7. A research chemist adds a measured amount of HCl gas to pure water at 25 ^{0}C and obtains a solution with $[H_3O^+] = 5\ 3.0 \times 10^{-4}$ M. Calculate $[OH^-]$. Is the solution neutral, acidic, or basic?

8. 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 $[OH^-] = 5.0 \times 10^{-12}$ 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 M $HC_2H_3O_2$ and 1.0 M $C_2H_3O_2^-$?

$$\mathrm{HC_2H_3}\,O_2\mathrm{(aq)} + H_2O(aq) \rightleftharpoons H_3O + \mathrm{(aq)} + C_2\,\mathrm{H_3O_2}^-\mathrm{(aq)}$$

UNIT 2

ELECTROCHEMISTRY

Unit Outcomes

After completing 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 interconversion of chemical and electrical energy*
- *distinguish between metallic conduction and electrolytic conduction*
- *identify and describe the functioning of the components of electrolytic and 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 and contrasting, communicating, asking question, measuring, relating cause and effect and problem solving.*

2.1 Oxidation-Reduction 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*

Start-up Activity

Form a group and discuss the following questions,

1. What are oxidation-reduction (redox) reactions?
2. List the redox-reactions taking place in your body, and the surroundings After discussion, share your idea with other groups.

2.1.1 Oxidation

When do we say a substance is oxidized?

The term **oxidation** was originally defined in terms of the adding of 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.

2.1.2 Reduction

When do we say a substance is reduced? Can oxidation occur without reduction and vice versa?

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.

Consider the following example

$$\overset{0}{Mg}(s) + 2\overset{1+}{H}Cl(aq) \rightarrow \overset{2+}{Mg}Cl_2(aq) + \overset{0}{H}_2(g)$$

In the above reaction 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’.

Activity 2.1

Form a group and discuss the following questions and present your answers to the class.

1. Which of the following reactions are redox reactions? Explain your answer for each case.
   a. $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
   b. $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
   c. $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
2. Use the given chemical equation to answer the following questions;

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

Identify the: a. oxidized substance b. reduced substance.
c. oxidizing agent. d. reducing agent.

3. Calculate the oxidation number of:
   a. C in $C_2O_4^{\ 2-}$ b. Cr in K_2CrO_4 c. Cl in $HClO_4$

2.1.3 Balancing Oxidation-Reduction (Redox) Reactions

What scientific law is used in balancing chemical equations?

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.

Balancing Redox Reactions Using Change in Oxidation-Number Method

How do you balance redox reactions using the change in the 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 number s changes
5. 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

$$\overset{+2}{Pb}\overset{-2}{S}(s) + \overset{0}{O_2}(g) \rightarrow \overset{+2}{Pb}\overset{-2}{O}(s) + \overset{+4}{S}\overset{-2}{O_2}(g)$$

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

Step 2: Assign oxidation numbers to the elements that change their oxidation number

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 N

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 to balance the six NO_3^- ions that are present in three . Therefore, the coefficient of 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 isequal to the number of atoms in the product side.

Exercise 2.1

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

   c $H_2S + HNO_3 \rightarrow S + NO + H_2O$

Balancing Redox Reactions using Half-Reaction Method

Why do you balance chemical equations?

In half-reaction method, the overall reaction is divided into two half-reactions, 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 half-reaction
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 side in the reduction half-reaction and to the right side in the oxidation half-reaction.

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

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

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

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 we have only one electron for the oxidation half-reaction and six electrons for the reduction half-reaction, so we need to multiply the oxidation half-reaction by 6 and write

$$\begin{array}{c} 6(Fe^{2+} \rightarrow Fe^{3+} + e^-) \\ 14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ \hline 6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + 6e^- \end{array}$$

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 a 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 (MnO_4^-) in basic solution to yield molecular iodine (I_2) and manganese (IV) oxide (MnO_4^-).

$$MnO_4^- + I^- \rightarrow MnO_2 + I_2$$

Solution:

Step 1: The two half-reactions are

Oxidation: $I^- \rightarrow I_2$

Reduction: $MnO_4^- \rightarrow MnO_2$

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:

$$MnO_4^- \rightarrow MnO_2 + 2H_2O$$

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

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

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 half-reaction by 2 as follows:

$$3(2I^- \rightarrow I_2 + 2e^-)$$

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

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

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

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

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

Exercise 2.2

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

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

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

   c. $H_5IO_6 + Cr \rightarrow IO_3^- + Cr^{3+}$

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

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

2.2 Electrolysis of Aqueous Solutions

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.* H_2SO_4, *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* $CuSO_4$ *solution using* Ni *electrodes and* Cu *electrodes.*
- *write electrode half reactions and overall reactions for the electrolysis of dil.* H_2SO_4, $NaOH$, *dil* $NaCl$, *conc.* $NaCl$ *and* $CuSO_4$ *solutions*
- *distinguish between molten electrolytes and aqueous electrolytic solutions.*

Before we study the electrolysis of aqueous solutions, let us 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.

Activity 2.2

Form a group and discuss the following points and present your answers to the class. Your teacher will help you to form groups.

1. How does conduction occur in metals and in electrolytes?
2. What do substances need in order to conduct electricity?
3. Can ionic compounds conduct electricity in the solid state? If your answer is "No", why?

Metallic conduction

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. In metallic conductors

- There is only flow of electrical energy but there is no transfer of matter.
- Electrical conduction through metals does not bring about any chemical transformations.
- Free and mobile electrons of the metallic atoms or their solid solutions such as alloys are responsible for electrical conductance.
- Conductivity of metal decreases with increase in temperature due to the enhanced thermal vibration of metal atoms disrupting the movement of electrons passing through them.

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.

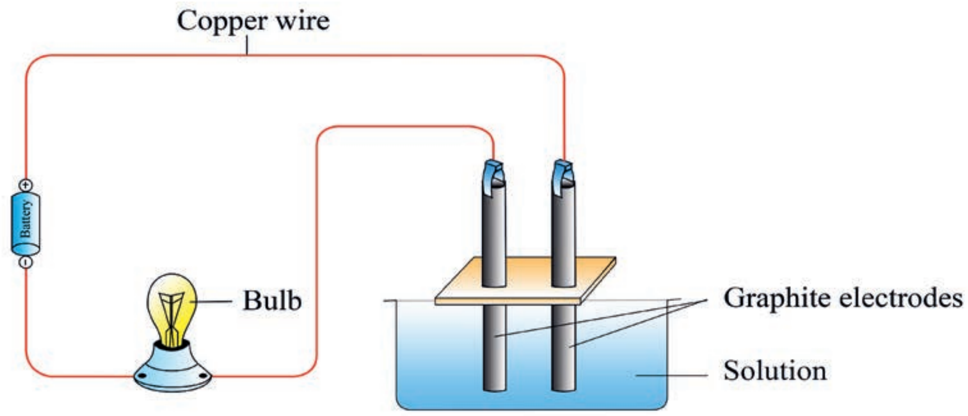


Figure 2. 1: Electrical Conductivity Apparatus

Exercise 2.3

1. Which of the following substances are capable of conducting electricity? Give reason for your answer.

   a. Iron
   b. Sulphur
   c. Solid sodium chloride
   d. Molten calcium chloride

Experiment 2.1

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_3COOH solution, 1 M sugar solution, magnesium ribbon and an iron nail.

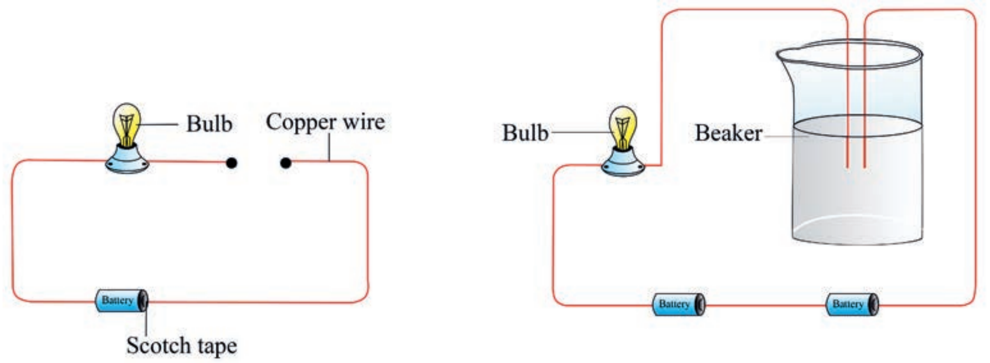


Figure 2. 2 (a) Electrical conductivity apparatus for solid materials. (b) Electrical conductivity apparatus for liquids and solutions.

Procedure:

1. 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.
2. 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 observation.

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

Results and Discussion:

1. Why is it important to polish the magnesium ribbon and iron nail before use?
2. Classify the materials you used as conductors, strong electrolytes, weak electrolytes and non-electrolytes.
3. Label the two ends of the wire in **Figure 2.2b** as cathode and anode.

Electrochemical 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 1.5-volt cell which is used to power many electrical appliances such as TV remotes and clocks. There are two types of electrochemical cells. These are Galvanic cells (also known as Voltaic cells) and Electrolytic cells

2.2.1 Electrolytic Cells

Activity 2.3

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Describe the migration of ions during electrolysis?
2. Observe **Figure 2.3** and answer the following questions.

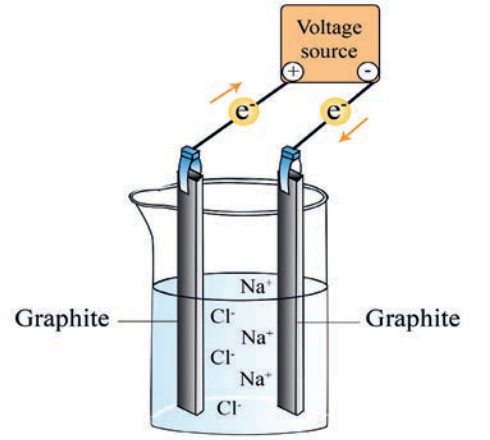


Figure 2. 3: Electrolytic cell containing molten sodium chloride.

a. Label the anode and the cathode.

b. Indicate the migration of sodium ions and chloride ions.

c. Write the reduction half-reaction, oxidation-half reaction, and the overall reaction.

2.2.2 Preferential Discharge

What does preferential discharge mean?

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 Sr Ca Na	Displaces H_2 gas from cold water, steam and acids and forms hydroxides
Mg Al Zn Cr Fe Cd	Displaces H_2 gas from steam and acids and forms hydroxides but do not displace hydrogen from cold water.
Co Ni Sn Pb	Displaces H_2 gas from acids only and forms hydroxides
H_2	Included for comparison
Cu Hg Ag Pt Au	Unreactive with water or acids.

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 **c**annot 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:

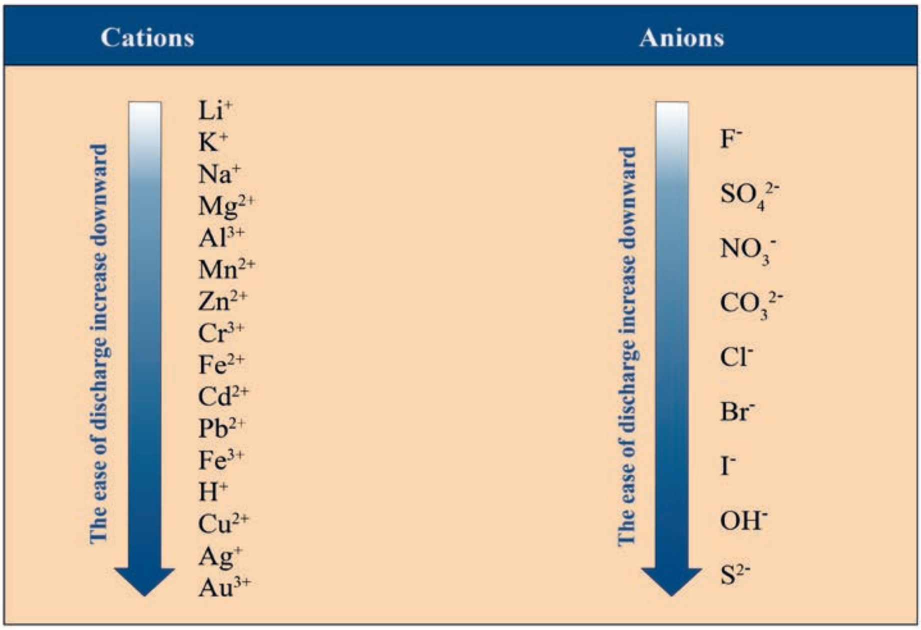
$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

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.



Cations

The ease of discharge increase downward

Li^+
K^+
Na^+
Mg^{2+}
Al^{3+}
Mn^{2+}
Zn^{2+}
Cr^{3+}
Fe^{2+}
Cd^{2+}
Pb^{2+}
Fe^{3+}
H^+
Cu^{2+}
Ag^+
Au^{3+}

Anions

The ease of discharge increase downward

F^-
SO_4^{2-}
NO_3^-
CO_3^{2-}
Cl^-
Br^-
I^-
OH^-
S^{2-}

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

How is concentration of an ion affect preferential discharge?

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

How do electrodes affect the preferential discharge of ions?

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.

- $\mathrm{CuSO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4{}^{2-}(aq)}$
- Anode: $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$
- Cathode: $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$

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

Exercise 2.4

1. Define the following terms:
   a. preferential discharge
   b. inert electrode
   c. reactive or active electrode.
2. 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.

2.2.3 Electrolysis of Some Selected Aqueous Solutions

Activity 2.4

Form a group, and discuss each of the following:

1. Prior to electrolysis, why sodium chloride must be in molten state?
2. For the electrolysis of molten KCl, 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? After the discussion, share your ideas with the rest of the class.

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)

Which ions are discharged at the cathode and anode?

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 −0.83V compared to −2.71V 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 increase. 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.

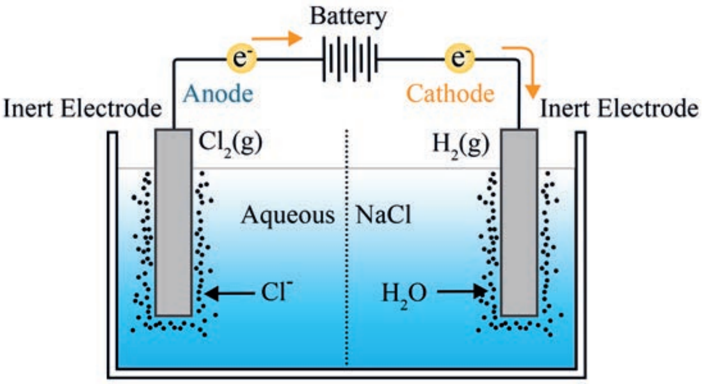


Figure 2. 4: Electrolysis of brine solution.

Electrolysis of Dilute Sodium Chloride Solution

Activity 2.5

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. For the electrolysis of dilute solution of sodium chloride.
   a. List all ions present in the solution.
   b. Identify ions that migrate towards the anode and the cathode.
   c. Write the electrode half-reactions and overall reaction

Experiment 2.2

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.

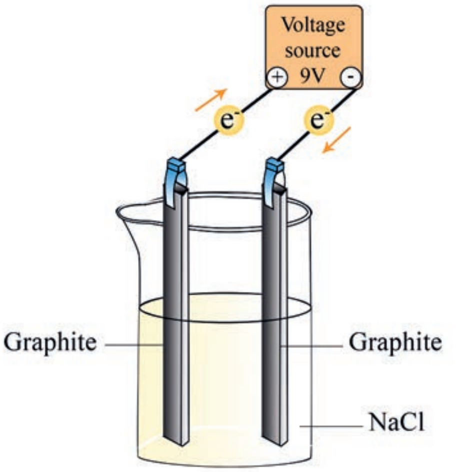


Figure 2. 5: Electrolysis of sodium chloride solution

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

Electrolysis of Dilute Sulphuric Acid Solution

Which ions are discharged at the cathode and anode?

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

Which ions preferentially discharged at the cathode and anode if copper (II) sulphate solution is electrolysed, using platinum (inert) electrodes?

Electrolyte $CuSO_4$ dissociates in to $Cu\ ^+$ 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:

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

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Are the copper electrodes reactive or inert in the electrolysis of $CuSO_4$ solution?
2. Write the reactions occurring at the anode and at the cathode during the electrolysis of $CuSO_4$ solution, using copper electrodes.
3. What is the net result of the electrolysis of $CuSO_4$ 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.

Exercise 2.5

1. For the electrolysis of dilute $NaOH$ solution,
    a. write the balanced chemical equations for the reduction half-reaction 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.

2.3 Quantitative Aspects of Electrolysis

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*
- ☞ *do calculations related to Faraday's second law of electrolysis.*

Is it possible to calculate the amount of product formed at the electrodes?

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

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,

$m \propto Q$ or

$m = zQ$

where, z is a proportionality constant called electrochemical equivalent

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

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 $E = \frac{\text{Molecular mass (M)}}{\text{Valence (n)}}$

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

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 (6.02×10^{23} electrons) to the cathode.

Example 2.3

1. 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 yield one chlorine molecule and releases two electrons. Therefore, the formation of 1 mole of chlorine results in 2 moles of electrons supplied by the Cl^- 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

Calculate the mass of calcium metal and chlorine gas that can be produced when a current of 0.452 A is passed through molten $CaCl_2$ 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 × time or charge.

$$\text{Charge } (Q) = \text{current } (I) \text{ in A} \times \text{time } (t) \text{ in s}$$

$$Q = I \times t = (0.452\ \text{A}) \times (1.5 \times 60 \times 60\ \text{s})$$

= 2.44 × 103 A s = 2.44 × 10^3 C

1 mol e^- = 96,500 C

$\boldsymbol{x}$ = 2.44 × 10^3 C

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

2 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 mol e– = 1 mole Ca = 40.08 g *Ca* 0.0253 mol e– = *x*

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

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 Cl_2= 1 mole Cl_2 0.0253 mol e^-= *x*

$$\Rightarrow x = \frac{0.0253\ mol\ e^-\ x\ 71\ g\ Cl_2}{2\ mol\ e^-} = 0.898\ g\ Cl_2$$

Exercise 2.6

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 amperes 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?

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, $m \alpha E$ Or $m_1 \alpha E_1, \; m_2 \alpha E_2, \; and \; m_3 \alpha E_3 \; etc$

Replacing the proportionality by the proportionality constant, the equation become

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

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 .**

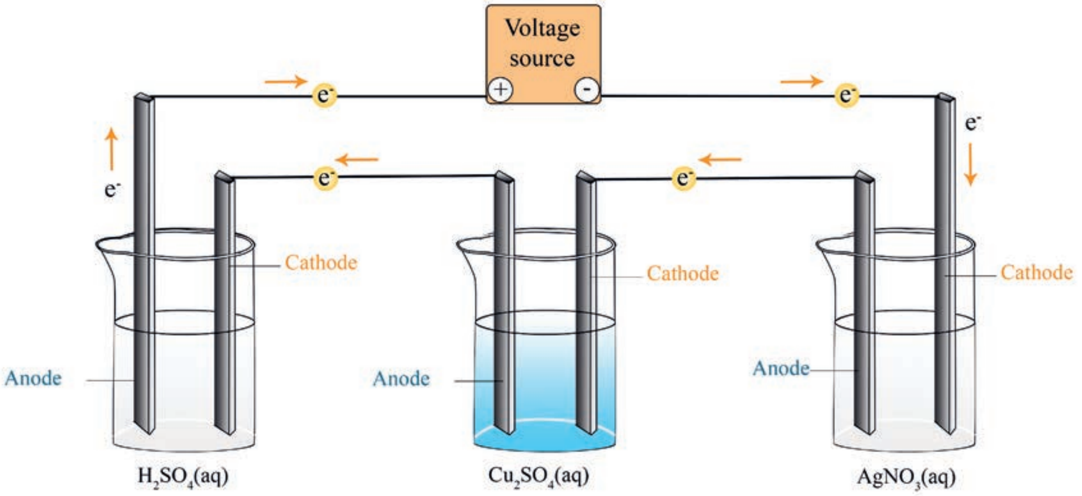


Figure 2. 6: Solutions connected in series to a battery.

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

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

$$= \frac{\text{mass of silver}}{\text{equivalent mass of silver}}$$

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.

$$\frac{m_{Ag}}{E_{Ag}} = \frac{m_{Cu}}{E_{Cu}} \Rightarrow m_{Cu} = \frac{E_{Cu} m_{Ag}}{E_{Ag}}$$

$$= \frac{31.75\ g/eq\ x\ 0.108\ g}{108\ g/eq} = 0.032\ g\ of\ Cu\ is\ deposited$$

Exercise 2.7

1. 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?
2. 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?

2.4 Industrial Application of Electrolysis

After completing this subunit, you will be able to:

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

Electrolysis has many industrial applications. Some of them are the following.

The production of chemicals

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

Electrosynthesis of Metals

Electro synthesis is the method of producing substances through electrolysis reactions. Electro synthesis has different applications such as extraction of metals, electroplating of metals, electro refining of metals, electro synthesis of nonmetals and compounds.

Extraction of Metals

Activity 2.7

Discuss each of the following questions. After the discussion, share your ideas with your classmates.

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.

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 aluminium, 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 (O^{2-}) anions are attracted to the anode, where they are oxidized to release oxygen gas.

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

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

Electrolytic refining of Metals

Activity 2.8

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

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

Many metals, such as copper, zinc, tin, nickel, silver, gold etc. are refined by electrolysis. In this process, the impure metal is made the anode and a thin strip of pure metal is made the cathode. The solution of the metal salt is used as an electrolyte. When current passes through electrolyte, the pure metal from the anode dissolves into the electrolyte. An equivalent amount of pure metal from the electrolyte is deposited on the cathode. The insoluble impurities settle down at the bottom of the anode and are known as anode mud whereas the soluble impurities go into the solution**(Figure 2.7).**For example: In the electrolytic refining of copper, the electrolyte is a solution of acidified . The anode is impure copper, whereas the cathode is a strip of pure copper. On passing electric current, pure copper is deposited on the cathode.

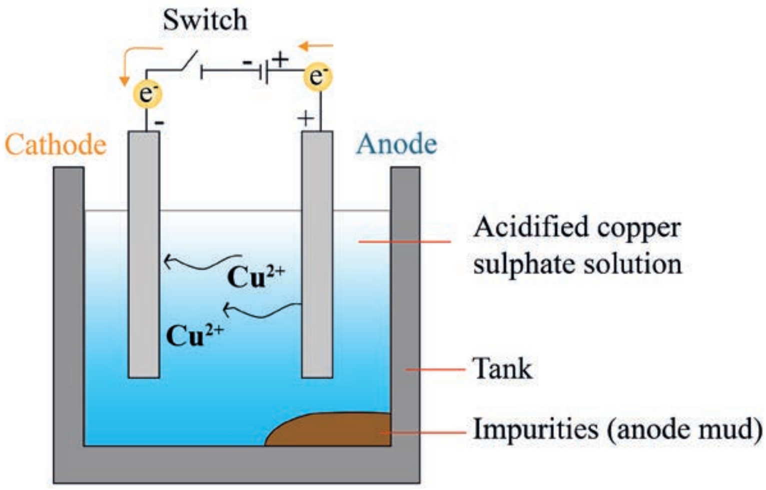


Figure 2.7: Purification of Copper by Electrolysis

Electroplating of Metals

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 salt solution of the metal which is to be deposited is taken as electrolyte.

Experiment 2.3

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, 1M H_2SO_4 solution, copper rode and an iron key

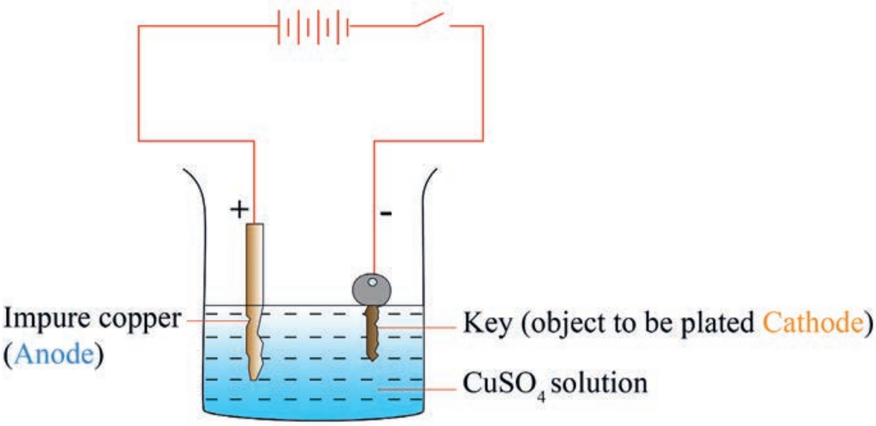


Figure 2. 8: Electroplating of an iron object with copper

Procedure:

1. Dissolve two teaspoonfuls 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 $CuSO_4$ solution?
5. What will happen to the copper plate connected to the positive terminal of the battery?

Electrosynthesis of Nonmetals and Compounds

Activity 2.9

Form a group and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

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?
4. Explore a compound that is prepared by electrolysis.
5. Write the oxidation half reaction, reduction half reaction and overall reaction for compound's you mention in question number 1.

Electro Synthesis of Compounds

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 d) 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:

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

2.5 Volatic Cells

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*
- *explain the different methods of the prevention of corrosion.*

What makes a Galvanic cell different from an electrolytic cell?

Construction of Voltaic Cells (Zn-Cu voltaic Cell)

Activity 2.10

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

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.

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

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 (Zn and Cu) and solutions ($ZnSO_4$ 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 **(Figure 2. 9).**

During the course of the overall redox reaction, electrons flow externally from the anode (Zn electrode) through the wire and light bulb to the cathode (Cu electrode). In the solution, the cations (Zn^{2+}, Cu^{2+}, and K^{+}) move toward the cathode, while the anions (SO_4^{2-} 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:

$$MnO_{\text{ü}}^{\,-}(aq) + 16H^{+}(aq) + 10I^{-}(aq) \rightarrow 2Mn^{2+}(aq) + 5I\ \ (s) + 8H\ \ O(l)$$

$$graphite\,|\,I^{-}(aq)\,|\,I_2(s)\,||\,MnO_4^{\,-}(aq), H^{+}(aq), Mn^{2+}(aq)\,|\,graphite$$

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

$Zn(s)|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu(s)$ or

$Zn(s)|Zn^{2+}(aq,1M)||Cu^{2+}(aq,1M)|Cu(s)$

$$\textit{anode}\rightarrow \underset{\text{Oxidation half reaction}}{Zn|Zn^{2+}\text{(aq, 1.00M)}}\ \underset{\textit{salt bridge}}{||}\ \underset{\text{Reduction half reaction}}{Cu^{2+}\text{(aq, 1.00M)}|Cu(s)} \leftarrow \textit{cathode}$$

- Half-cell components usually appear in the same order as in the half-reaction, 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 $Cr(s)|Cr^{3+}(0.20M)||(0.020M)Ag^{+}|Ag(s)$

Exercise 2.8

1. Write the cell notation for a Galvanic cell consisting of an Al electrode placed in 1M $Al(NO_3)_3$ solution and a Ag electrode placed in a 1M $AgNO_3$ solution.
2. Explain the use of a salt bridge.

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 half-reaction and a reduction half-reaction. The general forms of these half-reactions are

- Anode (Oxidation): $\text{Re}\,duction\ Species \rightarrow Oxidized\ Species + ne^{-}$
- 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:

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

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

$$2H^+(aq;\ 1M) + 2e^- \rightarrow H_2(g;\ 1\ atm), \quad E^0{}_{reference} = 0.00V$$

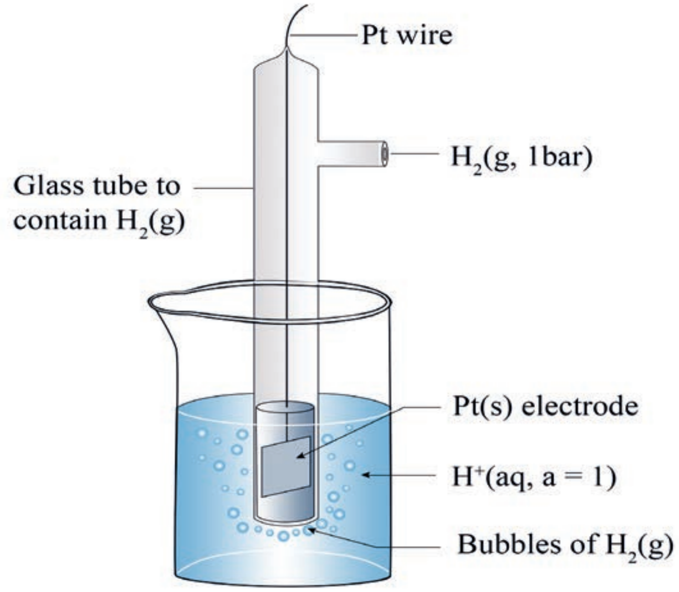


Figure 2. 10: The Standard Hydrogen Electrode (SHE)

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 half-cell. 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:

$$\begin{aligned} E^0{}_{cell} &= E^0{}_{cathode} - E^0{}_{anode} \\ &= E^0{}_{unknown} - E^0{}_{reference} \\ &= E^0{}_{unknown} - 0.00V \\ &= E^0{}_{unknown} \end{aligned}$$

- 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 $Zn(s)|Zn^{2+}(1M)||H^+(1M)|H_2(1\ atm)|Pt(s)$

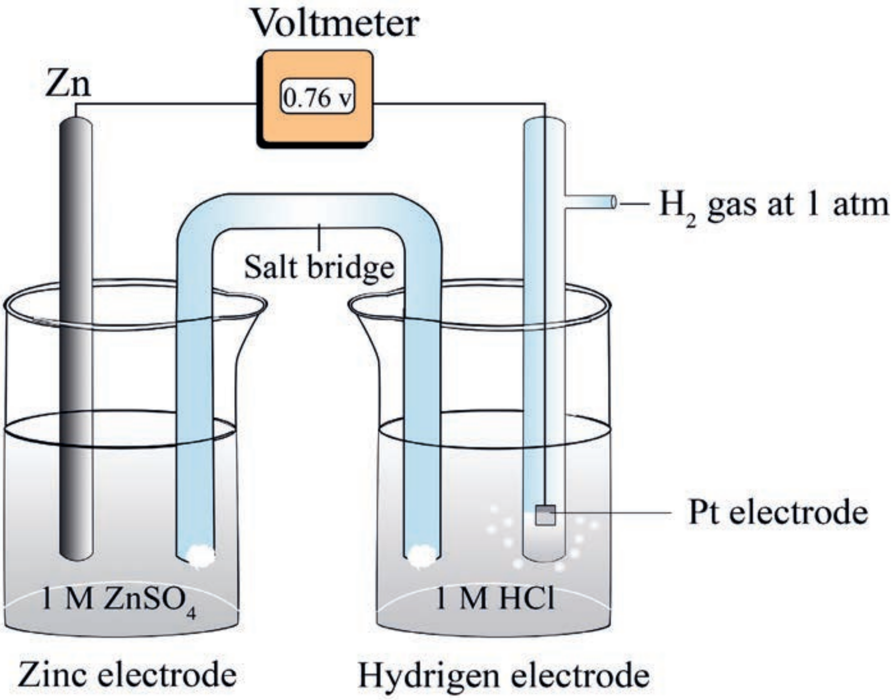


Figure 2.11: A cell consisting of a zinc electrode and a hydrogen electrode.

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^0_{zinc}:

We can write the half-cell reactions as follows:

- Anode (Oxidation): $Zn(s) \rightarrow Zn^{2+}(1M) + 2e^-$
- 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, $\boldsymbol{E^0_{cell}}$, which is composed of a contribution from the anode and a contribution from the cathode, is given by $E^0_{cell} = E^0_{cathode} - E^0_{anod}$ where both $E°_{cathode}$ 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 V

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:

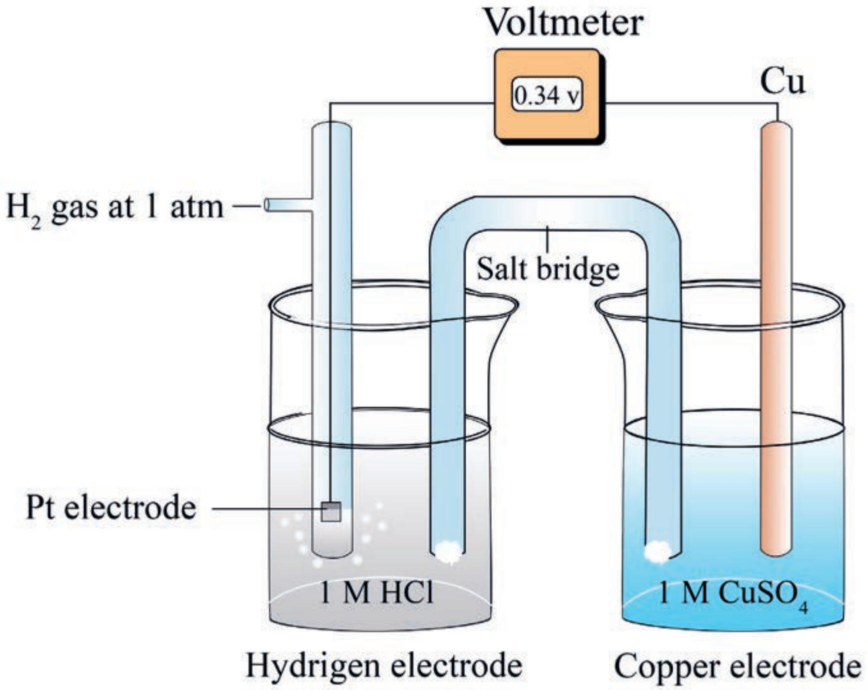


Figure 2.12: A cell consisting of a copper electrode and a hydrogen electrode

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

- Anode (Oxidation): $H_2(1\ atm) \rightarrow 2H^+(1M) + 2e^-$
- Cathode (Reduction): $Cu^{2+}(1M) + 2e^- \rightarrow Cu(s)$
- Overall Reaction: $H_2(1\ atm) + Cu^{2+}(1M) \rightarrow 2H^+(1M) + Cu(s)$

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, $E^0_{Cu^{2+}/Cu}$, is 0.34 V, where the subscript means $Cu^{2+} + 2e^- \rightarrow Cu$

For the Daniell cell shown in **Figure 2.10,** we can now write

- Anode(Oxidation): $Zn(s) \rightarrow Zn^{2+}(1M) + 2e^-$
- Cathode(Reduction): $Cu^{2+}(1M) + 2e^- \rightarrow Cu(s)$
- Overall Reactio: $Zn(s) + Cu^{2+}(1M) \rightarrow Zn^{2+}(1M) + Cu(s)$

The EMF of the cell is

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

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

$$= 0.34\ V - (-0.76\ V)$$

$$= 1.10\ V$$

we 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°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + 2e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^-(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbsO_4(s) + 2H_2O$	+1.70
$Ce^{3+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$2Cl(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^-(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(s) + 4H^+(aq) + 3e^- \longrightarrow NO(aq) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow NO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
$PbSo_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	-1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.90
$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05

Increasing Strength as oxidizing agent

Increasing Strength as reducing agent

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

1. 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

   $$F_2(1\ atm) + 2e^- \rightarrow 2F^-(1M),\ \ E^0 \ = \ 2.87\ V$$

   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 ***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 2.3 increase in strength from bottom to top and the reducing agents (the species on the right-hand side of the half-reactions) increase in strength from top to bottom.

2. 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.

3. Under standard-state conditions, any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located below it in Table 2.3**.** This principle is sometimes called the diagonal rule. In the case of the Daniell cell,

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

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

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.

4. Changing the stochiometric coefficients of a half-cell reaction does not affect the value of E^o_{red}, because electrode potentials are intensive properties. This means that the value of E^o_{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^0 does not change if we multiply the half-reaction by 2

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

5. 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 2.3 we 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 2.3

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ &= E^0_{Ag^+/Ag} - E^0_{Mg^{2+}/Mg} \\ &= 0.80V - (-2.37V) \\ &= 3.17V \end{aligned}$$

The positive value of E^0_{cell} shows that the forward reaction is favored.

Experiment 2.4

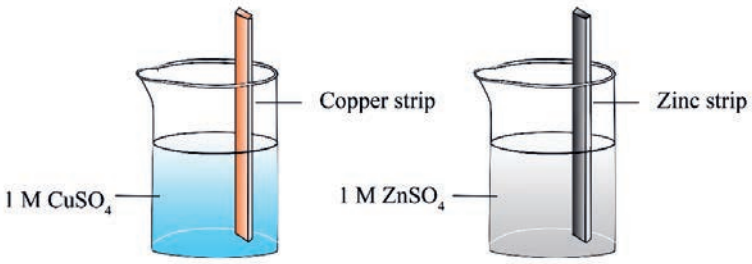
Determination of Cell Potential of Daniell Cell

Objective:

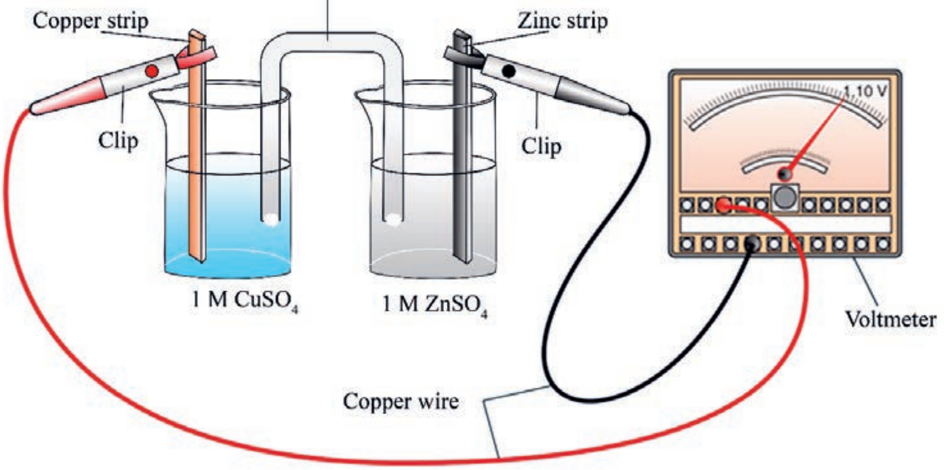
- To determine cell potential of Daniell cell and
- To identify the cathode and anode.

Apparatus and chemicals:

Voltmeter, copper strip, zinc strip, 1 M $ZnSO_4$, 1 M $CuSO_4$, saturated KCl solution, two 100 mL beakers, U-tube, a fine sandpaper or file and cotton.



a) Copperhalf cell **b) Zinc half cell**



c) Setup of Galvanice Cell

Figure 2.13: Daniell Cell.

Procedure:

1. Fill each U-tube with saturated KCl and plug each end with cotton. Be sure not to trap 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 metal strip in a 50 mL of 1 M 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

Exercise 2.9

1. Can Sn reduce Zn^{2+} (aq) under standard-state conditions?
2. What is the standard emf of a galvanic cell made of a Cd electrode in a 1.0 $\boldsymbol{M}\,Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 $\boldsymbol{M}$ $Cr(NO_3)_3$ solution at 25 °C?
3. 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.

Electromotive Force (EMF)

Activity 2.11

Form a group. Discuss the following question.

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?
   After the discussion, share your ideas with the rest of the class.

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 is called electromotive force (EMF).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.

1. When oxidation potential of anode and cathode are taken into account

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

2. When reduction potential of cathode and anode are taken into account

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

Dependence of Cell Potential EMF on Concentration

What is the effect of changing the concentration of reactants on cell potential?

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 $\Delta G^0 = -nFE^0{}_{cell}$ the equation becomes

$$-nFE_{cell} = -nFE^0{}_{cell} + RT \ln Q$$

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

$$E_{cell} = E^o{}_{cell} - \frac{RT}{nF} \ln Q \quad or \quad E_{cell} = E^o{}_{cell} - \frac{2.303RT}{nF} \log Q \quad \textbf{\textit{Nernst equation}}$$

If you substitute 298 K (25 ^{0}C) for the temperature in the Nernst equation and put in values for R and F, you get (using common logarithms)

$$E_{cell} = E^o{}_{cell} - \frac{0.0592}{n} \log Q \ \text{(Value in volts at 25 }^0\text{C)}$$

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 $E^{o}_{cell} - \frac{0.0592}{n}\log Q$ 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:

$$PV = nRT$$

$$\frac{P}{RT} = \frac{n}{V}$$

$$\frac{1\ \text{atm}}{0.0821\ \frac{\text{L atm}}{\text{K mol}} \times 298.15} = 0.041$$

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

1. 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,

$$\ln K = \frac{nE^{0}{}_{cell}}{0.0257\ V}$$

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

The half-reactions are:

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

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

From the above reaction and using Table 2.3, we can calculate the cell potential,

$$\begin{aligned} E^{0}{}_{cell} &= E^{0}{}_{\text{red}}\ (cathode) - E^{0}{}_{red}\,(\text{anode}) \\ &= E^{0}{}_{\text{red}}\ (Cu^{2+}/Cu^{+}) - E^{0}{}_{red}\,(Sn^{2+}/Sn) \\ &= 0.15\ V - (-0.14\ V) = +\ 0.29\ V \end{aligned}$$

$E^{0}{}_{cell}$ is 0.29 V, and n = 2 (because 2 mol of electrons are consumed in the reaction), then,

$$\ln k = \frac{nE^{0}{}_{cell}}{0.0257\ V} = \frac{2\ x\ 0.29\ V}{0.0257\ V} = 22.6$$

$$\Rightarrow K = e^{22.6} = 6.532\ x\ 10^{9}$$

The reaction favors the formation of products.

Example 2.9

1. Calculate the standard free-energy change for the following reaction 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): $3Ca^{2+}(1.0M) + 6e^- \rightarrow 3Ca(s)$

$$\begin{aligned} E^0{}_{cell} &= E^0{}_{\text{red}}\ (cathode) - E^0{}_{red}\,(\text{anode}) \\ &= E^0{}_{\text{red}}\ (Ca^{2+}/Ca) - E^0{}_{red}\,(Au^{2+}/Au) \\ &= -2.87\ V - 1.5\ V = -\ 4.37\ V \end{aligned}$$

The overall reaction shows that n = 6 (6 moles of electrons are involved). Now we can calculate ΔG^o, using the following equation:

$$\Delta G^0 = -\ nFE^0{}_{cell}$$

$$= -\ 6 \times (96500\ \text{J/V mol}) \times (-\ 4.37\ \text{V})$$

$$= 2.53 \times 106\ \text{J/mol} = 2.53 \times 103\ \text{kJ/mol}$$

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,

$$Zn \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu$$

Calculate the standard EMF of the given cell

$$E^0_{Zn^{2+}/Zn} = -\,0.76\ V \quad \text{and} \quad E^0_{Cu^{2+}/Cu} = +\,0.34\ V$$

Solution: Half-cell reactions

Anode Reaction: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode Reaction: $Cu^{2+} + 2e^- \rightarrow Cu$

Over all Reaction: $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

$$\begin{aligned} E^0_{cell} &= E^0_{cathode} - E^0_{\text{anode}} \\ &= E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} \\ &= 0.34\ V - (-\,0.76\ V) = 1.1\ V \end{aligned}$$

Example 2.11

1. What is the cell potential of the following voltaic cell at 25⁰C?

$$Zn(s) \mid Zn^{2+}(1.0\ x\ 10^{-5}\ M) \parallel Cu^{2+}(0.100M) \mid Cu(s)$$

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

$$\text{K} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1.0\ x\ 10^{-5}}{0.100} = 1.0\ x\ 10^{-4}$$

The standard cell potential is 1.10 V, so the Nernst equation becomes

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n} \log\ K$$

$$= 1.10 - \frac{0.0592}{2} \log\ (1.0\ x\ 10^{-4})$$

$$= 1.10 - \ (-0.12) = 1.22\ V$$

Exercise 2.10

1. 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: $\left[Zn^{2+}\right]=0.010M$,$\left[H^+\right]=2.5M$, $pH_2 =$ 0.30 atm . Calculate E_{cell} at 298.15 K.
2. A concentration cell consists of two Ag/Ag^{2+} half-cells. In half-cell A, the electrolyte is 0.010 M $AgNO_3$; in half-cell B, it is 4.0 x 10 — 4M $AgNO_3$. What is the cell potential at 298.15 K?
3. What is the cell potential of the following voltaic cell at 25C?

   $Zn(s)\,|\,Zn^{2+}(0.200\ M)\,||\,Ag^{2+}(0.002M)\,|\,Ag(s)$

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 $\boldsymbol{E}_{\text{cell}}$ 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 M Cu^{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 1.0M Cu^{2+} in the cathode half-cell **(Figure 2. 14):**

Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq;\ 0.1\ M) + 2e^{-}$

Cathode reaction: $Cu^{2+}(aq;\ 1.0\ M) + 2e^{-} \rightarrow Cu(s)$

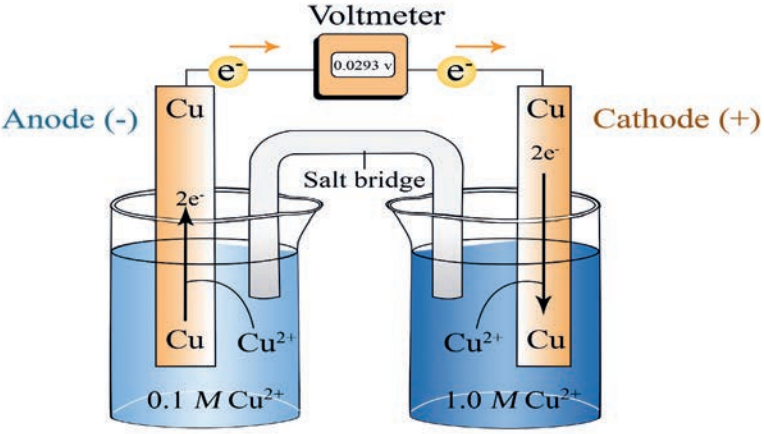


Figure 2.14. A concentration cell based on the Cu / Cu^{2+} half-reaction; E$_{cell}$ > 0 as long as the half-cell concentrations are different.

The overall cell reaction is the sum of the half-reactions:

$$Cu^{2+}(aq;\ 1.0\ M) \rightarrow Cu^{2+}(aq;\ 0.1\ M) \quad E_{cell} = ?$$

The cell potential at the initial concentrations of 0.10 M(dilute) and 1.0 M(concentrated), with n = 2, is obtained from the Nernst equation:

$$E_{cell} = E^{0}{}_{cell} - \frac{0.0592\ V}{2} \log \frac{\left[Cu^{2+}\right] dilute}{\left[Cu^{2+}\right] conc.}$$

$$= 0\ V - \left(\frac{0.0592\ V}{2} \log \frac{0.10 M}{1.0 M}\right)$$

$$= 0\ V - \left(\frac{0.0592\ V}{2} (-1.00)\right)$$

$$= 0.0296\ V$$

Since $E^{0}{}_{cell}$ 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 $\left[Cu^{2+}\right]$ 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 1atm. 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 0.76V, 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 $\left[H^{+}\right]$ 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? $pH=-\log\left[H^{+}\right]$

The result is $E_{cell} = 0.76 - 0.0592\,pH$ Which you can 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.

Exercise 2.11

1. 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 $\left[Co^{2+}\right] = 0.25M$ and $\left[Fe^{2+}\right] = 0.94M$
2. 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 $E^0_{Zn} = 0.76\ V$.

The main difference between electrolytic and voltaic cell is summarized in the following table

Table 2.4: Comparison of Galvanic Cell / Voltaic Cell and Electrolytic Cell

Galvanic Cell / Voltaic Cell	Electrolytic Cell
Energy released by spontaneous redox reaction is converted to Electrical energy	Electrical energy is used to derive non-spontaneous redox reaction.
In these electrochemical cells, the anode is negatively charged and the cathode is positively charged.	These cells feature a positively charged anode and a negatively charged cathode.
The electrons originate from the species that undergoes oxidation.	Electrons originate from an external source (such as a battery).
Oxidation half reaction $Y \rightarrow Y^{+} + e^{-}$	Oxidation half reaction $Z^{-} \rightarrow Z + e^{-}$
Reduction half reaction $Z^{+} + e^{-} \rightarrow Z$	Reduction half reaction $Y^{+} + e^{-} \rightarrow Y$
Overall reaction $Y + Z^{+} \rightarrow Y^{+} + Z \quad (\Delta G < 0)$	Overall reaction $Y^{+} + Z^{-} \rightarrow Y + Z \quad (\Delta G > 0)$

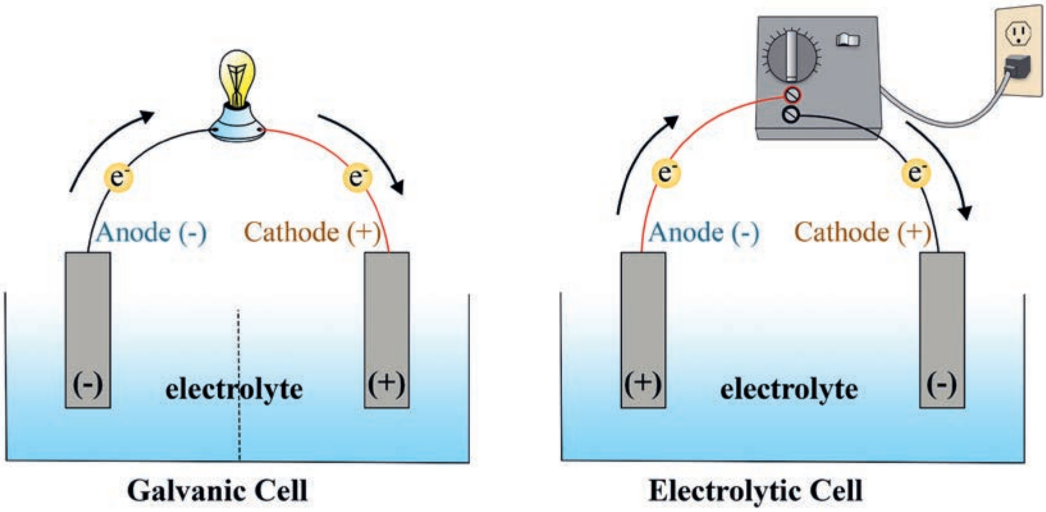


Figure 2. 15: An electrochemical cell:

a) galvanic (voltaic) cell **b) electrolytic cell**

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-cells-one 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 remains 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.

Batteries

Activity 2.12

Form a group. Discuss the following questions, and share your idea with other groups.

1. Collect some used and disposed batteries;
    - i. classify them as:
        - a. primary battery or secondary battery.
        - b. dry cell or alkaline battery etc.
    - ii. Identify the parts of the batteries, which you have collected.
    - iii. Describe the type of electrodes as well as physical and chemical nature of the electrolyte present in each battery.
2. The electrolyte in a discharged lead storage battery freezes at higher temperature than a fully charged battery. Explain this observation to your class.
3. Go to a nearby automobile garage and ask the garage mechanic:
    - a. About the working principle of car battery;
    - b. how do they come to know whether a car battery needs recharging;

Caution! Wear gloves while collecting the disposed 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 self-contained and requiring no auxiliary components such as salt bridges. Here you will discuss types of batteries that are in widespread use.

Fuel cells

What makes fuel cell different from battery?

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

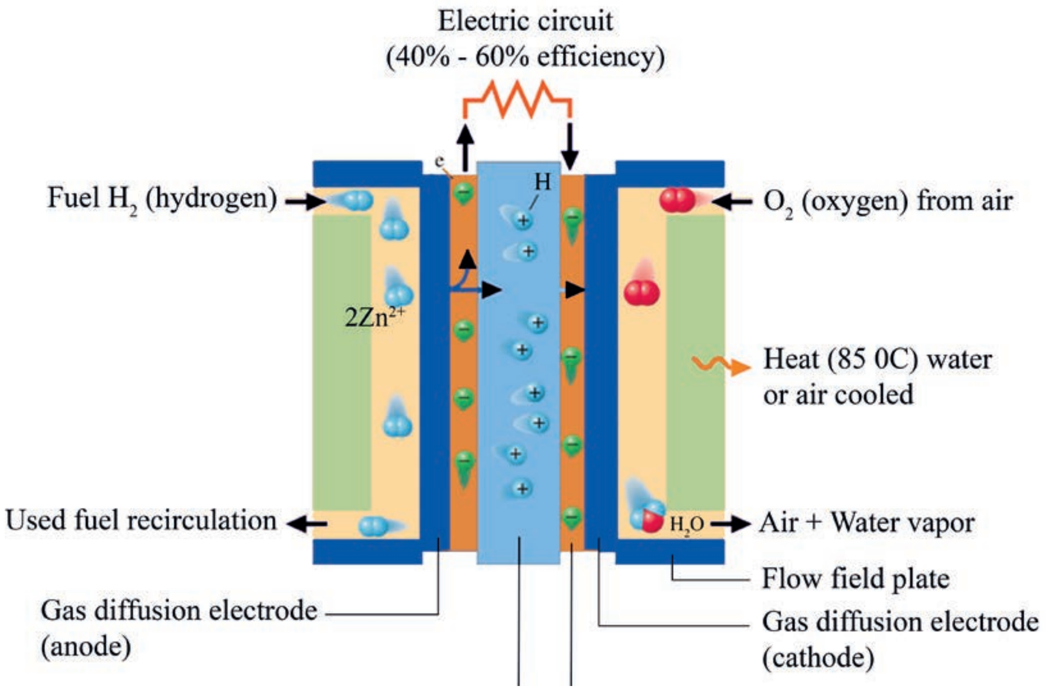


Figure 2.16: A hydrogen – oxygen fuel cell.

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:

$$\text{Anode:} \quad H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

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 $O_2(g)$

$$\text{Cathode:} \; O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(g)$$

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 both half-reactions is given by:

$Overall: 2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$, 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.

Exercise 2.12

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. a. What is the electrolyte in a dry cell?
   b. Write the half-reactions for the reducing and oxidizing agents in a dry cell.

Corrosion of Metals

What are the causes of corrosion?

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

What is the economic disadvantage of iron corrosion?

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 $\left[H^+\right]$).
- 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):**

   $$\text{Anodic region; Oxidation}: \text{Fe(s)} \rightarrow \text{Fe}^{2+}\text{(aq)} + 2\text{e}^-$$

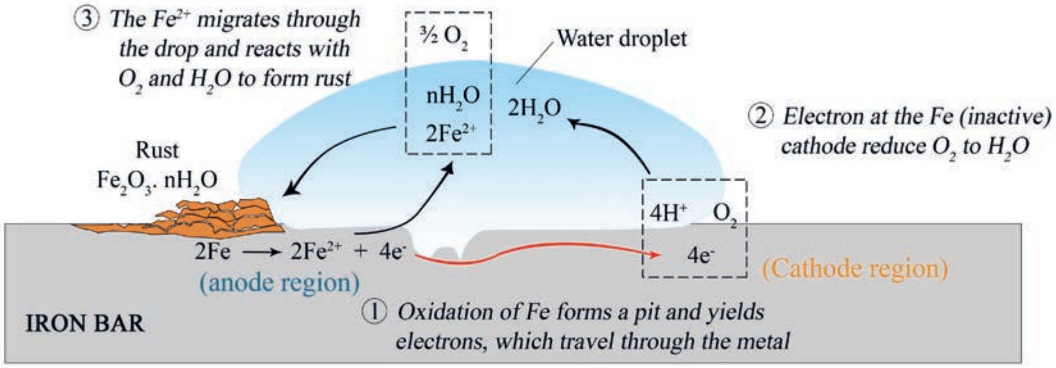


Figure 2.17: A small area of the surface, showing the steps in the corrosion process.

Once the iron atoms lose electrons, the damage to the object has been done, and a pit (depression or hollow) form 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:

➢ $Cathodic\ region;\ reduction: O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

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 $\left[H^+\right]$ 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 $\left[H^+\right]$).

Ionic 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 ($Ag\ S$).

Exercise 2.13

1. Define corrosion.
2. Explain the negative effects of corrosion.
3. Aluminum does not rust as iron does. Why?

Protecting Against the Corrosion of Iron

Activity 2.13

Form a group and discuss each of the following questions. After the discussion, share your ideas with the other groups.

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

1. 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.

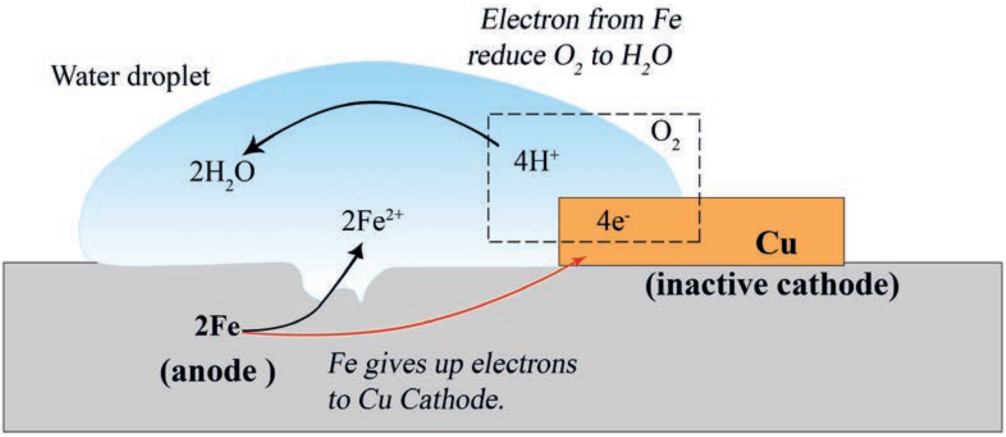


Figure 2.18: The effect of Metal-metal contact on the corrosion of iron; *Fe* in contact with *Cu* corrodes faster.

2. 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.

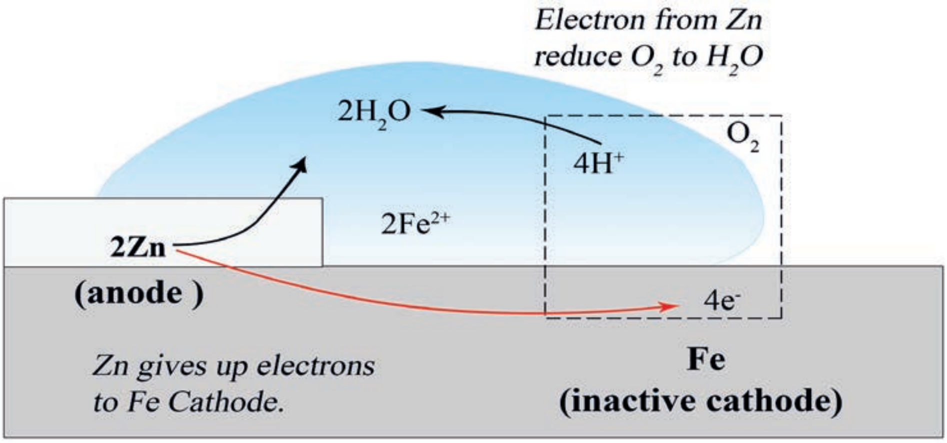


Figure 2. 19: The effect of Metal-metal contact on the corrosion of iron; *Fe* in contact with *Zn* does not corrode. This method of preventing corrosion is known as cathodic protection

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 cells, 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) half-cells, 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_{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 $\left[H^+\right]$, 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.

CHECK LIST

KEY TERMS

- *Anion*
- *Anode*
- *Battery*
- *Brine solution*
- *Cathode*
- *Cation*
- *Cell notation*
- *Concentrated solution*
- *Conductivity*
- *Corrosion*
- *Daniell cell*
- *Dilute solution*
- *Dry cell*
- *Electrochemical series*
- *Electrolysis*
- *Electrolyte*
- *Electrolytic cell*
- *Electroplating*
- *Faraday's first law*
- *Faraday's second law*
- *Galv*
- *Galvanic Cell / Voltaic Cell*
- *Nernst equation*
- *Oxidation*
- *Oxidation number*
- *Oxidizing agent*
- *Preferential discharge*
- *Primary batteries*
- *Redox reaction*
- *Reducing agent*
- *Reduction*
- *Salt bridge*
- *Secondary batteries*
- *SHE*
- *Standard electrode potential*

REVIEW EXERCISE ON UNIT 2

Part I: Multiple Choice Questions

1. What is the oxidation number of chromium in the ionic compound ammonium dichromate? $(NH_4)_2Cr_2O_7$?

   a. + 3
   b. + 4
   c. + 5
   d. + 6

2. What are the oxidation numbers for nickel, sulfur, and oxygen in $Ni_2(SO_4)_3$?

   a. Ni +3; S +6; O -2
   b. Ni +2; S +4; O -2
   c. Ni +3; 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 regarding voltaic cells is ***not correct***?

   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+}--> Zn is – 0.76 V, what is the standard reduction potential of

$Mg^{2+} \rightarrow Mg$? $Mg \mid Mg^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn \quad E^{\circ} = +1.61$ V

a. – 0.85 V
c. + 2.37 V
b. + 0.85 V
d. – 2.37 V

8. Use the Table of Standard Reduction Potential stable, which species would react with Al^{3+}?

a. Pb only
c. Fe and Pb
b. Au^{3+} only
d. Both Mg and K

9. 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 cell?

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta G^{\circ} = -474$ kJ/mol

a. 2.46 V
c. 1.23 V
b. 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. $K = RT \ln \Delta G^{o}$
d. $\Delta G^0 = RT \ln K$

11. What is ΔG° for the following balanced reaction, if $E^{\circ} = +2.431$ V?

$Al(s) + Fe^{2+}(aq) \rightarrow Al^{3+} + Fe(l) \quad E^{\circ} = +2.431$ V

a. -704 kJ/mol
c. -235 kJ/mol
b. +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, $\left[Cu^{2+}\right] = 1.0M$ and

$\left[Zn^{2+}\right] = 0.025M$

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. a fuel cell is rechargeable, while a battery is not.
    b. a 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.

Part II: Short Answer Questions

1. Define each of the following terms:
    a. oxidation
    b. reduction
    c. Galvanic cell
    d. electrolytic cell
    e. corrosion
2. Balance each of the following chemical equations, using oxidation state change method.
    a. $2Al(s)+3H_2SO_4(aq)\rightarrow Al_2(SO_4)_3(aq)+3H_2(g)$
    b. $Cu+HNO_3\rightarrow Cu(NO_3)_2+NO_2+H_2O$
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. $H_2S+NO_3^{-}\rightarrow S_8+NO$
    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 $2H_2O(l) + 2e^{-} \rightarrow H_2(aq) + 2OH^{-}(aq)$

   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^{0}C for the following reaction? $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ Is this reaction spontaneous at 1000 ^{0}C and 1 atm?

8. Using standard electrode potentials, calculate the standard free-energy change at 25C 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?
    c. S

UNIT 3

INDUSTRIAL CHEMISTRY

Unit outcomes

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

- *list the renewable and non-renewable natural resources and appreciate their importance to the industry as raw materials*
- *describe the relationship between natural resources and industry*
- *list some chemicals and related industries in Ethiopia*
- *list some important chemicals used for the manufacture of valuable products*
- *explain the major steps in the industrial production of ammonia, nitric acid, sulphuric acid, sodium hydroxide, sodium carbonate and aluminum sulphate and di-ammonium phosphate and other Nitrogen fertilizers; and*
- *list some important direct uses of* NH_3, HNO_3 , H_2SO_4 , *and* Na_2CO_3 *and their uses as raw materials in the production of other products*
- *list some important uses of DAP,* $(NH_4)_2\,HPO_4$, *nitrogen fertilizers, insecticides and Herbicides*
- *prepare insecticides from locally available material*
- *describe the uses of the common insecticides and pesticides that are manufactured in chemical industries*
- *discuss the important steps in the production of glass, ceramics, cement, sugar and paper and pulp*
- *describe the important steps in the production of soaps and detergent, and beverage*
- *prepare soap on a small scale from the available resources*
- *describe the tanning process*

- *apply local methods of tanning*
- *use local methods of food preservation*
- *develop inquiry skills along this unit: observing, predicting, classifying, communicating, and inferring.*

Start-up Activity

From your grade 10 lesson, you have learnt about the occurrence and extraction of some important metals and non-metals.

Thus in small groups discuss and present to the class the occurrence and importance of some metals and non-metal that are used as a raw material for the production of desired products.

3.1 Introduction

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

- *define industrial chemistry*
- *list general characteristics of chemical industries*
- *mention the role of industrial chemistry in the society*

Activity 3.1

1. Discuss in groups of three and comment on the following statement "It is very difficult to think of life without the chemical industry."
2. List at least five products that are manufactured by Ethiopian chemical industries. Then, report your answer to your classmates.

The 19th century industrial revolution began the development of chemical industries at a very high rate. Following this, the demand for goods produced through chemical processes increased. Today, chemical industries in both developed and developing countries produce a number of very useful products. This includes synthetic fibers, plastics, rubber fertilizers, dyes, drugs and many other products.

Chemistry and chemical technology are very important for economic growth and development especially for developing countries like Ethiopia. Ethiopia has minerals (metal ores) deposits which are sources of iron, lead, copper, gold, platinum, tantalum and many rare-earth metals. Moreover, rock salt gypsum, coal, and crude oil are found. So, Ethiopia needs industrial revolution to use its mineral deposits to produce various chemicals on a large scale.

So, in this context, what is meant by industrial Chemistry?

Industrial chemistry is a branch of chemistry which applies physical and chemical procedures toward the transformation of natural raw materials and their derivatives in to products that have beneficial to humanity.

Industrial chemistry differs from classical chemistry in that it closes the gap created in concepts between chemistry as it is taught in schools, and chemistry as it is practiced commercially.

Industrial chemistry is the basis of the chemical industry. The chemical industry is an institution involved in producing chemical products such as food, medicine, building materials, plastics, etc. The chemical industry involves the use of chemical processes such as chemical reactions and refining methods to produce a wide variety of materials with desirable properties and quality to satisfy social needs. Most of these products, in turn, can be used by other chemical industries to manufacture other items or can be used directly by consumers.

Generally, chemical industries

- use naturally or artificially available raw materials to produce the desired products.
- involve chemical reactions to transform raw materials into finished and semi-finishe products.
- consume relatively large quantities of energy during the manufacturing process.
- use safe operation methods in their manufacturing processes, and
- test their products during and after manufacture in their quality control laboratories to ensure that the products meet the required specifications.

Exercise 3.1

1. Define "industrial chemistry"?
2. Discuss how chemical industries are considered to be the prominent one when dealing with manufacturing industries.
3. List the characteristics of chemical industries.

3.2 Natural Resources and Industry

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

- ☞ *define natural resources*
- ☞ *list the types of natural resources*
- ☞ *classify chemical industries based on the raw materials they use to manufacture their products*
- ☞ *classify chemical industries based on the type of product they manufactured*
- ☞ *describe the applications of minerals in industry.*

Activity 3.2

Discuss the following questions in groups and present your findings to your classmates.

1. How can animals and plants be replaced once they die?
2. What are fossil fuels?
3. Can fossil fuels be renewed?
4. Explain the importance of natural resources for chemical industries using examples?

3.2.1 Natural Resources (Raw Materials)

Natural resources are the raw materials for the chemical industry which are obtained from the natural environment. The raw materials are obtained from the different components of the natural environment. These are listed below

- **From the atmosphere:** The earth's atmosphere has approximately 5×10^{15} tons of gases. It is composed of different gases namely N_2, O_2, CO_2, Ne, Ar, Kr and Xe. They are important industrial raw materials. Thus, the natural supply of these gases is unlimited.
- **From the hydrosphere:** Ocean water which amounts to about 1.5×10^{21} liters contains about 3.5 percent by mass dissolved material. Seawater is a good source of sodium chloride, magnesium and bromine.
- **From the lithosphere:** The vast majority of elements are obtained from the earth's crust in the form of mineral ores, carbon and hydrocarbons. Coal, natural gas and crude petroleum besides being energy sources are also converted to thousands of chemicals.
- **From the biosphere:** Vegetation and animals contribute raw materials to the so-called agro-based industries. Oils, fats, waxes, resins, sugar, natural fibres and leather are examples of thousands of natural products.

Classification of Natural Resources

Natural resources can be classified as renewable and non-renewable resources.

Renewable resources: The resources that can be replenished through rapid natural cycles are known as renewable resources. These resources are able to increase their abundance through reproduction and utilization of simple substances. Examples of renewable resources are plants, (crops and forests) and animals which are being replaced from time to time because they have the power to reproduce and maintain life cycles. There are also renewable resources without any life cycle. These include wood and wood-products, natural rubber, fibers (e.g.; cotton, jute, animal wool, silk, and synthetic fibers), pulp products, and leather. Furthermore, resources, water, and soil are also classified as renewable resources. Moreover, solar energy is considered a renewable resource as much as solar stocks are inexhaustible on the human scale.

Non-Renewable Resources: The resources that cannot be replenished (regenerated) through natural processes are known as non-renewable resources. These are available in limited amounts and cannot be increased. These resources include fossil fuels (petrol, coal etc.), metals (iron, copper, gold, silver, lead, zinc etc.), minerals and salts (carbonates, phosphates, nitrates etc.). Once a non-renewable resource is consumed, it is gone forever. Thus, a substitute for it is necessary.

Activity 3.3

Although renewable resources can be replenished by natural process they are practically getting depleted. Similarly nonrenewable resources are also over used that they may be exhausted shortly. Think how chemical knowledge can be used to tackle such problems and share your views to the class?

3.2.2 Industry

Industry is a well-organized facility with a high degree of automation and specialization where large-scale manufacturing of goods take place. Nevertheless, it can also include other commercial activities that provide goods and services such as agriculture, transportation, hospitality, and many others.

Manufacturing industry: Manufacturing industry is a compartment of industry or economy which is concerned with the production or making of goods out of raw materials by means of a system of organized labor.

Classification of manufacturing industry

Manufacturing industries use different type of raw materials, skills, and technologies. As a result, different types of products are manufactured.

Chemical Industry: Chemical industry is a facility where industrial chemicals are manufactured. The products result from:

a. Chemical reaction between organic materials, or inorganic materials, or both

b. Extraction, separation, or purification of natural products, with or without the aid of chemical reactions

c. The preparation of specifically valuable materials

Classification of the chemical industry based on raw material used for production

1. Chemical industries use natural raw materials (resources)

   For example, Sugar industries use sugar cane to manufacture sugar.

2. Chemical industries use products from other industries to manufacture their products. For example: Detergent and soap manufacturing industries use preprocessed products like caustic soda, caustic potash and related compounds to manufacture their products.

Classification based on the product type

Examples are:

- Food processing industries,
- Beverages industries
- Textiles industries,
- Wearing apparel industries,
- Leather industries
- Paper and chemical industries etc.

Exercise 3.2

1. List the types of manufacturing industries based on their products.
2. Give examples of renewable and non-renewable natural resources

3.3 Manufacturing of Valuable Products/ Chemicals

At the end of this section, you will be able to

- ☞ *describe the general methods of "manufacturing of valuable products in industries"*
- ☞ *explain the important steps for the production of NH_3 in Haber process*
- ☞ *use Lechaterier's principles to explain how the yield of ammonia can be increased in Haber process*
- ☞ *consult the internet or other reference materials to inspect some important direct uses of H_2SO_4 , HNO_3 and Na_2CO_3*
- ☞ *examine the physical and chemical properties of H_2SO_4 , HNO_3, and Na_2CO_3*
- ☞ *describe the important steps for the production of HNO_3 in Ostwald Process*
- ☞ *list the physical and chemical properties of HNO_3*
- ☞ *explain how the production of H_2SO_4 is considered as the vital to measure the development of a Nation*
- ☞ *draw the schematic diagram which shows the steps followed in the production of H_2SO_4 in contact process*
- ☞ *state the raw material used to manufacture Na_2CO_3*
- ☞ *draw the schematic diagram which shows the steps followed in production of Na_2CO_3 in Solvay process*
- ☞ *discuss the uses of DAP, $(NH_4)_2HPO_4$, Nitrogen fertilizers, herbicides and insecticides in the agriculture sector*
- ☞ *apply indegenious knowledge to produce natural compost*
- ☞ *use local resources to prepare insecticides.*

Manufacturing of some valuable products: Manufacturing of valuable products involve a number of chemical processes. The process is designed to produce a desired product from a variety of starting raw materials using energy through a succession of treatment steps integrated in a rational fashion **(Figure 3.1).** The treatment steps could be either physical or chemical in nature.

Figure 3.1: Basic steps in a manufacturing process.

Valuable products include every industrial product. These products are either directly used or serve as raw materials to synthesize products that are important to solve the society demands in different necessities. Both organic and inorganic chemicals could be used in the manufacturing process.

3.3.1 Ammonia (NH_3)

Activity 3.4

Discuss in group and present your answer to the class.

1. Why ammonia is highly soluble in water?
2. List and describe the conditions that are required to get high yield of ammonia using Le Chatelier's principle?

Properties

Ammonia is lighter than air with a density of 0.769 kg/m³ at STP. Ammonia is commercially and commonly available as an aqueous solution; the most common commercial formulation is 28–30% NH_3. In the aqueous solution ammonia is partially ionized according to the equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

and it is often referred to as ammonium hydroxide. It is a weak base. It is colorless with sharp and intensely irritating gas at room temperature. Its melting point is -77.7 ^{O}C. Its boiling point is -33.35 ^{O}C. Its solubility in water at 25 ^{O}C is 34% (w/w).

Uses

Ammonia is an important compound, essential to man for a variety of diverse uses. It is used as a cleaning agent, antimicrobial agent, a raw material for the production of nitrogen fertilizers, raw material in the manufacturing of explosives such as nitrocellulose and trinitrotoluene (TNT), used in the production of soda ash and in the Ostwald process to get nitric acid etc. Such a diverse applicability has caused large demand for its production.

Preparation

Ammonia is easily made in the laboratory by heating an ammonium salt, such as ammonium chloride NH_4Cl with a strong alkali, such as sodium hydroxide or calcium hydroxide.

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_3(g)$$

The gas may also is made by warming concentrated ammonium hydroxide. However, its diverse applicability has caused large demand for its production. The development of the Haber-Bosch process for ammonia production has made it possible to meet this demand. So, the principal commercial method of production of ammonia is the Haber process, the direct combination of nitrogen and hydrogen under high pressure in the presence of a catalyst.

The Haber process was found by the German chemist, Fritz Haber, in the early 20th century. It involved the practical use of atmospheric hydrogen and nitrogen to produce ammonia. Carl Bosch was tasked with scaling up the process to an industrial production. The efforts of both these men were recognized in the form of Nobel prizes that were awarded to them in 1918 and 1931, respectively. This also led to the process being called the Haber-Bosch process. Presently, about 454 million tons of nitrogen fertilizers are produced using the Haber-Bosch process. They are extensively used to increase crop yields.

Steps Involved in Ammonia Production

Step 1: The primary requirements for the production of ammonia are hydrogen (H_2) and nitrogen (N_2). H_2 was initially obtained by electrolyzing water, thus, splitting the water molecule into its components – hydrogen and oxygen. In recent times, this method has been replaced by the use of methane as a source. Methane is easily acquired from natural gas, and requires very less external energy to produce hydrogen. The other substrate, nitrogen, is obtained by carrying out fractional distillation of air.

Step 2: The hydrogen and nitrogen are then, introduced into a chamber containing iron particles or lined internally with iron, and a pressure of 15 – 25 MPa at a temperature of 300 – 500 °C is applied to the gases. These conditions cause the gases to react and produce ammonia, and the following reaction occurs:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Step 3: The hot mixture of gases is then passed through a condenser. Since ammonia condenses easily as compared to nitrogen and hydrogen, the liquefied ammonia is collected and removed, and the leftover nitrogen and hydrogen gases are re-introduced into the reactor. Thus, pressure is maintained, and there is no loss or wastage of reactants. This recycling of the raw materials allows a 97% conversion of initial reactants into ammonia, which is, then, used to produce a variety of products. The steps are shown in **Figure 3.2.**

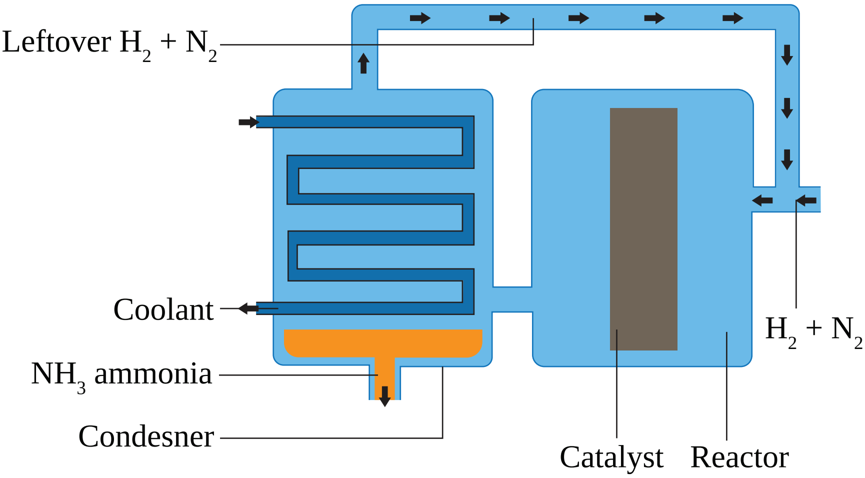


Figure 3.2: production of NH_3 using Haber-Bosch process

Experiment 3.1

Preparation and Testing of Ammonia

Objective:

- to prepare ammonia
- to test its solubility
- to test its alkaline nature

Material Required

Eye protection or eye goggles, stand and clamp, a dried boiling tube with stopper and delivery tube (see diagram below), beaker100 mL, beaker, 250 mL or bigger, Bunsen burner, spatula and test tube to collect ammonia gas.

Chemicals Required

Ammonium chloride, Calcium hydroxide, Calcium oxide, Concentrated hydrochloric acid, red litmus paper, blue litmus paper and Universal indicator paper.

Safety Precautions

Wear eye protection throughout. Ammonia gas is toxic and dangerous for the environment and pungent-smelling and must not be inhaled. The experiments must only be carried out in a fume cupboard or in a well-ventilated laboratory.

Procedure

1. In a 100 ml beaker, mix 2 spatulas of the ammonium chloride with 2 spatulas of the calcium hydroxide together. The two solids begin to react immediately on mixing.
2. Hold a piece of each color of litmus paper over the mixture and observe the color change. Test also with a piece of universal indicator paper.
3. Transfer the mixture of ammonium chloride and calcium hydroxide into a boiling tube and set up the apparatus as shown in the diagram.

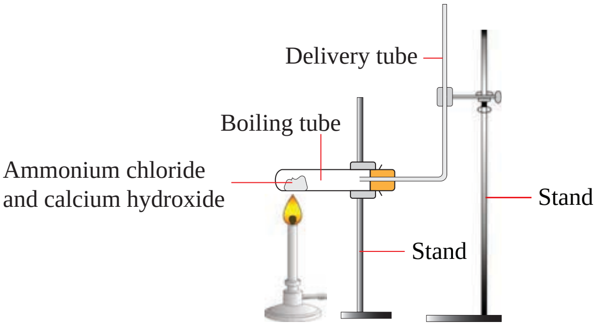


Figure 3.3: The setup required for producing ammonia gas

4. Optional: put the lump of calcium oxide into the boiling tube containing the ammonium chloride/calcium hydroxide mixture. The calcium oxide will absorb the water produced in the reaction and ensure that the ammonia gas is dry.
5. Gently warm the reaction mixture.
6. Collect a test tube which contains a few drops of concentrated hydrochloric acid. Remove the stopper from this test tube and hold the open end near the end of the ammonia gas delivery tube. Observe what happens. Replace the stopper on the test tube of hydrochloric acid and return the test tube to its original place.
7. Two-thirds fill a large beaker with water. This is needed for step 10.
8. Continue to gently warm the reaction mixture. Hold one of the dry boiling tubes in position as shown in the diagram below. Notice that the ammonia is collected with the boiling tube upside down. This is because ammonia is less dense than air.

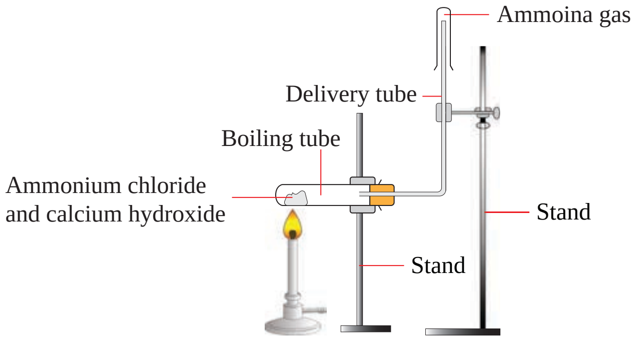


Figure 3.4: The equipment setup required to collect the ammonia gas.

9. Test around the open end of the collecting boiling tube with universal Indicator paper to check that the collecting tube is full of ammonia.
10. Hold the tube of ammonia upside down then quickly put it, mouth still downwards, into water in a beaker. The ammonia dissolves in the water and the level of the water should rise up inside the test tube. If you want to try this a second time, use a fresh dry boiling tube.

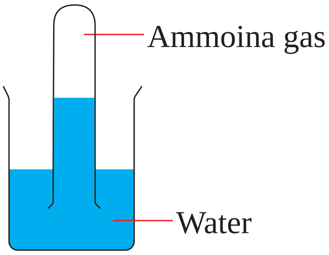


Figure 3.5: A setup showing ammonia gas dissolved in water

Observation and Analysis

A. Why a dried boiling tube is required?

B. What is the purpose of putting the lump of calcium oxide into the boiling tube containing the ammonium chloride/calcium hydroxide mixture?

C. What do you think is the white fume (‘smoke’) that is produced when the ammonia gas is collected into the HCl?

D. What is the nature of ammonia? Is it alkaline or acidic gas? If it is alkaline, please write the reaction equation that shows its alkalinity?

Experiment 3.2

Ammonia Fountain Demonstration

Objective: To make a miniature chemical fountain using only soluble ammonia and atmospheric pressure

Materials Required

Water, 2-L round bottomed flask, 2-L beaker, 2-hole stopper syringe, Glass tube connected with rubber tube, stand with ring and clamp, test tube, tong, bunsen burner and heat proof mat

Chemicals Required

NH_4Cl and NaOH or NH_4OH (ammonia solution) or dry NH_3 gas, water and Phenolphthalein

Procedure:

(I) Preparing dry ammonia and filling the flask

a. Set up the flasks as shown in **Figures 3.6a** and **3.6b**

b. Add 50 ml of concentrated ammonia solution to a 100 mL test tube

c. place the test tube in a test tube holder and fit it into the mouth of conical flask that is inverted upside down and supported by stand

d. Heat the test tube with Bunsen burner while holding it with a test tube holder so that ammonia gas produced is collected by the upward displacement of air. Alternatively, use a 1:1 mixture of NH_4Cl: NaOH in the conical flask.

(II) Demonstration (Figure 3.6b)

e. Fill the beaker with water. To this, add 1 mL of phenolphthalein indicator solution.

f. Position a clamp so that the flask will be held with the tube well below the level of the water. Bear in mind that the flask will be heavy when filled with water so take care that it will not overbalance

g. fill the syringe with water, dry the nozzle and carefully fit it into the second hole of the two-holed stopper (see diagram).

h. Remove the plain stopper from the inverted gas-filled flask and quickly fit the stopper which holds the jet and syringe. Be careful not to prematurely inject water from the syringe.

i. Use the syringe to squirt a few mL of water into the flask.

j. As the gas dissolves, a partial vacuum forms inside the flask and the external air pressure will force water up the tube and through the jet - forming a fountain. The ammonia gas dissolves in the water emerging from the jet and the indicator changes colour.

k. The fountain continues for some minutes, depending on the size of the flask and the width of the jet. When the fountain finishes, a bubble of gas remains.

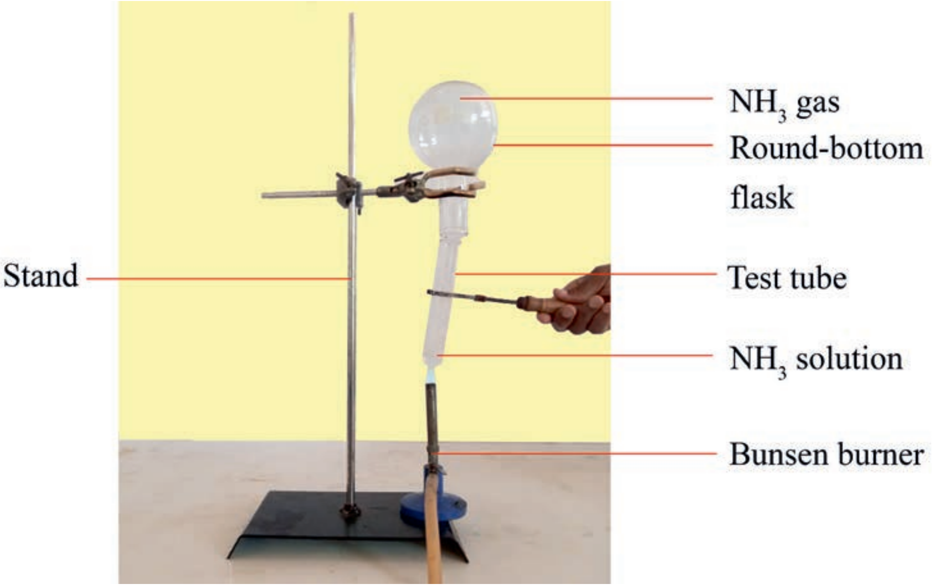


Figure 3.6a: Generation of ammonia

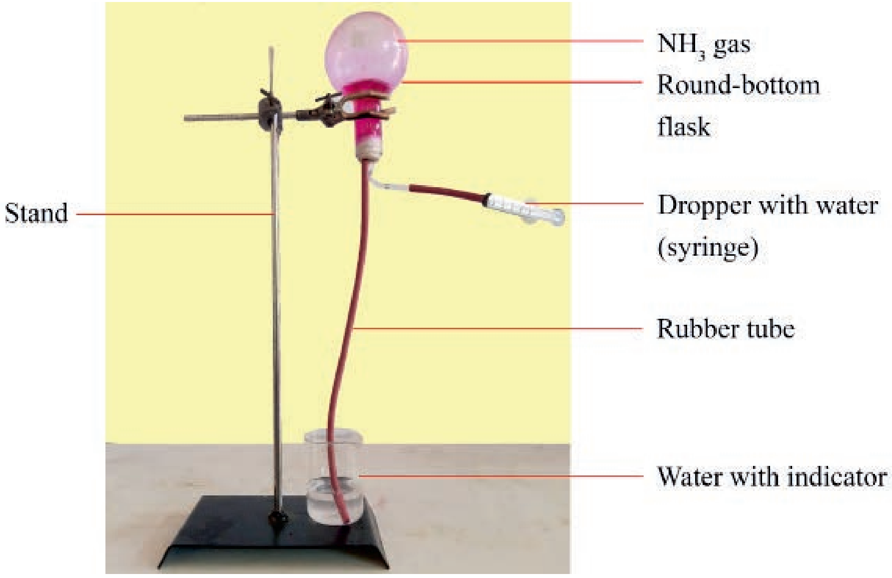


Figure 3.6b: Set-up of ammonia fountain demonstration Experiment

Observation and Analysis

A. What happens to the colour of the soultion after addition of phenoolphtalin? What does its change shows?

B. As ammonia (NH_3) getting dissolved in the water what will happen?

C. Why does fountain formed in flask?

Exercise 3.3

1. Write a balanced chemical equation for the formation of ammonia by the Haber process.
2. What is the purpose of adding finely divided iron in the Haber process?
3. Why are high temperature conditions required in production of ammonia in the Haber process?
4. Predict the product formed and write the reaction equation when you heat an ammonium salt, such as ammonium chloride NH_4Cl, with a strong alkali, such as sodium hydroxide or calcium hydroxide, in a laboratory.

3.3.2 Nitric Acid

Activity 3.5

Discuss in a group and present your answer to the class.

1. Why is nitric acid considered a highly corrosive mineral acid?
2. Why is nitric acid used to manufacture explosives such as trinitrotoluene (TNT) and nitroglycerine?

Properties

Pure nitric acid has a density of 1.51 g/cm^3. It is a colorless liquid, with a highly pungent odor, in appearance similar to water, but on exposure to light, it turns brown because of slight decomposition into NO_2 (brown) and O_2.

$$4HNO_3(l) \rightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)\text{brown}$$

Nitric acid is a strong acid and dissociates completely to give H_3O^+ and NO_3^- in a dilute aqueous solution. Nitric acid forms a large number of salts, called nitrates, which are typically very soluble in water. Nitric Acid is a highly corrosive mineral acid. Nitric acid and its salts are strong oxidizing agents, particularly when it is hot and concentrated. This fact explains the violence of the reactions with metals, which result in the release of hydrogen. It reacts readily with numerous substances and produces heat when dissolved in water. A significant proportion of reactions involving it are even explosive.

Concentrated nitric acid is highly hazardous to health. Upon contact with the skin, it causes severe burns and even necrosis.

Uses

Neutralization of nitric acid with ammonia results in ammonium nitrate – the most important component of mineral fertilizers used worldwide. In addition, HNO_3 can be used for soil acidification in horticulture. In the chemical industry, nitric acid is primarily a precursor to organic nitrogen compounds, such as nitrobenzenes. When combined with aromatic compounds, it yields substances used to make explosives such as TNT and nitroglycerine.

Another important application is rocket fuel. For this purpose, a mixture of HNO_3, dinitrogen tetroxide and hydrogen peroxide, also known as red fuming nitric acid, is prepared. Nitric acid's potential for plastic production is also noteworthy. Other less popular uses of nitric acid include:

- production of organic dyes and lacquers;
- pharmaceutical industry;
- production of fungicides;
- cleaning and etching of metal surfaces;
- refining of precious metals for the jewellery industry (in preparation of aquaregia);
- the artificial ageing of wood to obtain the desired shade;
- production of household cleaning products;
- detection of traces of metals in laboratory test substances.

Preparation

Nitric acid can be obtained by reacting nitrogen dioxide with water. Under laboratory conditions, an alternative production method is the reaction of potassium nitrate with sulphuric acid to produce pure nitric acid.

$$2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$$

(Salt of more volatile acid + less volatile acid → displaces more volatile acid). There is a basic principle that a more volatile acid can be displaced from its salt by a less volatile acid.

For commercial purposes, the basic production method is the so-called Ostwald process. This is the catalytic oxidation of ammonia to nitric oxide, which, using special absorption towers, yields concentrated HNO_3 acid. For purchase, a concentration of 65–68% is most desirable.

Ostwald processes: The principle or mechanism behind the Ostwald process is "the conversion of ammonia to nitric acid simply occurs as a result of oxidation. This particular oxidation reaction gives us the corresponding nitric oxide. Further, when the nitric oxide is oxidized nitrous gases are formed, and those gases can trap water molecules. As a result, we obtain nitric acid. Catalytic oxidation involving O_2 is used where ammonia will give rise to the product."

Production of Nitric Acid

Nitric acid is produced industrially from ammonia by the three-step Ostwald process:

Step 1: Ammonia is burned in excess oxygen over a platinum catalyst to form nitric oxide (NO):

$$4NH_3(g) + 5O_2(g) \xrightarrow[5atm,\ Pt]{850\ 0c} 4NO(g) + 6H_2O(g)$$

Step 2: Additional air is added to cool the mixture and oxidize NO to NO_2:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Step 3: The NO_2 gas is bubbled into the warm water, where it reacts to give nitric acid and nitric oxide:

$$3NO_2(g) + H_2O(l) \rightarrow 2NHO_3(aq) + NO(g)$$

The nitric oxide (NO) is recycled in Step 2.

The production of nitric acid with the Ostwald process is summarized in **Figure 3.7.**

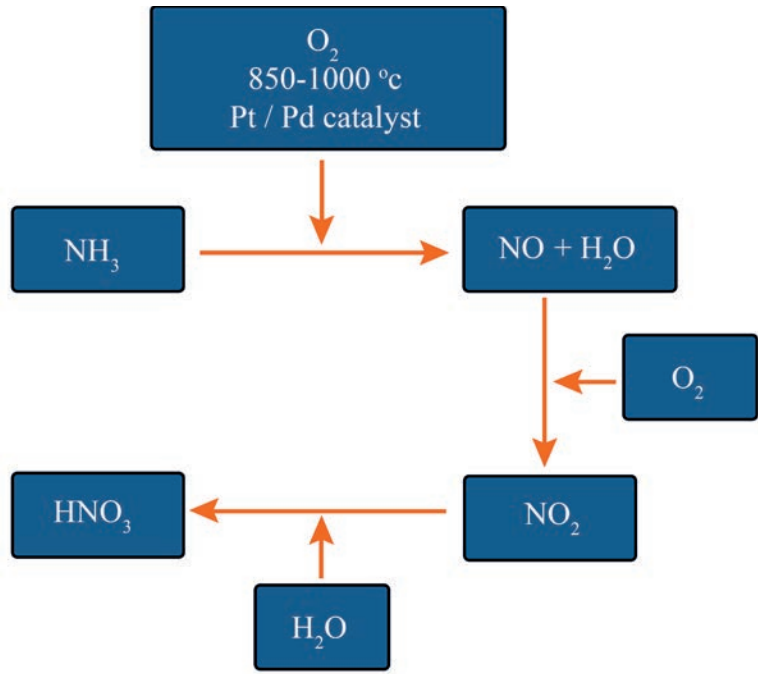


Figure 3.7: Simplified diagrams that show the Nitric acid manufacturing process

Experiment 3.3

Preparation of Nitric Acid in Laboratory

Objective: To prepare nitric acid in laboratory

Materials Required

Round-bottomed borosilicate flask (Preferably thick-walled), delivery tube, glass stopper, glass retort, Tripod stand, Bunsen burner, ice-cold water

Chemicals Required

Potassium Nitrate and concentrated sulphuric acid

Safety Precautions

Concentrated nitric acid is corrosive and oxidizing - wear goggles or face shield. The use of nitrile gloves is recommended.

Procedure

1. Place a 50 gm of potassium nitrate (KNO_3) and 25ml of concentrated sulphuric acid (H_2SO_4) in a round bottom flask.
2. Heat the reactants to about 200 °C taking care that the temperature does not cross 200 °C
3. Observe nitric acid's vapors cooled and condensed to a brown liquid in a receiver cooled under cold water. See its collection as shown in the diagram below.

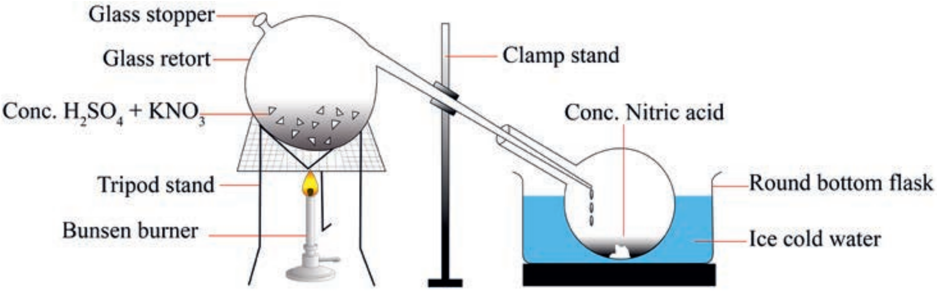


Figure 3.8: Set-up of laboratory preparation of Nitric acid

Observation and Analysis

A. What do you observe in the formation of nitric acid in this experiment?

B. Write a reaction equation that explaining Nitric acid's formation in this experiment.

Experiment 3.4

Properties of Nitric Acid

Objective: To investigate oxidizing property of Nitric acid

Materials Required

round-bottomed borosilicate flask (Preferably thick-walled), clamp stand, delivery tube, test tube, tong, glass wool bowl or trough safety screens (if in an open lab).

Chemicals Required

5 g copper turnings and 40 ml concentrated nitric acid

Safety Precautions

Concentrated nitric acid is corrosive and oxidizing - wear goggles or a face shield. The use of nitrile gloves is recommended.

Procedure

1. Fill the test tube flask with water and add the acid to the round-bottomed flask
2. Clamp the round bottomed flask into position and check that the delivery tube, when in place, is at the bottom of the flask
3. Loosely plug the neck of the conical flask with glass wool, leaving the delivery tube in position, ready to be removed when the copper is added
4. Add the copper and fit the delivery tube.
5. After about 80 seconds, the reaction will slow and observe what will happen
6. The setup for the experiment is represented in the figure below

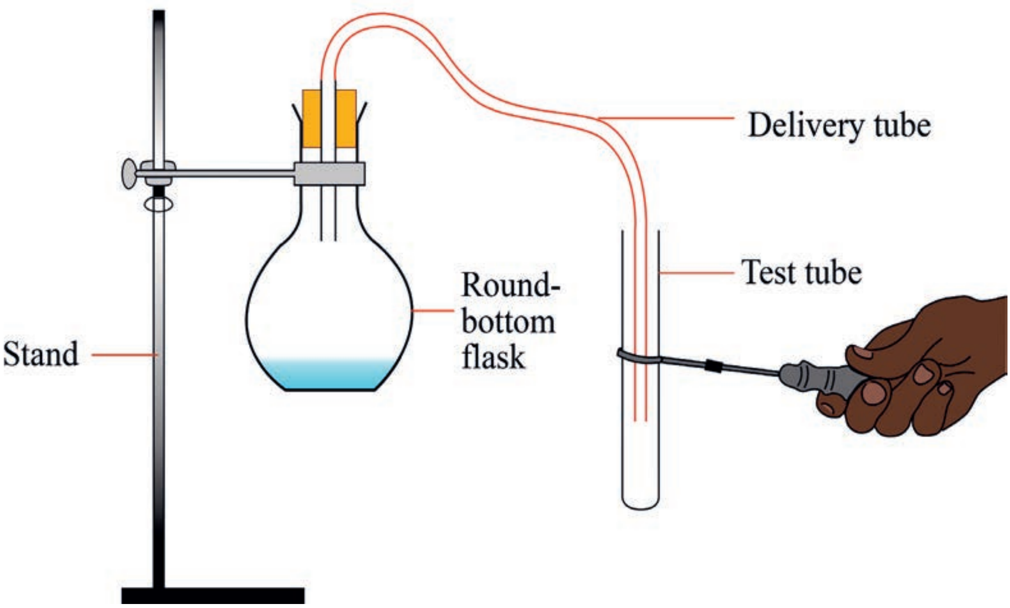


Figure 3.9. Set up for reaction of nitric acid with Copper

Observation and Analysis

A. As the copper is added, what color is observed or developed in the solution?

B. What gas evolved during the reaction? what is the color of this gas?

C. Write the reaction equation, which shows the reaction of copper with concentrated nitric acid.

Exercise 3.4

1. Describe the properties of nitric acid.
2. State the preparation of nitric acid by the Ostwald process.
3. What are the main uses of nitric acid?
4. Predict the product of the reaction between potassium nitrate with sulphuric acid.

3.3.3 Nitrogen-Based Fertilizers

Activity 3.6

Discuss in a group and present your opinion to your classmates.

1. Describe why a large-scale use of synthetic fertilizers can be harmful to the environment
2. What is the purpose of adding nitrogen stabilizers in the soil after the addition of nitrogen-based fertilizers?
3. What is the role of nitrifying bacteria in the reaction of nitrogen-based fertilizers?

The common forms of N-based fertilizer include anhydrous ammonia, urea, urea-ammonium nitrate (UAN) solutions and Diammonium Monohydrogen Phosphate (DAP) with represented by chemical formula $(NH_4)_2HPO_4$.

Anhydrous Ammonia

Anhydrous ammonia (NH_3) is the most basic form of nitrogen fertilizer. Ammonia, a gas at atmospheric pressure, must be compressed into a liquid for transport, storage and application. Consequently, it is applied from a pressurized tank and must be injected into the soil to prevent its escape into the air.

Although almost 80 percent of the earth's atmosphere is comprised of nitrogen, it is in a chemically and biologically unusable form for plants. Using a complex method called the Haber-Bosch process (refer section 3.3.1 for this process), nitrogen is captured from the air, combined with a hydrogen source and converted into a form that can be used by growing plants. Ammonia in this form is also known as ammonia gas or anhydrous ("without water") ammonia.

Application

Anhydrous ammonia is applied by injection 6 to 8 inches below the soil surface to minimize escape of gaseous NH_3 into the air. NH_3 is a very hygroscopic compound and once in the soil, reacts quickly with water and changes to the ammonium (NH_4^+) form. As a positively charged ion, it reacts and binds with negatively charged soil constituents including clay and organic matter. Thus, it is held on the soil exchange complex and is not subject to movement with water.

Soil reactions - Over time and with appropriate soil temperatures that support biological activity, NH_4^+ ions are converted to the nitrate (NO_3^-) form by the action of specific soil bacteria in a process known as nitrification. Nitrification generally occurs at soil temperatures above 50 °F, and increases as temperatures rise above this level. However, some limited activity occurs below 50 °F as well. Ammonium is converted first to nitrite (NO_2^-) by the action of *Nitrosomonas* bacteria, and then to nitrate by *Nitrobacter* and *Nitrosolobus* bacteria:

$$NH_4^+ \xrightarrow{\text{Nitosomonas}} NO_2^-$$

$$NO_2^- \xrightarrow[\text{Nitrosolobus}]{\text{Nitrobacteria } \&} NO_3^-$$

Urea

Urea is a solid fertilizer with high N content (46%) that can be easily applied to many types of crops and turf. Its ease of handling, storage and transport, convenience of application by many types of equipment, and ability to blend with other solid fertilizers has made it the most widely used source of N fertilizer in the world.

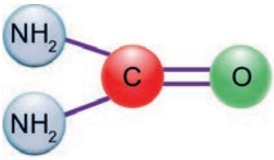
Production

Urea is manufactured by reacting CO_2 with NH_3 in the following two step reactions:

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4 \ (\text{ammonium carbamate})$$

$$NH_2COONH_4 \xrightarrow[\textit{high}\ T]{\textit{high}\ P} (NH_2)_2CO + H_2O \ (urea + water)$$

The urea molecule has 2 amide (NH_2) groups joined by a carbonyl (C=O) functional group.



Urea Molecule

Urea readily dissolves in water, including soil moisture. Thus, it can be "incorporated" into the soil by sufficient rainfall or irrigation.

Soil Reactions - If urea is applied to the soil surface and not incorporated by water or tillage, it is subject to volatilization losses of nitrogen. This occurs as urea undergoes hydrolysis to carbon dioxide and ammonia:

$$(NH_2)_2CO + H_2O \rightarrow CO_2 + 2NH_3$$

Urea-ammonium nitrate (UAN) Solutions

Urea-ammonium nitrate (UAN) solutions are also popular nitrogen fertilizers. These solutions are made by dissolving urea and ammonium nitrate (NH_4NO_3) in water.

Urea-ammonium nitrate (UAN) solutions are mixtures of urea, ammonium nitrate, and water in various proportions i.e. 35%, 45% and 20% respectively. All common UAN solutions are formulated to contain 50% of actual N as amide, (from urea), 25% as ammonium (from ammonium nitrate), and 25% as nitrate (from ammonium nitrate).

Production

Liquid urea-ammonium nitrate (UAN) fertilizer is relatively simple to produce. A heated solution containing dissolved urea is mixed with a heated solution of ammonium nitrate to make a clear liquid fertilizer. Half of the total nitrogen comes from the urea solution and half from the ammonium nitrate solution.

Soil Reactions - The urea portion of UAN solutions reacts just as dry urea does (see the reaction of urea). If applied on the surface, the amide-N in the solution may incur losses due to volatilization when urease hydrolysis releases NH_3. But if UAN is incorporated by tillage or sufficient water, the NH_3, quickly reacts with soil water to form NH_4^+. This ammonium, as well as the ammonium nitrogen derived from ammonium nitrate in the solution, adheres to soil components at the application site and is not subject to loss in the short term. Like N applied as anhydrous ammonia, this nitrogen will eventually be taken up by plants in the ammonium form, or if not, eventually converted to nitrate by soil bacteria.

Diammonium Monohydrogen Phosphate(DAP), $(NH_4)_2HPO_4$

Diammonium monohydrogen phosphate (DAP) is a white crystalline compound.

Production

Diammonium monohydrogen phosphate (DAP) is formed by the reaction between ammonia and phosphoric acid by the following two steps:

Step 1: Anhydrous ammonia reacts with phosphoric acid to form monoammonium dihydrogen phosphate and diammonium monohydrogen phosphate

$$3NH_3(g) + 2H_3PO_4(l) \rightarrow NH_4H_2PO_4(s) + (NH_4)_2HPO_4(s)$$

Step 2: Recycling monoammoniumdihydrogen phosphate for further reaction with anhydrous ammonia yields DAP:

$$NH_4H_2PO_4(s) + NH_3(g) \rightarrow (NH_4)_2HPO_4(s)$$

DAP is used as a fertilizer. It temporarily increases soil acidity, but over the long term, the soil becomes more acidic than before upon nitrification of the ammonium. DAP has the advantage of having both nitrogen and phosphorus, which are essential for plant growth.

DAP can be used as fire retardant. It lowers the combustion temperature of the material, decreases weight-loss rates, and causes an increase in the production of residue or char.

DAP is also used as a yeast nutrient in wine making and beer brewing.

Exercise 3.5

1. Write the chemical reaction that shows the synthesis of urea?
2. Write the reaction which shows soil reactions of urea?
3. Describe the industrial production of DAP. Write the chemical equations too.
4. Describe the properties and major uses of DAP.
5. Calculate the percentage composition of phosphorus and nitrogen in DAP.

3.3.4 Sulphuric Acid

Activity 3.7

Which chemical do you think is produced in the largest volume in the world? And why?

Properties

Anhydrous, 100% sulphuric acid is a colorless, odorless, heavy, oily liquid. It is heavier than water, with 98 gram/mole molar mass. Pure H_2SO_4 melts at 10.5 °C and boils at 338 °C. It is soluble in all ratios with water. This chemical is highly corrosive, reactive and soluble in water. The sulphuric acid can be diluted by water to get acids in various strengths for different purposes. During the mixing process, sulphuric acid should be added to water, not the other way around. Since the dissolution of sulfuric acid in water is very exothermic i.e. a large amount of heat is released and the solution may even boil. It has a very high oxidizing power and thus, acts as a strong oxidizing and dehydrating agent. It can oxidize both metals as well as non-metals. Moreover, it itself reduces to sulphur dioxide.Example

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$$

$$2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O$$

33.5 % sulphuric acid commonly called battery acid while 62.18 sulphuric acid is known as chamber acid used for production of fertlizers

Uses

Activity 3.8

Discuss in group and present your answer to your classmates.

By referring different sources such as internet and reference books list the various uses of sulphuric acid.

Preparation

Sulphuric acid is manufactured industrially by the contact Process which involves the following four major steps:

Step 1: Burning sulphur in air (preparation of sulphur dioxide):

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Step 2: Converting SO_2 to SO_3 (Oxidation of sulphur dioxide to prepare sulphur tri oxide)

$$2SO_2(g) + O_2(g) \underset{400\,^\circ C}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3(g)$$

The conversion of SO_2 to SO_3 is slow, but it is increased by heating the reaction mixture to 400 °C in the presence of V_2O_5 catalyst. Because the SO_2 and O_2 molecules react on contact with the surface of V_2O_5, the process is called the contact process.

Step 3: Passing SO_3 into concentrated H_2SO_4 (addition reaction of sulphur trioxide and sulphuric acid to give oleum):

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

Sulphur trioxide is absorbed into 98 % sulphuric acid to form oleum which is also known as fuming sulphuric acid.

Step 4: Addition of water to oleum i.e. Dilution of oleum to produce concentrated sulphuric acid

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

Oleum is diluted with water to form concentrated sulphuric acid, as indicated in the above reaction. The production of sulfuric acid with the contact process is summarized in **Figure 3.10.**

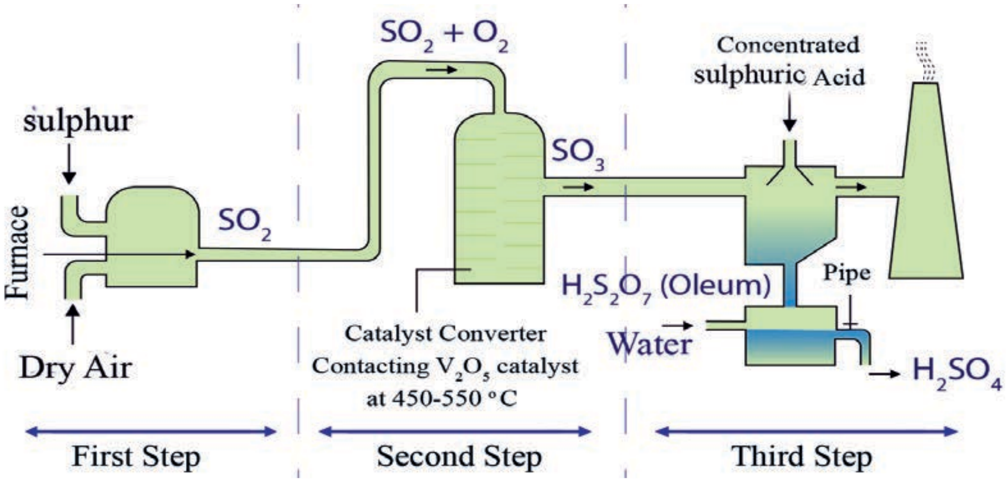


Figure 3.10: Production of sulphuric acid (contact process)

Exercise 3.6

1. Describe the industrial production of H_2SO_4. Write the equations and state the conditions of each step.
2. State the properties and major uses of sulphuric acid.
3. Draw a schematic diagram that involves the four major steps in the production of sulphuric acid along with chemical reactions.
4. When an active metal reacts with concentrated sulfuric acid, the active metal gets oxidized while the sulphuric acid gets reduced to H_2S , S and SO_2. Predict the product formed and write the reaction equation “when eight mole of aluminium react with 15 moles of concentrated sulphuric acid”

Project 3.1

Write a paper, not less than three pages, comparing and contrasting natural fertilizers, that are processed locally, like manures and compost, with commercial fertilizer. Tip- include their impacts, sustainability, accessibility, and composition in your discussion. Submit a report to your teacher.

3.3.5 Some Common Pesticides and Herbicides

Activity 3.9

Make a group of five students and list up to five names and specific uses of natural and commercial pesticides and herbicides that Ethiopian farmers use to treat insect, pests and weeds. Share your discussions with the rest of the class.

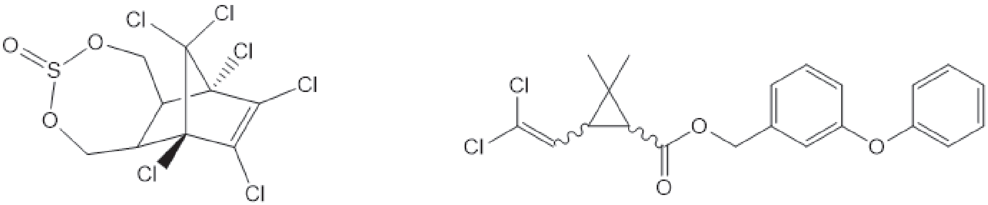
Pesticides

Pesticides are chemicals used to prevent or control pests, diseases, weeds and other plant pathogens. It decreases yield losses, and maintain high product quality. Chemical pesticides can be classified according to their chemical composition. This method allows the uniform and scientific grouping of pesticides to establish a correlation between structure, activity, toxicity and degradation mechanisms, among other characteristics. Table 3.1, shows the most important pesticides and their general characteristics, and **Figure 3.11** show examples of some chemical structures of pesticides.

Table 3.1: General characteristics of some pesticides

Pesticides	Characteristics	Main composition
Organochlorines	• Soluble in lipids • They accumulate in the fatty tissue of animals and transferred through the food chain • toxic to a variety of animals • long-term persistence	Composed of Carbon, Hydrogen, Chlorine, and Oxygen atoms. They are nonpolar and lipophilic

Pesticides	Characteristics	Main composition
Organophosphates	• Soluble in organic solvents but also in water • They infiltrate reaching groundwater, less persistent than chlorinated hydrocarbons • some affect the central nervous system • They are absorbed by plants and then transferred to leaves and stems which are the supply of leaf-eating insects or feed on wise.	Possess central phosphorus atom in the molecule. In relation whit organ chlorines, these compounds are more stable and less toxic in the environment. The organophosphate pesticides can be aliphatic, cyclic and heterocyclic.
Carbamates	• Carbamate acid derivatives • kill a limited spectrum of insects • highly toxic to vertebrates • Relatively low persistence	Chemical structure based on a plant alkaloid Physostigma venenosum
Pyrethroids	• Affect the nervous system but less than compared to the other pesticides • the safest in terms of their use • some are used as household insecticides	Compounds similar to the synthetic pyrethrins (alkaloids obtained from petals of Chysanthemun cinerariefolium
Biological	• Only the Bacillus thuringiensis (Bt) and its subspecies are used with some frequency • are applied against forest pests and crops • Particularly against butterflies and also affect other caterpillars	Viruses, microorganisms or their metabolic product



Endosulfan (*6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzadiaxathiepin 3-oxide*)

A)

Permethrin (*3-phenoxybenzyl (1RS)-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate*)

B)

Carbofuran (*2,2-Dimethyl-2,2-dihydrobenzofuranyl-7 N-methylcarbamate*)

C)

Malathion (*Diethyl 2-dimethoxyphosphinothioyl sulfanylbutanedioate*)

D)

Figure 3.11: Examples of chemicals structure of pesticides (A) Organochloride (B) Pyrethroid (C) Carbamate (D) Organophosphate

On the other hand, there are also traditionally produced pesticides by Ethiopian farmers. Traditionally, farmers of different districts produce pesticides from botanical origins and then apply it to fruits, vegetables and other crops. These pesticides are called botanical pesticides. Botanical pesticides are extracted from various plant parts (stems, seeds, roots, leaves and flower heads) of different plant species. Botanical pesticides are hailed for having a broad spectrum of activity, being easy to process and use, having a short residual activity and for not accumulating in the environment or in fatty tissues of warm-blooded animals. The following are some of the common natural pesticides commonly used in some areas of Ethiopia: Neem Leaf, Salt Spray and Onion and Garlic Spray. Let us see the detail of Neem Leaf which is one of traditionally produced pesticides.

Neem Leaf

Neem has long been used for its medicinal and culinary properties. It is also known to be used as a deterrent to pests. This medicinal herb has a bitter taste and strong odour that may keep the bugs away from your plants, but non-toxic to animals, birds, plants and humans. It's best to spray Neem oil on young plants where it is said to be effective for about 22 days. Add some Neem oil to a dash of liquid soap and some warm water and stir slowly. Add it to a spray bottle and use it immediately. This serves as an insect/pest repellant. Even you can cut down and collect the Neem leaf around your environment and put it simply in your home/table as it serves also as pests/insect repellant. **Figure 3.12** shows a Neem leaf that is grown in most gardens.

Figure 3.12: Neem Leaf (Azadirachta indica)

Project 3.2

Please collect information from your parents or concerned body and write a report about one of the common traditionally produced pesticides by Ethiopian farmers other than Neem Leaf. And submit the report to your teacher..

Herbicides (chemical weed killers)

Herbicides also commonly known as weed killers which are substances used to control unwanted plants. Selective herbicides control specific weed species, while leaving the desired crop relatively unharmed. Non-selective herbicides (sometimes called total weed killers in commercial products) since they kill all plant material with which they come into contact. Herbicides have largely replaced mechanical methods of weed control in countries where intensive and highly mechanized agriculture is practiced.

Types of Herbicides

The most important groups of herbicides and the crosponding examples are given in Table 3.2.

Table 3.2 Common groups of herbicides

S.No	Types of herbicide group	Examples of Herbicides
1	Chlorophenoxy acids	2,4-D and 2,4,5-T
2	Triazines	Atrazine, hexazinone, and simazine
3	Organic phosphorus chemicals	Glyphosate
4	Amides	Alachlor and metolachlor
5	Thiocarbamates	Butylate
6	Dinitroanilines	Trifuralin
7	Chloroaliphatics	Dalapon and trichloroacetate
8	Inorganic chemicals	Various arsenicals, cyanates, and chlorates

Exercise 3.7

1. What are insecticides?
2. List and describe the types of pesticides.
3. List the most common groups of herbicides.

3.3.6 Sodium Carbonate

Activity 3.10

Discuss in groups the following questions and present your opinion to the class?

1. What are the raw materials for glass production? How is glass manfuctured?
2. Why does Solvay plant situated near water mass?

Properties

Sodium carbonate (washing soda) is a white crystalline solid powder. It exists as a decahydrate ($Na_2CO_3.10H_2O$) compound. It has a density of 2.54 g/cm3, a purity of > 98 %. It has a high melting point 851°C and a high boiling point 1,600 °C. It has hygroscopic properties in nature. There are two forms of sodium carbonate available, light soda and dense soda. Light soda and Dense soda are both chemically identical compounds, with the only difference being their densities and size. Light soda has a lower density of 0.7 g/ml, while dense soda has about 0.9 g/ml.

Sodium carbonate can be easily dissolved in water to form an aqueous solution with moderate alkalinity and dissolved in acids by liberating CO_2. But it is insoluble in alcohol. Anhydrous Sodium Carbonate is unaffected by heat. It melts without disintegrating. The release of OH^-(aq) ions during hydrolysis makes Sodium Carbonate aqueous solutions somewhat alkaline.

$$Na_2CO_3(s) + 2H_2O\ (l) \rightarrow H_2CO_3(aq) + 2Na^+(aq) + 2OH^-(aq)$$

Its aqueous solution has the property of absorbing carbon dioxide from the air, and produces sodium Hydrogen Carbonate.

$$Na_2CO_3(aq) + H_2O + CO_2(g) \rightarrow 2NaHCO_3(aq)$$

Uses

Sodium carbonate has wide applications in various kinds of fields around the world. One of the most important application of sodium carbonate is for the manufacturing of glass. Based on statistics information, about half of the total production of sodium carbonate is used for the manufacturing of glass. During the production of glass, sodium carbonate acts as a flux in the melting of silica. It is also largely used in production of detergents and soaps. In addition, as a strong chemical base, it is used in the manufacturing of pulp and paper, textiles, drinking water. In addition, it can also be used for tissue digestion, dissolving amphoteric metals and compounds, food preparation as well as acting as a cleaning agent. It is also used in the brick industry.

Production Method (Solvay process)

Sodium carbonate at present is mostly mined from its natural deposits. It also is manufactured synthetically by **Solvay (or ammonia-soda) process**. The natural production of sodium carbonate currently has surpassed its synthetic production.

The Solvay process involves a series of partial reactions. The first step is calcination of calcium carbonate to form lime and CO_2. Lime is converted to calcium hydroxide. The most crucial step of the process involves reacting brine solution with carbon dioxide and ammonia to produce sodium bicarbonate and ammonium chloride. Sodium bicarbonate converts to sodium carbonate. The calcium hydroxide and ammonium chloride react to form calcium chloride as the by-product. The partial reactions are shown below:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2NaCl + 2CO_2 + 2NH_3 + 2H_2O \rightarrow 2NaHCO_3 + 2NH_4Cl$$

$$2NaHCO_3 \rightarrow \mathbf{Na_2CO_3} + H_2O + CO_2$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The overall reaction:

$$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$$

Exercise 3.8

1. List the four major raw materials that are used to manufacture Na_2CO_3 in the Solvay process.
2. What is the main byproduct in manufacturing of Na_2CO_3 in the Solvay Process?
3. Write the chemical equation of the reaction when sodium hydrogen carbonate is heated in the Solvay process.
4. What is the purpose of burning coke in the Solvay process?
5. Write the chemical formula of the following compounds:
   a) Washing soda b) soda ash c) baking soda

3.3.7 Sodium Hydroxide (NaOH)

Activity 3.11

Discuss in groups and present your opinion to the class.

1. During the manufacturing process of NaOH from brine, Cl_2 is produced in the process. What are the uses of this Cl_2?
2. Why do you take care while doing experiments that involves sodium hydroxide?

Properties

Sodium hydroxide (NaOH) is a white, translucent crystalline solid with a melting point of 591 k. It is a stable compound. NaOH is often referred to as caustic soda, due to its corrosive action on many substances: it decomposes proteins at room temperatures and may cause chemical burns to human bodies. It dissolves readily in water and moderately soluble in alcohol; its solution has bitter and has a soapy feeling". It is strongly alkaline in nature commonly used as a Base.

Manufacturing process

NaOH does not occur in nature. It has been manufactured at large scale for many years from readily obtainable raw materials. It is manufactured from sodium chloride (NaCl) and water (H_2O) in electrolysis process. Its preparation involves various methods like;

1. Castner-Kellner process
2. Nelson Diaphragm cell
3. Loewig's process

Castner-Kellner process

Principle: In the Castner-Kellner method, electrolysis of brine solution is performed in order to obtain sodium hydroxide.

Castner-Kellner cell: It is a steel tank that is rectangular. Ebonite is lined inside the tank. Titanium acts as an anode and a layer of mercury at the bottom of the tank acts as the cathode. Ionization of brine solution occurs according to the following reaction:

$$2NaCl \rightarrow 2Na^{+} + 2Cl^{-}$$

When the brine solution comes in contact with electric current, ionization takes place. As a result positive and the negative ions move towards the electrodes. Sodium ions get deposited at the mercury cathode forming a sodium amalgam. Chlorine ions move towards the anode and exit the cell from the top.

Reaction at the anode: $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$

Reaction at the cathode: $2Na^{+} + 2e^{-} \rightarrow 2Na$

NaOH

The amalgam formed is then transferred to another chamber called denuder. In the denuder, it is treated with water to obtain a sodium hydroxide solution. On evaporation of the solution, solid sodium hydroxide is formed. This is a very efficient process in order to obtain pure caustic soda.

Mercury is toxic so care must be taken to prevent mercury losses.

Safety

- Due to its strong corrosive qualities, exposure to sodium hydroxide in its solid or solution form can cause skin and eye irritation
- Pure NaOH has a high affinity for water and may form hydrates depending on the concentration. Since some hydrates have melting points greater than 0 °C, insulation or heating during storage.

Uses

It is widely used in numerous industrial processes such as in pulp and paper manufacturing, alumina extraction from bauxite in aluminum production, as well as in the textiles industry and drinking water production. NaOH is also an important compound in the manufacture of soaps and detergents (i.e. a cleansing agent and in the manufacturing of washing soda), in waste gases scrubbing, saponification and etherification and esterification reactions; as well as in basic catalysis.

Exercise 3.9

1. List the uses of NaOH in industrial processes or manufacturing of other valuable products
2. What is the role of caustic soda in the industrial cleaning process?
3. What are the health effects of caustic soda?

3.4 Some Manufacturing Industries in Ethiopia

At the end of this section, you will be able to

- *list some manufacturing industries in Ethiopia*
- *outline the important steps in the production of ceramics*
- *mention some uses of ceramics*
- *Write the important steps in the production of cement, ceramics, glass, sugar and ethanol*
- *predict the product of sugar fermentation*
- *prepare ethanol from locally available ingredients*
- *compare and contrast the indigenous and industrial methods of: food preservation and packing, making ethanol, and processing skin and hide.*
- *compare and contrast locally made clay materials with ceramics*
- *outline the important steps in the production of pulp and paper, soaps and detergent and dry detergents*
- *explain how tanning is carried out*
- *mention some uses of skin and hides*
- *present a report to the class after visiting a nearby food factory.*

Activity 3.12

Discuss in groups and present your opinion to the class.

1. Do you know where in Ethiopia most of chemicals /manufacturing industries are located?
2. List as many of the manufacturing chemical industries in Ethiopia, and write the products manufactured by them in tabular form?

The chemical industry in Ethiopia is still at a nascent stage. Therefore, there is a strong demand to develop the chemical industry to meet the requirements of the rapidly growing Ethiopian economy. Currently, imports fulfil domestic demand for chemicals/manufacturing products. According to ADDISBIZ.com news of the year 2022, more than 2228 manufacturing industries are available in the country.

In this subsection emphasis is given to the production of final products like glass, cement, ceramics, sugar, alcoholic beverages, food packing and preservation, soaps and dry detergent, tanning and paper.

3.4.1 Glass Manufacturing

Activity 3.13

Discuss the following questions in groups and present your answer to the class.

1. What is glass?
2. List the types of glasses with their corresponding main functions.
3. Is glass manufactured in Ethiopia?

Glass is an amorphous or non-crystalline solid material. It is inexpensive to make, easy to shape when it's molten, reasonably resistant to heat when it's set, chemically inert (glass jar doesn't react with the things inside it). It can be recycled any number of time. The main component of glass is silica.

Quartz glass is made by melting pure silica, SiO_2, at a temperature of about 2300°C and pouring the molten viscous liquid into moulds. It is of high strength, low thermal expansion and highly transparent.

Soda-lime glass is ordinary glass. It is a mixture of sodium silicate and calcium silicate. It is made by heating a mixture of silica sand, sodium carbonate or sodium sulphate and limestone. The reactions that take place in forming soda-lime glass are the following:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

Soda-lime glass accounts for about 90% of manufactured glass. This type of glass is widely used for window panes, bottles, dishes etc.

Borosilicate glass is commonly known as Pyrex. It is manufactured using boron (III) oxide, B_2O_3, instead of limestone or calcium oxide. This glass has high resistance to chemical corrosion and temperature changes and is widely used to make ovenware and laboratory equipment such as flasks, beakers, and test tubes.

Project 3.3

Have you ever wondered how glass retains different colors? Consult books in your library and make list of the compounds added to impart color to the glass. Submit your findings to your teacher?

Steps in glass production

i) **Batch preparation:** refers to the preparation of the raw materials according to the appropriate combinations. The raw materials are mixed in a proportion of 60% sand, 21% sodium carbonate and 19% limestone.

ii) **Glass melting:** The raw materials and recycled glass (according to their colour) are fed into a glass-melting furnace. The materials are then heated to a temperature of about 1600°C to form a molten viscous liquid. Why glasses are separated according to the colour?

The furnace operates continuously, producing glass 24 hours a day. Substances that give the glass different colours or improved chemical and physical properties such as transparency, thermal and chemical stability and mechanical strength are added during this process.

iii) **Glass forming:** This is the stage in which the melted glass is made into a required shape.

iv) **Annealing:** This is a process that involves the removal of internal stresses by reheating the glass followed by a controlled slow-cooling cycle during which the stresses are relieved.

v) **Inspection:** It involves testing of the glass product to check whether it fulfills desired quality requirements or not.

vi) **Packing and dispatching** is the final stage before distribution

Exercise 3.10

1. Predict the type of glass produced if potassium carbonate is used instead of sodium carbonate? What would be its properties?
2. What type of color will impact by the iron compounds which is often contained as impurities in the sand used in manufacturing of ordinary glass?
3. To produce glass industrially, two types of furnaces are used, what are the two types of furnaces, and what type of glass is produced in each type?

3.4.2 Manufacturing of Ceramics

Activity 3.14

Form a group of three to discuss the questions below and share your reflection's to the class

1. Discuss the traditional pottery industry in Ethiopia and present your answer to the class?
2. List the similarities and differences between pottery and Ceramics.
3. Prepare a list of ceramics products used in daily life.

Ceramic is an inorganic, non-metallic solid prepared by the action of heat and subsequent cooling. Traditional ceramics, such as porcelain, tiles, and pottery are formed from minerals such as clay, talc and feldspar. Most industrial ceramics, however, are formed from extremely pure powders of specialty chemicals, such as silicon carbide, alumina, barium titanate, and titanium carbide.

The minerals used to make ceramics are dug out of the earth and are then crushed and ground into a fine powder. Manufacturers often purify this powder by mixing it in a solution and allowing a chemical precipitate (a uniform solid that forms within a solution) to form. The precipitate is then separated from the solution. The powder is heated to drive off impurities including water.

The steps of manufacturing ceramics include:

A. **Moulding:** After purification, small amounts of wax are often added to bind the ceramic powder and make it more workable. Plastics may also be added to the powder to give the desired pliability and softness. The powder can be shaped into different objects by various moulding processes.

B. **Densification:** The process of densification uses intense heat to condense a ceramic object into a strong, dense product. After being moulded, the ceramic object is heated in an electric furnace to temperatures between 1000 °C and 1700 °C. As the ceramic heats, the powder particles coalesce, much as water droplets join at room temperature. As the ceramic particles merge, the object becomes increasingly dense, shrinking by up to 20 percent of its original size.

The goal of this heating process is to maximize the strength of ceramic by obtaining an internal structure that is compact and extremely dense.

In general, most ceramics are hard and wear-resistant, brittle, refractory, thermal and electrical insulators, non-magnetic, oxidation-resistant, and chemically stable. Due to the wide range of properties of ceramic materials, are used for a multitude of applications.

- **Well-known uses of ceramics: -** they are commonly found in art sculptures, dishes, platters, and other kitchenware, kitchen tiles and bath room structures.
- **Lesser-known uses for ceramics:** - they are used as electrical insulators, computer parts, tools, dental replacements, engine parts, and tiles on space shuttles and to replace bones such as the bones in hips, knees, and shoulders.
- **Future uses of ceramics: -** In the future, ceramics might be used to remove impurities from the drinking water and to replace diseased heart valves.

Do you know a ceramic industry in Ethiopia?

Figure 3.13 shows some photos of ceramics and pottery products in Ethiopia.

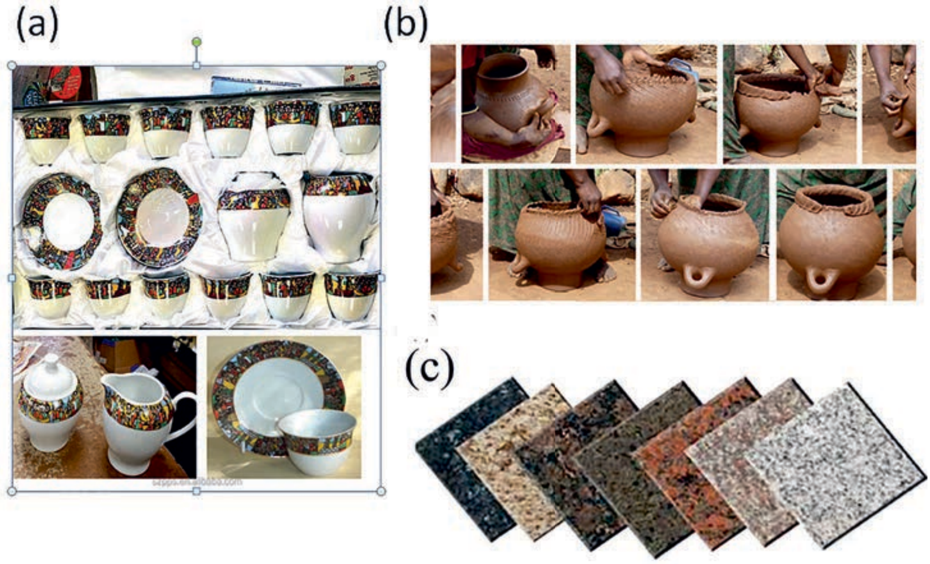


Figure 3.13: Some ceramics and pottery products in Ethiopia (a and c) Ceramic (b) Pottery

3.4.3 Cement

Activity 3.15

Discuss in groups and present your answer to the class:

1. Is there any cement factory in Ethiopia? If there, where are they located?
2. Why Cement manufacturing plants are preferably located close to the sources of the raw material?
3. Why most cement factories are located in rural areas of Ethiopia?

Cement production has been increasing because of the opening of new cement companies and also the upgrade of the old ones.

Availability of cement raw materials in Ethiopia

The raw materials for the production of cement are limestone, clay, silica sand, gypsum, calcium silicate, calcium aluminate, iron (III) oxide, magnesium oxide and pumice. Limestone is the major ingredient for the production of cement. It is abundantly available in Africa. Ethiopia has huge amounts of reserve raw materials.

Manufacturing Process

Cement is made by heating limestone (chalk), alumina (Al_2O_3) and silica-bearing materials such as clay to 1450 °C in a kiln. This process is known as calcination. Calcination results a hard substance called clinker. The clinker is then ground with a small amount of gypsum into a powder. The resulting cement is known as Ordinary Portland cement (OPC).

When gypsum is included in the process, cement known as Portland cement is produced. Portland cement was first discovered in England. On setting, it hardens to a stone-like mass and was compared to the famous Portland Rock of England.

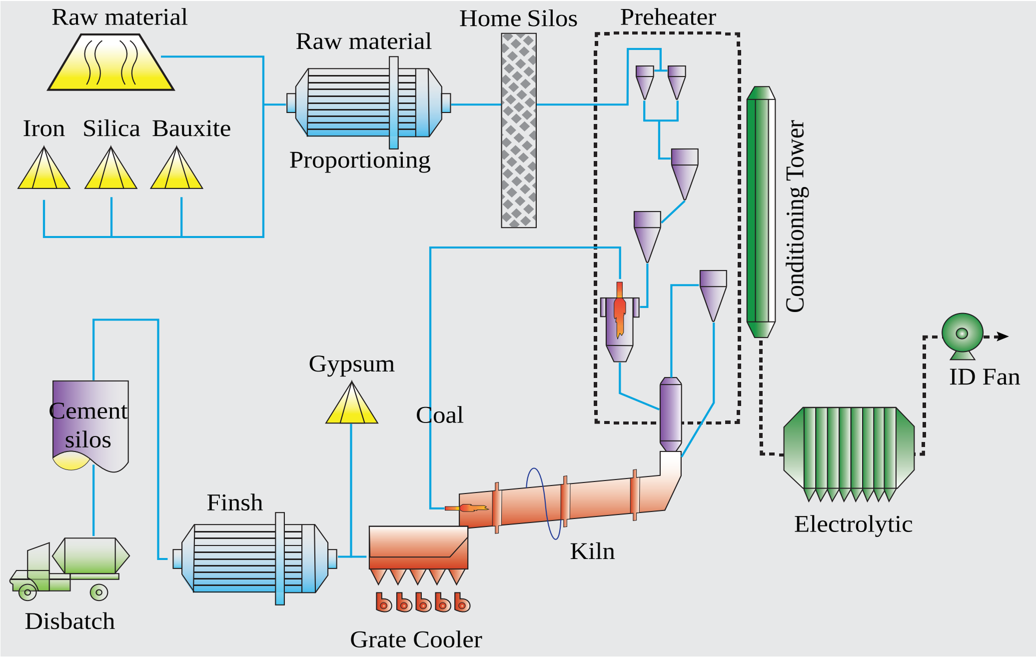


Figure 3.14: Cement manufacturing process.

Upper Part of the Kiln

$$Raw\,Material \xrightarrow{\blacktriangle} Complete\,elimination\,of\;moisture$$

Middle Part of the Kiln

Limestone decomposes to calcium oxide

$$CaCO_3(s) \xrightarrow{\blacktriangle} CaO(s) + CO(g)$$

Lower End of the Kiln

In this part, the temperature reaches about 1600 °C; the partly fused and sintered mixture undergoes a series of chemical reactions to form calcium aluminates and silicates.

$$2CaO + 2SiO_2 \rightarrow 2CaO.SiO_2\,(di - calcium\,silicate)$$

$$3CaO + 3SiO_2 \rightarrow 3CaO.SiO_2\;(tri - calcium\,silicate)$$

$$CaO + 3Al_2O_3\;\rightarrow 3CaO.Al_2O_3\,(tri - calcium\,aluminate)$$

$$4CaO\;+\;4Al_2O_3 + 4Fe_2O_3\;\rightarrow\;4CaO.Al_2O_3.Fe_2O_3\,(tetra\,calcium\,aluminate\;ferrate)$$

$$MgO + SiO_2 \rightarrow MgSiO_3\;(Magnesium\,silicate)$$

The resulting mixture of all these silicates and aluminates is called cement clinker. After cooling, it is mixed with 2-3% gypsum (calcium sulphate) and ground to a fine powder. Gypsum slows down the rate of setting of cement, so that the cement hardens adequately.

Table 3.2 The approximate composition of cement

Component	Percentage %
Calcium oxide (CaO)	50-60
Silica (SiO_2)	20-25
Alumina(Al_2O_3)	5-10
Magnesium Oxide (MgO)	2-3
Ferric oxide (Fe_2O_3)	1-2
Sulphur trioxide(SO_3)	1-2

Setting of Cement

When cement mixed with water, the cement first forms a plastic mass that hardens after sometime. This is due to the formation of three-dimensional cross-links between –Si–O–Si– and –Si–O– Al– chains. The first setting occurs within 24 hours, whereas the subsequent hardening requires about two weeks. In the hardening process of cement, the transition from plastic to solid state is called setting.

Project 3.4

Take a 0.5 kg of cement and mix it with correct proportion of sand and water. Mix the component well till a plastic mass is formed. Take this plastic mass and construct a model of any object. Start pouring water on the model starting from the second day onwards. Report the observations to the class 24 hours later and with the same procedure check any changes happened after two weeks.

3.4.4 Sugar Manufacturing

Activity 3.16

Work in pairs and reflect your answers to the whole class

1. List the foods and drinks in which sugar is an ingredient.
2. List the different sources of sugar?

Sugarcane is a perennial herb belonging to the grass family. Native to tropical and subtropical regions of the world, this tropical grass is about 3 meters tall. And it is used commonly as raw material for production of sugar.

Planting: Sugarcane is planted in fields by workers or mechanical planters. Typical cane soil is made from the mixture of silts, clay particles and organic matter. Fertilizers are applied from the time of planting up until the beginning of the ripening period, depending on the region where the crop is planted. Cane seasons last from 8-22 months.

Steps involved in sugar production:

1. Collecting the Harvest: Mature canes are gathered by a combination of manual and mechanical methods. The cane is cut at ground level, the leaves are removed, the top is trimmed off (by cutting off the last mature joint) the canes and transported to a sugar factory.

2. Cleansing and Grinding: The stalks are thoroughly washed and cut at the sugar mill. After the cleaning process, a machine led by a series of rotating knives, shreds the cane into pieces. This is known as “grinding”. During grinding, hot water is sprayed onto the sugarcane to dissolve the remaining hard sugar. The shredded cane is then spread out on a conveyer belt.

3. Juicing: The shredded sugarcane travels on the conveyor belt through a series of heavy-duty rollers which extract juice from the pulp. The pulp that remains, or “bagasse”, is dried and used as a fuel. The raw juice moves on through the mill to be clarified.

4. Clarifying: Carbon dioxide and milk of lime are added to the liquid sugar mixture, which is heated until boiling. The process of clarifying begins at this stage. As the carbon dioxide moves through the liquid, it forms calcium carbonate which attracts non-sugar debris (fats, gums and waxes) from the juice, and pulls them away from the sugar juice. The juice is then pushed through a series of filters to remove any remaining impurities.

5. Evaporation: The clear juice that results from the clarifying process is put under a vacuum where the juice boils at a low temperature and the water in it begins to evaporate. It is heated until it forms into thick, brown syrup.

6. Crystallization: Crystallization is the process of evaporating the water from the sugar syrup. Pulverized sugar is fed into a sterilized vacuum pan. As the liquid evaporates, crystals form. The remaining mixture is a thick mass of large crystals. These crystals are sent to a centrifuge that spins and dries them. The dried product is raw sugar, which is edible.

7. Refinery: Raw sugar is transported to a cane sugar refinery for the removal of molasses, minerals and other non-sugars that contaminate it. This is known as the purification process. Raw sugar is mixed with a solution of sugar and water to loosen the molasses from the outside of the raw sugar crystals, producing a thick matter known as “magma”. Large machines then spin the magma, separating the molasses from the crystals. The crystals are promptly washed, dissolved and filtered to remove impurities. The golden syrup that is produced is then sent through filters, and SO_2 is passed through it to remove the colour and water. The process of removing colour is known as bleaching. What is left is concentrated, clear syrup which is again fed into a vacuum pan for evaporation.

8. Separation and packaging: Once the final evaporation and drying process is done, screens separate the different- sized sugar crystals. Large and small crystals are packaged and labelled as white refined sugar.

Exercise 3.11

1. Write the chemical formula of the common sugar i.e. sucrose.
2. In Ethiopia most sugar industries produced by products in their sugar production process. List the main byproducts.

3.4.5 Paper and Pulp

Activity 3.17

Discuss the following issues in groups of three and present it to your classmates:

1. Wasting paper is like chopping down trees. Comment.
2. Some papers are cheap while others are expensive. What could be the reason?

Do you know what this textbook is made of?

Paper is not a chemical compound which can be expressed by a chemical formula. Paper is a mixture made from rags and wood pulp glued together with some additives, bleached and dried. Wood pulp is a dry fibrous material. The timber resources used to make wood pulp are referred to as pulp wood. Wood pulp is made from soft-wood trees, such as spruce, pine, fir, larch and hemlock, and from hard woods, such as eucalyptus, aspen and birch. Wood is composed of cellulose, lignin, oils and resins. Lignin is used to bind fibres of cellulose together. To provide wood pulp, the cellulose must be separated from the lignin.

Manufacturing of pulp and paper involves the following steps:

1. **Harvesting:** trees involves the cutting down of trees from their growing areas and transporting the timber to the paper and pulp industry.
2. **Preparation:** for pulping is a step in which the bark of the tree is removed and then the wood is chipped and screened to provide uniform sized chips (pieces).
3. **Pulping** is a step used to make wood pulp from the chipped wood pieces. This can be accomplished by either mechanical or chemical means depending on the strength and grade of paper to be manufactured.
   A. **Mechanical pulping:** It utilizes steam, pressure and high temperatures instead of chemicals to tear the fibres. The fibre quality is greatly reduced because mechanical pulping creates short, weak fibres that still contain the lignin that bonds the fibres together. Paper used for newspapers are a typical product of mechanical pulping.

B. **Chemical pulping:** Chemical pulp is produced by combining wood chips and chemicals in large vessels called digesters. Heat and the chemicals break down the lignin which binds the cellulose fibres together without seriously degrading the cellulose fibres. Chemical pulp is manufactured using the Kraft process or the Sulphite Process.

   I. The Kraft Process is the dominant chemical pulping method. It is the most widely used method for making pulp from all types of trees. The process uses aqueous sodium hydroxide and sodium sulphide as a digestion solution. After digestion for about four hours at a temperature of 170 °C, the pulp is separated by filtration. This process uses a basic digestion medium.

   II. The Sulphite Process uses a cooking liquor (digestion) solution of sodium bisulphate or magnesium bisulphate digester at pH of about 3 in a pulp. The action of the hydrogen sulphide ions at 60 °C over 6 to 12 hours dissolves the lignin and separates it from the cellulose. After the process is complete, the pulp is recovered by filtration. The wood pulp achieved from the Sulphite or Kraft processes is washed to remove chemicals and passed through a series of screens to remove foreign materials

4. **Bleaching:** It is the process of removing colouring matter from wood pulp and increasing its brightness. The most common bleaching agents are strong oxidizing agents such as chlorine, chlorine oxide, ozone and hydrogen peroxide.

5. **Making paper from pulp:** After bleaching, the pulp is processed into liquid stock that can be transferred to a paper mill. The suspension is poured onto a continuously moving screen belt and the liquor is allowed to seep away by gravity to produce paper sheet. The continuous sheet then moves through additional rollers that compress the fibres and remove the residual water to produce fine paper.

3.4.6 Tannery

Activity 3.18

Discuss in groups and present your answer to the class.

1. The leather products of Ethiopia are durable and relatively cheaper than the same products imported from outside. Why do people prefer to buy imported products? What can you suggest to change this attitude? Discuss this matter in class in relation to quality and availability of resources.
2. Why are leather products being replaced by synthetic products?
3. Do you know the traditional way of Tanning in Ethiopia? What are the procedures to be followed when it is compared to the modern method?

Tanning is a process of converting raw animal hides and skin to leather, using tannin. Leather is a durable and flexible material created by the tanning of animal hides and skin. Tannin is an acidic chemical that permanently alters the protein structure of a skin so that it can never return to raw hide or skin again.

Leather production involves various preparatory stages, tanning, and crusting:

1. **Preparatory stages** are those in which the hide or skin is prepared for tanning. This stage includes curing, soaking, flesh removal, hair removal, scudding, and deliming.
   a) **Curing:** This process involves salting or drying the hide once it has been removed from the animal. Curing is employed to prevent putrefaction of the protein substance, collagen, from bacterial infection. Curing also removes excess water from the hide and skin. Brine curing is the simplest and fastest method.

   b) **Soaking:** In this process, cured hides are soaked in water for several hours to several days to remove salt, dirt, debris, blood and excess animal fat from the skin.

   c) **Flesh removal:** In this process, animal hides are moved through a machine that strips the flesh from the surface of the hide.

d) **Hair removal:** In this step, the soaked hides and skins are transported to large vats where they are immersed in a mixture of lime and water. This process is called liming. It loosens the hair from the skin and makes hair-removal easier. After 1–10 days soaking, the hair is mechanically removed from the hide by a hair-removing machine.

e) **Scudding:** This is the process in which hair and fat missed by the machines are removed from the hide with a plastic tool or dull knife.

f) **Deliming:** This process involves the removal of lime from the skin or hides in a vat of acid. After this preparatory process, the skin or hide is ready for tanning.

2. **Tanning** is a process that converts the protein of the raw hide or skin into a stable material. There are two main types of tanning:

   a) **Vegetable or natural tanning:** The skin is placed in a solution of tannin. Tannins occur naturally in the barks and leaves of many plants. The primary barks used in modern times are chestnut, oak, tanoak, hemlock, quebracho, mangrove, wattle (acacia) and myrobalan. Naturally tanned hide is flexible and is used for making shoes, luggage and furniture.

   b) **Mineral tanning:** In this process, the skin is placed in solutions of chemicals such as chromium sulphate and other salts of chromium. Chrome tanning is faster than natural (vegetable) tanning and requires only twenty four hours. The leather is greenish-blue in colour derived from the chromium. This process produces stretchable leather that is used for making garments and handbags.

3. **Crusting:** This is the final stage in leather manufacturing and includes dyeing, rolling the leather to make it strong, stretching it in a heat-controlled room and performing a process that involves covering the grain surface with chemical compounds such as wax, oil, glazes etc. to make the leather very attractive.

3.4.7 Food Processing and Preservation

Activity 3. 19

What could be the reason for the rate of spoilage of food is faster in open air in comparison to foods kept inside the refrigerator. Discuss in groups and present your finding to the class.

Food preservation is the process of treating and handling food to stop or greatly reduce spoilage, loss of quality, edibility or nutritive value caused or accelerated by microorganisms. Preservation usually involves preventing the growth of bacteria, fungi and other microorganisms, as well as reducing the oxidation of fats which causes rancidity.

Activity 3.20

Discuss in groups and present it to the class.

1. What are the traditional methods used to preserve food for a long time without spoil at your home?
2. What modern methods of food preserving and processing do we use in Ethiopia?

Modern methods of food preservation are:

A. **Freezing:** This is one of the most commonly used processes, commercially and domestically, for preserving a very wide range of foods such as potatoes, as well as prepared foodstuffs that would not require freezing in their normal state.

B. **Freeze-drying:** Water vapour has easier access through the cell structure of any product compared to water-penetrating the product and evaporating from the surface of the product as in case of other drying methods. The gentle escape of water vapour in the freeze-drying process leaves the product close to its original shape, taste, and colour and there is no loss of aroma or flavour. For example, liquids such as coffee, tea, juices and other extracts, vegetables, segments of fish and meat products. Freeze-drying is a superior preservation method for a variety of food products and food ingredients.

C. **Vacuum-packing:** Stores food in a vacuum environment, usually in an air-tight bag or bottle. The vacuum environment strips bacteria of the oxygen needed for survival, slowing down the rate of spoiling. Vacuum-packing is commonly used for storing nuts to reduce loss of flavour from oxidation.

Inorganic and organic preservatives

Activity 3.21

Discuss in groups about the traditional method of preserving meat and present your answer to the class?

Some inorganic and organic preservatives are available for food preservation. Some examples of inorganic preservatives are sodium chloride (NaCl), nitrate and nitrite salts, sulfites, and sulfur dioxide (SO_2). NaCl lowers water activity and causes plasmolysis by withdrawing water from cells. Nitrites and nitrates are curing agents for meats (hams, bacons, sausages, etc.) to inhibit *Clostridium botulinum* under vacuum packaging conditions. Sulfur dioxide (SO_2), sulfites (SO_3^-), bisulfite (HSO_3^{-2}), and metabisulfites ($S_2O_5^{-2}$) form sulfurous acid in aqueous solutions, which is the antimicrobial agent. Sulfites are widely used in the wine industry to sanitize equipment and reduce competing microorganisms. Wine yeasts are resistant to sulfites. Sulfites are also used in dried fruits and some fruit juices. Sulfites have been used to prevent enzymatic and nonenzymatic browning in some fruits and vegetables (cut potatoes).

A number of organic acids and their salts are used as preservatives. These include lactic acid and lactates, propionic acid and propionates, citric acid, acetic acid, sorbic acid, and sorbates, benzoic acid and benzoates, and methyl and propyl parabens (benzoic acid derivatives).

For example, propionic acid and propionate salts (calcium most common) are active against molds at pH values less than 6. They have limited activity against yeasts and bacteria. They are widely used in baked products and cheeses. Acetic acid is found in vinegar at levels up to 4–5%. It is used in mayonnaise, pickles, and ketchup, primarily as a flavoring agent. Acetic acid is most active against bacteria, but has some yeast and mold activity, though less active than sorbates or propionates.

3.4.8 Manufacturing of Ethanol

Activity 3.22

Discuss the following questions in group and present your answer to your classmates.

1. List the most common local alcohol beverages that are produced in most of Ethiopian homes during a holiday?
2. What does fermentation in the absence of oxygen mean?

Ethanol is one of the constituents of all alcoholic beverages. ‘Tella’, ‘Tej’, beer, wine, ‘Katikalla’, ouzo, gin and whisky contain ethanol. There are a number of methods for preparing ethanol using different materials. Since it is the constituent of all alcoholic beverages it is better to describe its industrial preparation.

Industrial preparation of Ethanol

Ethanol is manufactured industrially by:

1. Fermentation of carbohydrates such as sugar: Fermentation is the slow decomposition of carbohydrates such as sucrose, starch and cellulose in the presence of suitable enzyme that results in the formation of ethanol and carbon dioxide.

$$\underset{\text{Sucrose}}{\mathrm{C_{12}H_{12}O_{11}}} \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{\mathrm{C_6H_{12}O_6}} + \underset{\text{Fructose}}{\mathrm{C_6H_{12}O_6}}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + H_2O \xrightarrow{zymase} \underset{\text{Ethanol}}{2CH_3CH_2OH} + 2CO_2$$

Fermentation can produce an alcoholic beverage whose ethanol content is 12 – 15% only. The alcohol kills the yeast and inhibits its activity when the percentage is higher. To produce beverages of higher ethanol content, distillation of the aqueous solution is required. Most liquor factories in Ethiopia use molasses, a by-product of sugar industries, as a raw material to produce ethanol. In the brewing industry, germinated barley called malt (in Amharic, 'Bikil') is used as the starting material. The whole process taking place in breweries is summarized as follows:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11})} \xrightarrow[\text{Maltase}]{nH_2O} \underset{\text{Glucose}}{2nC_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + nH_2O \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{CH_3CH_2OH} + CO_2$$

2. Catalytic Hydration of Ethene: Most ethanol is manufactured at present by this method. In this process, ethene is treated with steam at 573 K and 60 atm pressures in the presence of phosphoric acid, H_3PO_4, catalyst.

$$\underset{\text{Ethene}}{CH_2 = CH_2(g)} + H_2O(g) \xrightarrow[573\ k/60\ atm]{H_3PO_4} \underset{\text{Ethanol}}{CH_3CH_2OH(g)}$$

Experiment 3.5

Preparation of Ethanol by Fermentation

Objective: To prepare ethanol from sugar.

Materials required: Conical flask, glass rod, distillation flask, condenser, spatula, thermometer, watch glass, Bunsen burner, beaker, stopper and delivery tube.

Chemicals Required: Sugar, ammonium phosphate or ammonium sulphate, yeast, calcium hydroxide.

Procedure:

1. Take 50 mL of distilled water in a conical flask
2. Add 15 g of sugar to it and stir.
3. Add about 1 gram of yeast and a small amount of ammonium phosphate or ammonium sulphate to the solution.
4. Arrange the set-up, as shown below, and let the flask stand for three days at a warm place.

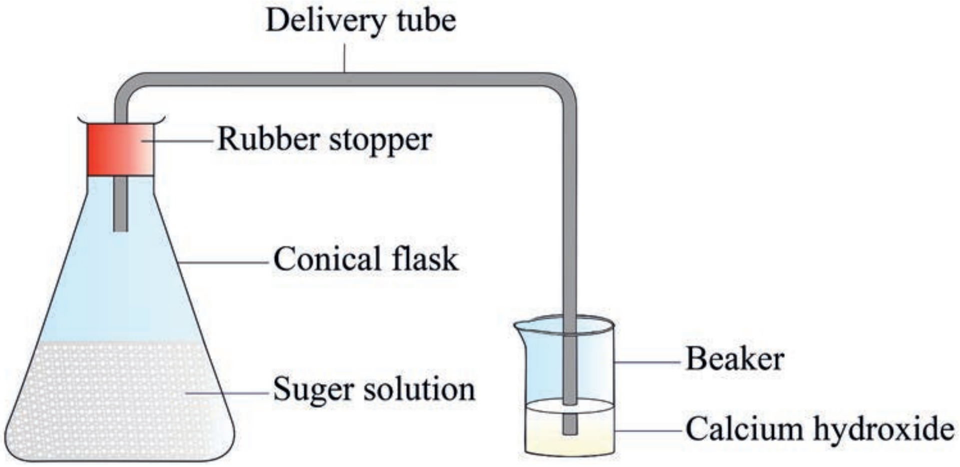


Figure 3.15: The Fermentation of sugar

Observations and analysis:

A. What is the purpose of adding yeast to the solution?
B. Why do we add ammonium phosphate or ammonium sulphate to the sugar solution?
C. What happened to the calcium hydroxide solution at the end of the first or second day? Which gas is produced?

D. What is the smell of the solution in the flask after three days?
E. What happened in the flask containing the sugar solution as it stood for three days?

5. After three days, filter the solution, and arrange the set up as in **Figure 3.16.** Pour 20 mL of the filtrate in to a distilling flask, heat the solution, and collect the liquid in a receiver.

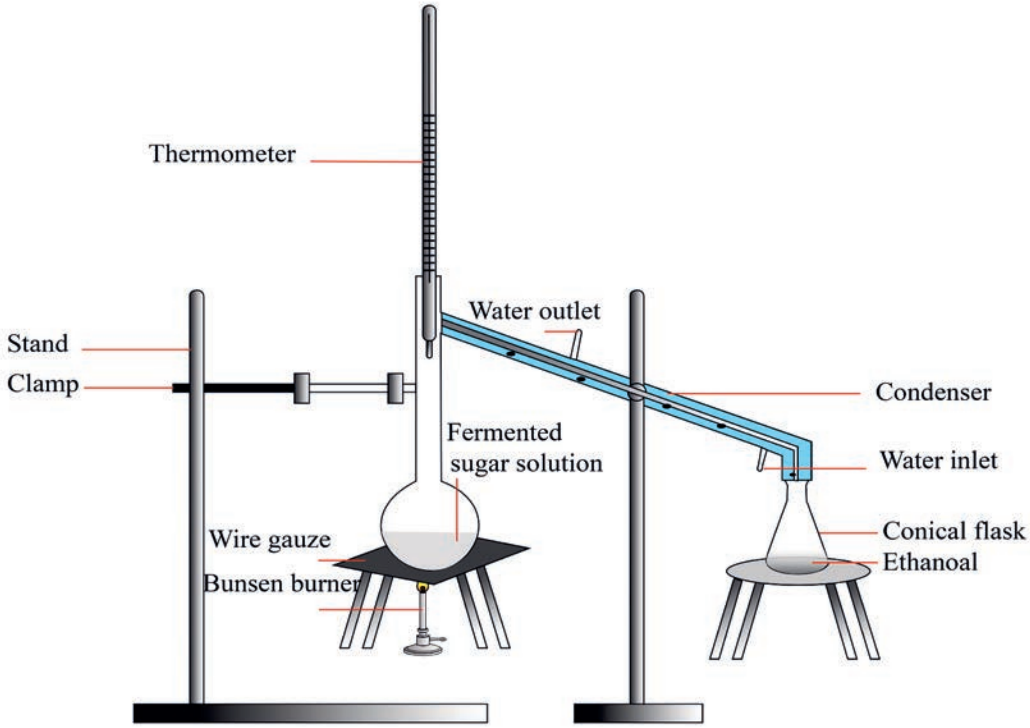


Figure 3.16: Separation of ethanol by distillation

Observations and analysis:

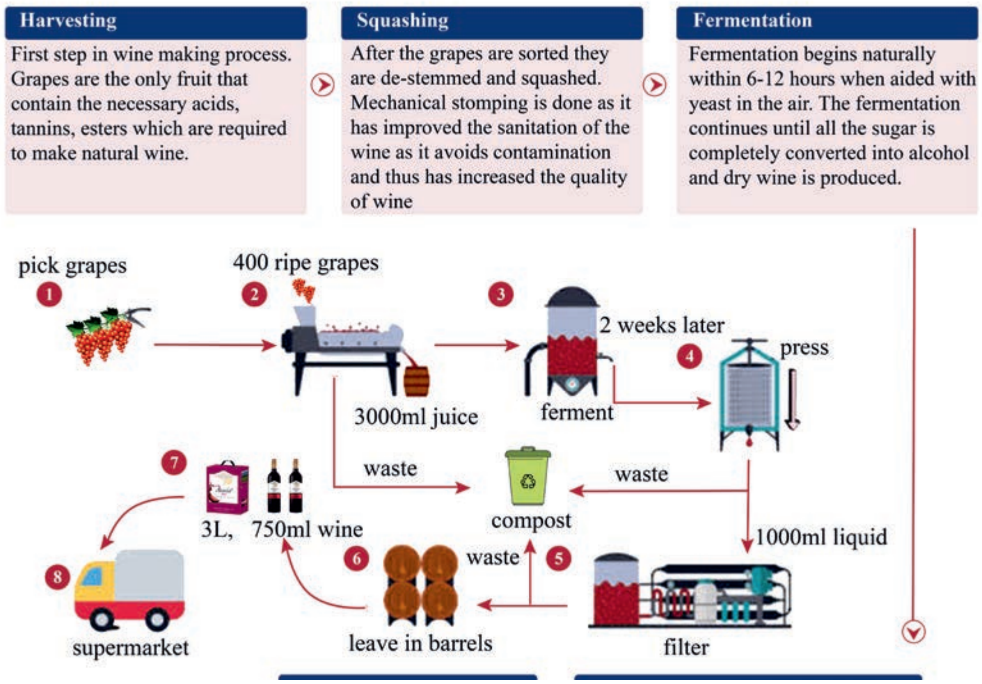
A. Observe the colour and identify the smell of the distillate.
B. Pour a small amount of the distillate on a watch glass, strike a match and bring the flame close to the distillate. Does it catch fire? Write a complete laboratory report on this experiment and submit it to your teacher.

Beer

The raw materials for beer are barley and hops. The first step is to bring the barley to germination whereby starch is converted into a type of sugar called malt sugar. Heat stops this process and the material is now called malt. After drying and grinding the barley, water is added in the mash tubes. After adding hops and yeast the process of fermentation begins. Then it is stored in tanks for a period of time as required by a type of the product. Later it is pasteurized and carbon dioxide is added under pressure and supplied to consumers. Although the type of beers produced in the world are too many, the average beer has alcohol content between 2-6 % by volume.

Wine

Although various other fruits can be used, grapes are the most common raw materials for producing wines. Grapes (or tether fruits) are first crushed and then steamed. The liquid that is derived from the crushing process is called must. It then goes to a fermentation takes place. The must then passes to a settling tank where sediment is allowed to settle, and proceeds from there to a filter. The clear liquid is cooled in a refrigerator tank and it is pasteurized as it passes through a flash pasteurizer. It finally goes to a storage tank where it is kept for months or years. The older a wine is kept, the more mature it becomes and usually is considered to have a higher quality fetching higher price. Most wines have an alcohol content varying from 10-16 per cent by volume. **Figure 3.17**, presented a schematic diagram which shows the major steps of Wine beverages.



Harvesting

First step in wine making process. Grapes are the only fruit that contain the necessary acids, tannins, esters which are required to make natural wine.

Squashing

After the grapes are sorted they are de-stemmed and squashed. Mechanical stomping is done as it has improved the sanitation of the wine as it avoids contamination and thus has increased the quality of wine

Fermentation

Fermentation begins naturally within 6-12 hours when aided with yeast in the air. The fermentation continues until all the sugar is completely converted into alcohol and dry wine is produced.

Figure 3.17:Schematic diagram which shows the major steps of Wine beverages

Liquor: Compared with beer and wine liquor contains a higher percentage of pure alcohol. Normally fermentation stops by itself, if the alcohol concentration riches 15 to 17 percent because yeast cells are not able to stay alive in alcohol of higher concentration.

To get drinks with higher concentration of alcohol the alcohol has to be separated from the solution by distillation. Thus liquors (e.g. cognac) are made by distillation of grape wine; rum is produced from sugar cane, and whisky from rye. Different types of liquors have different alcohol concentration. Most of them however range between 30-45 percent of alcohol by volume.

Local Preparation of Ethanol (Araki)

Araki: Araki is the local Ethiopian alcohol which is prepared almost everywhere with certain local differences. In fact, the differences are in the ingredients and not in the process of making it.

First, the barley is made into “Bikel” in the manner as was mentioned in the case of beer. Then with the help of water, the Bikel is mixed with Gesho (Rhamnuspronoides) powder to make starter “Tinses”. The starter is left to ferment for about four days. (It may vary from place to place depending upon the local’s humidity and temperature). Then the bread is baked from ingredients of Teff, Barley, Wheat, and Sorghum, depending upon their availability and local preferences. The bread is broken down into small pieces, mixed with the already prepared starter and left to stand to ferment for a couple of days (5 to 10 days). After it is fully fermented, a proportional amount of water is added to liquidity the tick dough-like mixture and left for 1 to 2 days for further fermentation. Finally, the liquid mixture is boiled and distilled in the traditional ways as depicted in **Figure 3.18.** The distillate is called “Araki”. While the leftover residue or the un-distilled component is locally called “ Atela” and it is usually used to feed cattle.

Figure 3.18: Preparation of Local Araki

Project 3.5

Do you know the raw materials that are used and the procedure to be followed to prapare “Tella” or Bordie (depending your locality) a local non distilled alcohol in most of Ethiopian homes? Please ask your parents and submit a report to your teacher?

3.4.9 Soap and Detergent

Activity 3.23

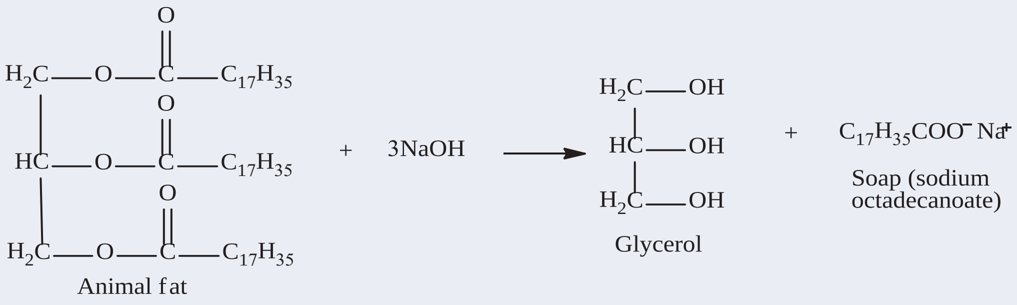
Do you know any local industry in your surrounding that Manufactures soaps? List them and discuss the raw materials that are used to manufacture soaps?

Soaps

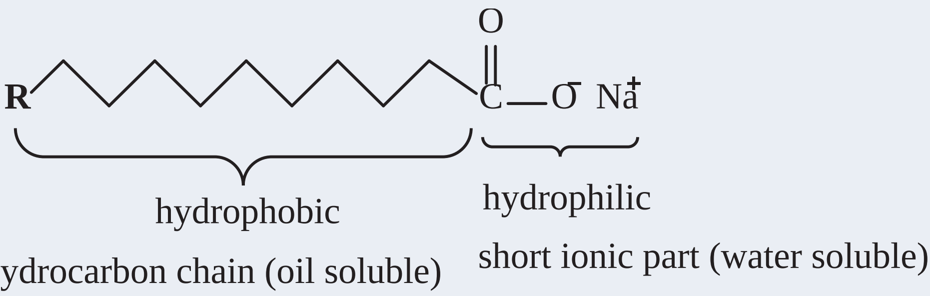
Organic chemicals are used for the synthesis of soaps. For example, animal fat and vegetable oils are used for manufacturing soap. Fats and oils are naturally occurring esters of glycerol and the higher fatty acids. Soaps are substances used to remove dirt. They are also called surfactants or surface-active agents. This is because they reduce the surface tension of water and change the surface properties.

Soaps are either sodium or potassium salts of higher (long-chain) carboxylic acids. Soaps that are sodium salts are called hard soaps and those that are potassium salts are soft soaps. Soaps are prepared by boiling animal fat or vegetable oil with a base. The reaction that produces soap is called saponification.

Example 3.1



The water-soluble group in ordinary soap ($C_{17}H_{35}COONa$) is – COONa and the fat-soluble part is the chain of 17 carbon atoms, $C_{17}H_{35}$. It is represented in the structure below.



In industry, tallow, lard, cotton seed oil, palm oil, castor oil, olive oil, whale oil and the oil of soybeans are used to prepare ordinary soap. When making hared soaps, the lye is usually caustic soda, but when a soft soap is desired, caustic potash (KOH) and potassium carbonate (K_2CO_3) are used and the glycerin is not salted out.

Industrially soap is produced in four basic steps:

Step 1. Saponification: A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and heated. The soap produced is the salt of a long chain carboxylic acid.

Step 2. Glycerine removal: Glycerine is more valuable than soap, so most of it is removed. Some is left in the soap to help make it soft and smooth. Soap is not very soluble in salt water, whereas glycerine is, so salt is added to the wet soap causing it to separate out into soap and glycerine in salt water.

Step 3. Soap purification: Any remaining sodium hydroxide is neutralized with a weak acid such as citric acid and two thirds of the remaining water removed.

Step 4. Finishing: Additives such as preservatives, colour and perfume are added and mixed in with the soap and it is shaped into bars for sale.

Figure 3.19 shows a flow chart that showing the soap making process.

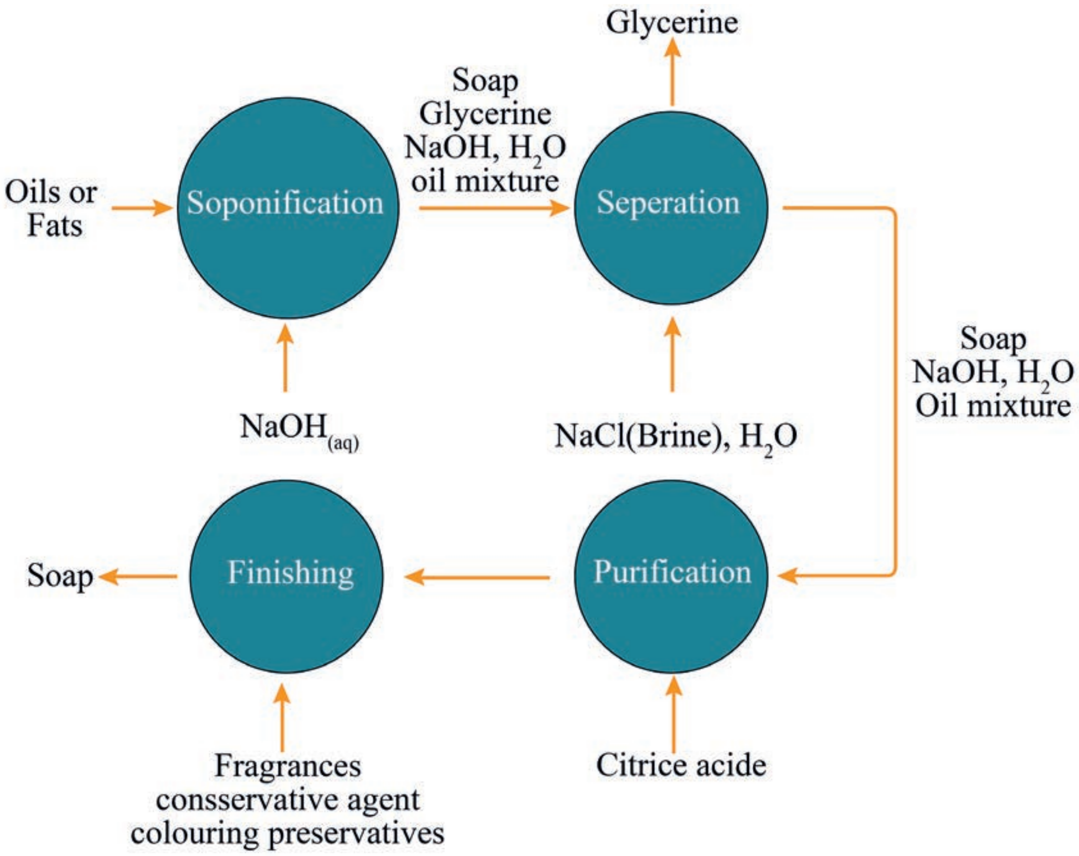


Figure 3.19: Flow chart showing the soap making process.

Experiment 3.6

Preparation of soap

Objective: to prepare soap from animal fat or vegetable oil.

Materials required: Measuring cylinder, beaker, glass rod, Bunsen burner, filter paper, funnel, conical flask, and test tube

Procedure:

1. Measure 3 mL vegetable oil or 3 g animal fat and place it in a 100 mL beaker;
2. add 3 mL of ethanol and 3 mL of 5M NaOH.
3. Stir the mixture vigorously with a glass rod and gently heat over a flame for 15 minutes or until it turns in to a paste.
4. When the paste begins to form, stir very carefully to prevent frothing. After all the paste has formed, set the beaker on the bench to cool.
5. Add about 15 mL of saturated NaCl solution to the paste mixture and stir thoroughly. This process is called salting out the soap.

   Filter off the soap mixture by suction filtration and wash the collected soap precipitate with 15 mL of ice water.

Observations and analysis:

A. Why do we add ethanol during the preparation?

B. What is the purpose of adding saturated NaCl solution to the paste mixture?

Write a lboratory report and present to the class

Detergents

These cleaning agents are often called, soap less soaps because they lather well, they are very different from ordinary soaps in their chemical composition. Long open-chain alcohols and alkyl benzene sulphonic acid can be used for the production of detergents. Detergents are sodium salts of sulphonated long chain organic alcohols.

$R\text{-}C_6H_4\,SO_3\,Na$, where:

R is an alkyl group with a chain of 10 to 18 carbon atoms. The water-soluble group is $-SO_3Na$ while the fat soluble one is the $-R\text{-}C_6H_4$ groups.

The advantage of detergents is, that they lather well with both soft and hard water and even with water that contains common salt or acids. They are more soluble than soap in water, form stable emulsions with grease and do not form a scum with hard water because their calcium and magnesium salts are soluble.

One example of detergents is sodium lauryl sulfate, $C_{12}H_{25}—O—SO_2—ONa$. It is prepared first by reacting dodecyl (lauryl) alcohol with sulphuric acid followed by reaction with sodium hydroxide. The reaction equation is:

$$\underset{\substack{\text{Dodecyl alcohol}\\\text{(lauryl alcohol)}}}{C_{12}H_{25}—OH} + \underbrace{HO—SO_2—OH}_{H_2SO_4} \longrightarrow \underset{\text{Lauryl hydrogen sulphate}}{C_{12}H_{25}—O—SO_2—OH} + H_2O$$

$$C_{12}H_{25}—O—SO_2—OH + NaOH \longrightarrow \underset{\text{Sodium lauryl sulphate}}{C_{12}H_{25}—O—SO_2—ONa} + H_2O$$

Experiment 3.7

Investigating the Chemical Properties of Soap and Detergent

Objective: Describe the chemical properties of soap.

Chemicals: Soap produced in **Experiment 3.3,** detergent

Equipment & Apparatus: Four 150 ml of beaker, cold water

Procedure

1. Weigh 3 g of your soap that you prepared in **Experiment 3.3** and **3** gram detergent as directed by your teacher.
2. Add 3 gram of the soap you produced in **Experiment 3.3** in solution (3 mL distilled water + 5 drops 3% magnesium chloride solution) in 150 ml of beaker labeled soap then add 100 ml of water. Do the same thing for 3 gram of detergent in a 150 of beaker labeled. Detergent. Stir both beakers. Observe in which beaker leather is well formed.

Observation and Analysis

Based on your observation in procedure 3, which reagent (soap or detergent) lathered well with hard water? Why?

Dry Cleaning

The qualities of some clothes decrease when they are washed with water using ordinary soap. In order to avoid this, other chemicals are used for washing purposes that remove dirt in the same manner as soaps. Dry cleaning refers to the use of different chemicals that are capable of dissolving grease and other dirt stains in a similar manner as soaps without the use of water. The most commonly used chemicals in dry cleaning are organic chemicals such as tetra chloromethane, CCl_4; tetra chloroethylene, $Cl_2C = CCl_2$; benzene and gasoline.

For example, Silk will turn yellow if it is treated with strong soap during laundering. Often the instruction for cleaning clothes contains the sentence: Use only lukewarm water for cleaning. Otherwise the quality of the product will decrease. Because natural fibers are mostly mixed with artificial ones, laundering should not be applied. Instead of laundering, dry cleaning is applied. To dry clean, means to use different chemical those are able to dissolve grease and stains in a similar manner as soaps, the only difference being that contact with water is avoided.

Project 3.6

Presently soap is prepared in a small scale (in the cottage industry) in most of the Ethiopian cities and has become a means of income generating. Do you know the raw materials that are used and the procedure to be followed to prepare the soap in such a cottage industry? Please visit the nearby cottage industry and submit a report to your teacher.

Exercise 3.12

Do the following questions individually.

1. Explain the difference between chemical and mechanical pulping.
2. How does natural tanning differ from mineral tanning?
3. Describe the modern methods of food preservation.
4. Explain the reason why the paper quality produced in industries differs.
5. What are the common chemicals that are used for mineral tanning?
6. What is the mechanism that makes food be preserved for a long time without spoiling?
7. How does the traditional way of preparation of Araki differ from industrially prepared liquor (Gin)
8. Explain the difference between hard soap that is used for cleaning us clothes and soft soap that is used for our body hygiene.
9. How do soap and detergent act on dirt particles during cleaning?
10. Describe how detergent is more effective in hard water than soap,. And show the mechanism of action by reaction equation that takes place during the cleaning action.

Unit Summary

- Before 19th century, chemistry and chemical technology were devoted to satisfying the needs of everyday life however the methods of production used were manual and small scale.
- In the 19th century as a result of Industrial revolution the chemical industries began to develop at a very high rate. The demands for goods produced through chemical processes increased.
- Ethiopia, as developing country, will find chemistry and chemical technology very important components of economic growth and development.
- Industrial chemistry as the branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw materials and their derivatives to products those are of benefit to humanity.
- The resources that can be replenished through rapid natural cycles are known as renewable resource. Examples: plants, (crops and forests), and animals
- The resources that cannot be replenished through natural processes are known as non-renewable resource. Examples: fossil fuels and, minerals.
- Ammonia is an important compound, essential to man for a variety of diverse uses. It is used as a fertilizer, cleaning agent, antimicrobial agent, etc. The process that used to manufactured ammonia in industries are called **Haber - Bosch process**
- Nitric Acid is a highly corrosive mineral acid. And it is a strong oxidizing agent and it is produced industrially from ammonia by the three-step **Ostwald process.**
- The largest percentage of nitric acid is used to synthesize ammonium nitrate, a water-soluble fertilizer. Large quantities are also used to make plastics, drugs, and explosives such as trinitrotoluene (TNT) and nitro glycerin.
- $H_2SO_4$the largest volume chemical produced in the world and rate of consumption of this acid is considered as a measure of a country’s industrialization.
- Most of the sulphuric produced in the world is manufactured industrially by the contact Process which involves four major steps. Sulfuric is used in the production of fertilizers, detergents, plastics, paints, explosives, as electrolyte in car batteries and as a catalyst in the manufacture of many chemicals.

- DAP has the advantage of having both nitrogen and phosphorus, which are essential for plant growth.
- The most common forms of N fertilizer include anhydrous ammonia, urea, and urea-ammonium nitrate (UAN) solutions.
- **Urea** is a solid fertilizer with high N content (46%) that can be easily applied to many types of crops and turf. It is manufactured by reacting CO_2 with NH_3 .
- Pesticides belong to a category of chemicals used worldwide to prevent or control pests, diseases, weeds and other plant pathogens in an effort to reduce or eliminate yield losses and maintain high product quality. Examples of common pesticides oregano-chlorine, oregano-phosphate and carbamates.
- A herbicide is a chemical used to kill or otherwise manage certain species of plants considered to be pests. Examples: chlorophenoxy acids such as 2,4-D and 2,4,5-T; triazines such as atrazine, hexazinone, and simazine.
- Sodium carbonate (washing soda) is a white crystalline solid. It exists as a decahydrate ($Na_2CO_3 . 10H_2O$) compound. Sodium carbonate is manufactured by Solvay process in industrial scale and has industrial and domestic uses.
- NaOH has been manufactured at large scale for many years from readily obtainable raw materials i.e. Rock salt "NaCl" sodium chloride & water "H_2O".
- Sodium hydroxide is used in numerous industrial processes such as in pulp and paper manufacturing, alumina extraction from bauxite in aluminum production, as well as in the textiles industry and drinking water production.
- The chemical/manufacturing industry in Ethiopia produces basic chemicals based on local raw materials and currently there are a total of 153 chemical and chemical-related product manufacturers according to CSA's raw data for the year 2014.
- Glass is an amorphous or non-crystalline solid material and is such a popular material in our homes because it has all kinds of really useful properties. Almost all glass contains silica as the main component.
- **Soda-lime glass** is ordinary glass which is a mixture of sodium silicate and calcium silicate.

- Traditional ceramics, such as porcelain, tiles and pottery are formed from minerals such as clay, talc and feldspar whereas industrial ceramics, however, are formed from extremely pure powders of specialty chemicals, such as silicon carbide, alumina, barium titanate, and titanium carbide.
- Ethiopia has a huge amount of reserve of raw materials for the production of cement. The major raw materials for the production of cement are limestone, clay, silica sand, gypsum, and pumice.
- Sugar is mainly manufactured from a raw material sugar cane with 8 stage industrial process starting from collecting the Harvest of sugar cane to for grinding to the last stage separation and packaging
- Paper is a mixture made from rags and wood pulp glued together with some additions, bleached and dried.
- Tanning is a process of converting raw animal hides and skin to leather, using tannin. Leather is a durable and flexible material created by the tanning of animal hides and skin.
- Food preservation usually involves preventing the growth of bacteria, fungi and other microorganisms, as well as reducing the oxidation of fats, which causes rancidity.
- The most common modern methods of food preservation are freezing, vacuum-packing and Freeze-drying
- The alcohol, which is the constituent of beverages, is known as ethyl alcohol or ethanol.
- The preparation of ethyl alcohol is atypical chemical process. It can be done from sugar by bacteria, without air (oxygen).

$$C_6H_{12}O_6 \xrightarrow[\text{bacteria}]{\text{zymase}} 2C_2H_5OH + CO_2$$

- The common alcoholic beverages in Ethiopia Beer, liquor (Araki), Wine, Tej and Tella
- There are many kinds of soap available on the market, but the methods used in making them are similar. It is expressed in the equation: Long chain fatty acids (Fat) + NaOH (Lye) → Soap + Glycerin represents the changes in practically all soap making. The soap making process is called saponification.

CHECK LIST

KEY TERMS

- *Alcoholic Beverages*
- *Araki*
- *ceramics manufacturing*
- *Chemical industry*
- *Contact process*
- *DAP*
- *Dry Detergents*
- *Food Preservation*
- *Glass manufacturing*
- *Haber - Bosch process*
- *Herbicides*
- *Industrial chemistry*
- *Le Chatelier's principle*
- *Nitrogen Based Fertilizers*
- *Non-Renewable Resources*
- *Ostwald Process*
- *Paper and Pulp*
- *Pesticides*
- *Renewable resources*
- *Setting of cement*
- *Soaps and detergents*
- *Solvay process*
- *Sugar manufacturing*
- *TanneryS*
- *Urea*
- *Valuable products*

REVIEW EXERCISE FOR UNIT 3

Part I. Write True if the statement is true and false if the statement is false

1. In early stage of industrial chemistry, the methods of production used were manual and small-scale.
2. The largest percentage of nitric acid is used to synthesize ammonium nitrate, a water soluble fertilizer.
3. H_2SO_4 is a leading economic indicator of the strength of many industrialized nations.
4. Diammonium monohydrogen phosphate (DAP) is a white crystalline compound that is insoluble in water
5. In Ethiopia's manufacturing/chemical industry is still at a nascent stage.
6. The present day paper is not completely different from the old papyrus which was used centuries ago.

Part II: Choose the best answer for the following questions among the given alternatives

1. What type of catalyst used in the Contact process?
   - a. V_2O_5
   - b. Fe
   - c. Pd
   - d. Pt
2. What is $H_2S_2O_7$?
   - a. Concentrated sulphuric acid
   - b. Sulfur trioxide
   - c. Oleum
   - d. Hydrogen sulfate
3. What are the uses of sulphuric acid?
   - a. In the manufacture of detergents and fertilizers
   - b. As food preservative
   - c. As a battery acid
   - d. As a bleach
   - e. a and c
4. In the Contact process, what happens to the equilibrium when the pressure is increased?
   - a. Shifts to the left
   - b. Shifts to the right
   - c. No change in equilibrium
   - d. None
5. What is the name of manufacturing process of sulphuric acid?
   - a. Contact
   - b. Frasch
   - c. Haber
   - d. Ostwald
6. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ + heat

   The equation above refers to the 2nd stage of Contact Process. What are the optimum conditions to favour the yield of sulphur trioxide?
   - a. Low Pressure
   - b. High Pressure
   - c. Low Temperature
   - d. High Temperature
   - e. b & c
7. Process in which sodium carbonate is manufactured is called
   - a. calcination
   - b. metallurgy
   - c. solvay process
   - d. carbonation

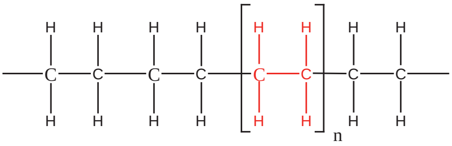
8. Pick out the wrong statement?
   a. High early strength cements are made from materials having high silica to lime ratio
   b. The function of gypsum in cement is to enhance its initial setting rate
   c. Acid resistant cements are known as silicate cement
   d. Major component of greyish Portland cement is tricalcium silicate
9. Among the following compounds which one is recycled in Solvay process during the production of Na_2CO_3
   a. NaCl
   b. CO_2
   c. NH_3
   d. $CaCO_3$
   e. B and C
10. The last step of the Solvay process is
    a. preparation of ammonical brine
    b. carbonation
    c. preparation of carbon dioxide and slaked lime
    d. recovery of ammonia
11. The third step of the Solvay process is
    a. preparation of ammonical brine
    b. carbonation
    c. filtration
    d. calcination
12. One of the following is the most common nitrogen based fertilizers.
    a. Anhydrous ammonia
    b. Urea
    c. urea-ammonium nitrate (UAN) solutions
    d. all
13. Which one of the following is the most important chemical groups of herbicides?
    a. chlorophenoxy acids such as 2, 4-D
    b. organic phosphorus chemicals such as glyphosate;
    c. amides such as alachlor and metolachlor
    d. all of the above
14. Which one of the following is a basic chemical or manufacturing product produced in Ethiopia from the local raw materials available?
    a. Sugar
    b. Cement
    c. soaps and detergent
    d. caustic soda
    e. All of the above

15. The product obtained by combining a material rich in lime, CaO with other materials such as clay, which contains silica, SiO_2, along with oxides of aluminum, iron and magnesium is:
    a. Glass b. Cement c. Steel d. Fertilizer
16. Which of the following is not a specific characteristic of chemical industries?
    a. using naturally available raw materials
    b. providing transport services to customers
    c. involving chemical reactions
    d. consuming energy
17. Which of the following is a non-renewable resource?
    a. soil c. water
    b. petroleum d. plants
18. In the tanning process, the purpose of putting the skin into slaked lime solution is to:
    a. facilitate the removal of unwanted flesh
    b. dehydrate the skin
    c. facilitate the removal of hair
    d. Soften the skin
19. The stage in which the shredded sugarcane travels on the conveyor belt through a series of heavy-duty rollers, which extract juice from the pulp in sugar manufacturing is called.
    a. Juicing c. Cleansing and Grinding
    b. Collecting the Harvest d. Clarifying
20. Preservation usually involves preventing ________________________
    a. The growth of bacteria
    b. The growth of fungi and other microorganisms,
    c. Reducing the oxidation of fats, which causes rancidity?
    d. All of the above
21. Which one of the following is a component to make soft soap along with the vegetable oil or animal fat
    a. Caustic soda c. K_2CO_3
    b. Caustic potash (KOH) d. B and C

Part III: Give Short Answer for the following Questions

1. Give a reason why among the essential aspects of industrial chemistry, the chemical industry is the prominent one?
2. In the production of ammonia in step 2 what conditions cause the gasses (nitrogen and hydrogen) to react and produce ammonia according to this reaction "$N_2 + 3H_2 \rightarrow 2NH_3$"
3. List the common uses of H_2SO_4.
4. What is the basic difference in the composition of glass and cement?
5. What are ceramics?
6. Write the main chemical equations involved in the production of cement.
7. Describe the refinery processes involved in sugar production
8. Write the key reaction during the Solvay process? And please describe how solid $NaHCO_3$ is formed.
9. What is the positive aspect of the application of pesticides?
10. Describe the process of production of the most local alcoholic beverages in Ethiopia.
11. Describe the cleaning action of soap and dry detergent.

UNIT 4



POLYMERS

Unit Outcomes

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

- *define polymers*
- *recognize that most of the materials around you may be polymers*
- *define the term monomer*
- *list and explain a variety of synthetic polymers and natural polymers and explain their differences*
- *classify polymers based on their response to heat*
- *predict monomers of the polymers by observing their structures*
- *distinguish addition and condensation polymerization*
- *recognize the relationship between properties and uses of plastics*
- *given a monomer/monomer, write polymerization reaction*
- *write structure of a polymer given structure of a monomer/monomers*
- *classify polymers into their types based on different criterion*
- *describe the properties of the different types of polymers*
- *describe the monomers, properties and uses of plastics, rubbers, carbohydrates and proteins*
- *list the applications of the different types of polymers*
- *describe the process of addition and condensation polymerization*
- develop inquiry skills along this unit: observing, predicting, classifying, communicating, and inferring.

4.1 Introduction to Polymers

At the end of this section, you will be able to

☞ *define the term monomer*
☞ *define the term polymer*
☞ *identify material with polymeric nature*

Activity 4.1

With your friends at your bench, look at the following materials. Then Set criteria and categorize them.

- the textile fibre of your clothes
- your hair and skin
- the wood from which your desk is made
- the glass of the window

Polymer

The word polymer is derived from the Greek words' 'poly' meaning many and 'meros' meaning part. It follows that this term applies to giant molecules built up of large numbers of interconnected repeating units. A polymer is a large chainlike molecule built up from many repeating smaller molecules.

A polymer is generally comprised of more than 100 monomers; structures with lower numbers of monomers are known as *oligomers*. These polymers or oligomers may be linear, slightly branched, or highly interconnected. In the branched case the structure develops into a large three-dimensional network. With few exceptions, the repeat unit in the polymer usually corresponds to the monomer from which the polymer was made. The size of a polymer molecule may be defined either by its mass or by the number of repeat units in the molecule. This latter indicator of size is called the *degree of polymerization*, DP. The relative molar mass of the polymer is thus the product of the relative molar mass of the repeat unit and the DP.

Example 4.1

Examples of polymers are:

- polyethylene,
- wood (cellulose),
- protein and

Monomers

The small molecules used as the basic building blocks for polymers are known as *monomers*. *Mono* means *one*.

Example 4.2

Example of monomers are:

- Glucose($C_6H_{12}O_6$) a monomer for cellulose (wood)
- ethylene a monomer for Polyethylene
- amino acid ($NH_2CH(R)(COOH)$) a monomer for protein

4.2 Polymerization Reactions

After completing this subtopic, you will be able to

- ☞ *describe polymerization reaction*
- ☞ *list the types of polymerization reactions*
- ☞ *give examples of addition polymers*
- ☞ *explain common uses of addition polymers*
- ☞ *give examples of condensation polymers*
- ☞ *explain the uses of these condensation polymers: nylon, polyester and Bakelite*
- ☞ *list the steps in addition polymerization*
- ☞ *identify whether a given monomer undergoes addition or condensation polymerization.*

Activity 4.2

Discuss in groups and present your answer to the class.

1. Long chains are made up of linkage of small metal rings(or other shapes). Use the anology of making chains to propose formation of large molcules.
2. Suggest another analogy for the formation of polymers.

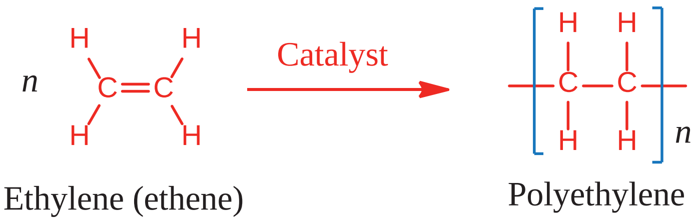
The chemical change by which monomer units combine to form a polymer is known as polymerization reaction. The essential feature of a monomer is to have two or more functional groups (polyfunctionality). This gives each monomer the capacity to form chemical bonds to at least two other monomer molecules.

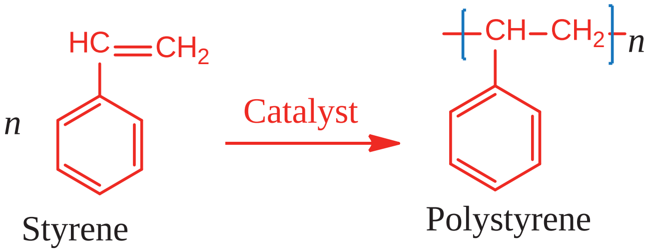
Bifunctional monomers can form only linear, chainlike polymers. Monomers with higher functionality yield cross-linked, network polymeric products.

Addition Polymerization

Addition polymerization is a reaction in which a chain reaction adds new monomer units to the growing polymer molecule one at a time. This type of polymerization is also known as chain-growth polymerization.

This type of polymerization reaction occurs by those involving unsaturated monomers. For example, the addition polymerization of many ethylene molecules yields polyethylene and that of styrene molecules gives polystyrene.





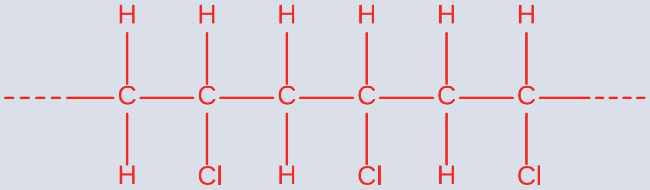
Note that the molecular formula of a polymer is *n* times that of the monomer and upon polymerization, the double bond is converted to a single bond. When monomers with triple bonds are used it is converted to double bonds.

Note also that: If a polymer is given, you can identify the monomer unit that is repeated in it.

If the mass of the polymer is known, the number of the monomer molecules is determined by dividing the molar mass of the polymer by the molar mass of the monomer.

Example 4.3

The addition polymer polyvinyl chloride (PVC) has the structure

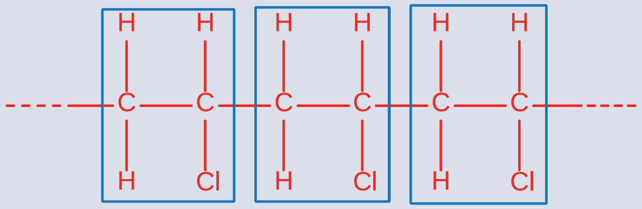


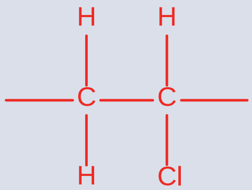
A. Draw the structure of the monomer from which PVC is made

B. How many monomer units are in a PVC polymer that has a molar mass of 1.33×10^5 g/mole

Solution:

A. We need to find the repeating unit from which this polymer chain is constructed



The repeating unit  and the monomer have carbon-carbon double bond.

B. If the PVC had a molar mass of 1.33×10^5 g/mol, how many monomer units (n) are there?

Given: Molecular mass of $CH_2=CHCl$ (Vinyl chloride) is 63.5g/mol

molar mass of the PVC 1.33×10^5 g/mol

Required: The number (n) of $CH_2=CHCl$

Relation:

$$\text{Number of monomer units }(n) = \frac{\text{Molar mass of the polymer}}{\text{Molar mass of the monomer}}$$

$$= \frac{1.33 \times 10^5 \text{ g/mol}}{62.5\text{g/mol}}$$

$$= 2128 \text{ vinyl chloride molecules}$$

Steps of addition polymerization

The addition polymerization process takes place in three distinct steps.

1. **Chain initiation step:** it is a time when the polymerization process is started by means of a reactive initiator molecule. The initiator molecules can be a free radical, a cation or anion. These reactive centres react readily with other monomers without eliminating the active centre.
2. **Chain propagation step**: It is the period when a monomer adds to the growing chain, with the free radical, cation or anioin transferring to the chain end. High molar mass polymers are formed right from the beginning of the reaction.
3. ***Chain termination step***: This is the step when the polymerization is stopped since chain reactions do not continue indefinitely. The radical, cation, or anion is "neutralized" stopping the chain propagation.

A polymerization reaction initiated by free radicals is called a free radical polymerization. The free-radical route to chain polymerization is the most important step in polymerization reaction.

A polymerization reaction initiated by a cation is called a cationic polymerization. A polymerization reaction initiated by an anion is called an anionic polymerization.

Example 4.4

Example for Free radical polymerization

1. Chain initiation:

The free radical on the initiator fragment, shown: as Ra·, attacks the covalent π bond in the monomer, leaving a free radical on the monomer

$$\underset{\text{initiator}}{Ra\cdot} + \underset{\text{monomer}}{CH_2{=}CH_2} \longrightarrow \underset{\text{monomer (free radical) (molecule)}}{Ra{-}CH_2{-}CH_2^{\cdot}}$$

2. Chain propagation

$$\sim\!\sim CH_2{-}CH_2^{\cdot} + CH_2{=}CH_2 \longrightarrow \sim\!\sim CH_2{-}CH_2{-}CH_2{-}CH_2^{\cdot}$$

3. Chain termination

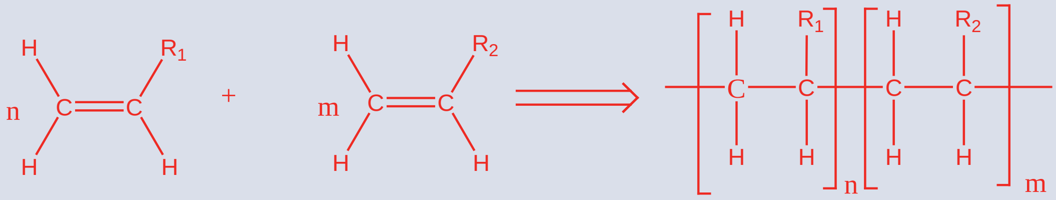
Termination is achieved in two possible processes.

A free radical is destroyed by the combination reaction when two chains link as

$$\sim\!\sim CH_2{-}CH_2^{\cdot} + \sim\!\sim CH_2{-}CH_2^{\cdot} \longrightarrow \sim\!\sim CH_2{-}CH_2{-}CH_2{-}CH_2\sim\!\sim$$

chain transfer may occur to continue polymerization of another chain

$$\sim\!\sim\!\sim\!\sim CH_2{-}CH_2^{\cdot} + H_2 \longrightarrow \sim\!\sim\!\sim\!\sim CH_2{-}CH_3 + H^{\cdot}$$



Separate the product

Polymers include polyethylene, polyvinyl chloride, acrylics, polystyrene, and polyoxymethylene (acetal) are made by addition polymerization.

Exercise 4.1

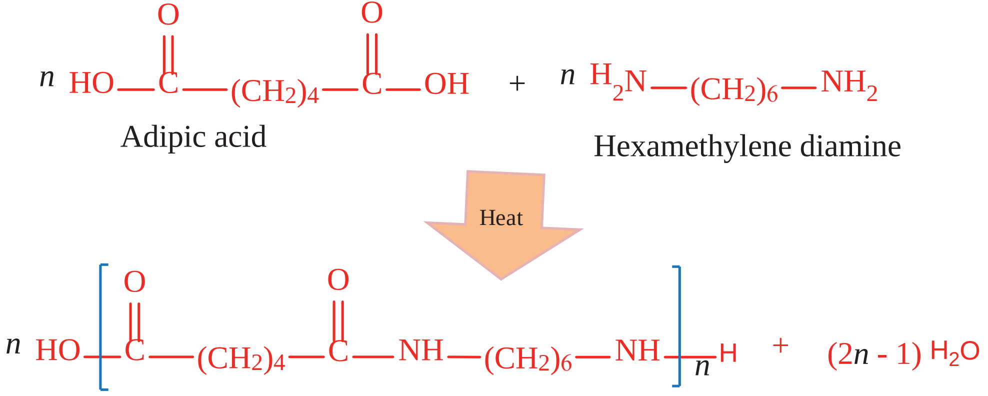
1. List the types of polymerization reactions.
2. Define addition polymerization reaction.
3. Show the steps followed in the polymerization of styrene to polystyrene. Describe each step.

Condensation polymerization

Condensation polymerization involves the combination of monomer molecules, with the release of simple molecules like water or methanol as by product. These products are normally referred to as condensate. This polymerization is also known as step growth polymerization. In order to produce a condensation polymer, the monomers involved two or more functional groups. Typically, such reactions take place between reactive components, such as dibasic acids with diamines to give polyamides, or dibasic acids with diols to form polyesters. Proteins, starch and cellulose are examples of natural condensation polymers. Whereas, Polyester (Polyethylene terephthalate or Dacron) and the polyamide Nylon 66 represented below, are two examples of synthetic condensation polymers.

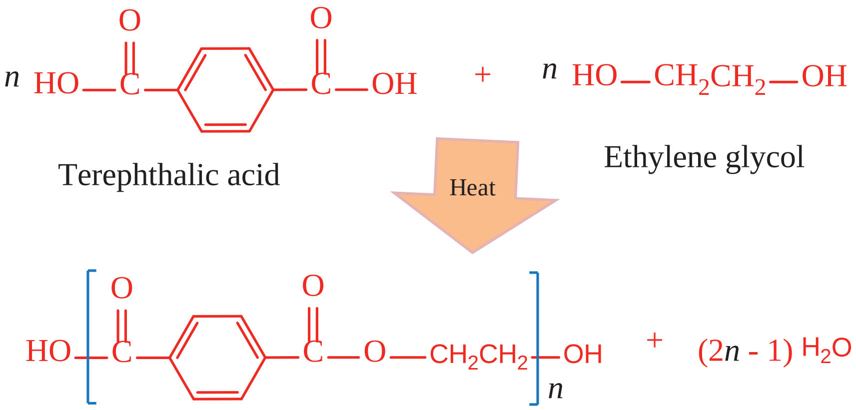
They can be produced by the condensation reaction of diacids and diamines. One of the most common polyamides is nylon 66 or nylon. It is a copolymer and is prepared by the condensation of 1, 6-diaminohexane (hexamethylene diamine) and 1,6-hexanedioic acid (adipic acid). The basic amine reacts with the acid to form a salt. Heating removes water and forms the amide bonds.

Dacron is a copolymer and is formed when equimolar amounts of 1, 4-benzene dicarboxylic acid (terephthalic acid) and 1, 2-ethanediol (ethylene glycol) react.



$$n\ HO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH \;+\; n\ H_2N-(CH_2)_6-NH_2$$

$$\xrightarrow{\text{Heat}}\; n\ HO-\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH\right]_n-H \;+\; (2n-1)\ H_2O$$



Polyethylene terephthalate (PTE)

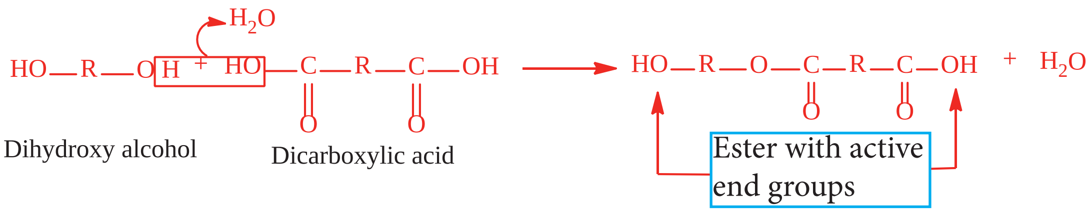
Nylon 66 (the numbers indicate there are six carbon atoms each in hexamethylene diamine and adipic acid)

Dacron is a strong and impact resistant. It is colourless and has high transparency. It is mainly used for synthetic fibbers. Mixing with various amounts of cotton it gives fabrics that are durable, easily dyed and crease-resistant. It is also used for making bottles and packaging materials.

Uses of nylon include making parachutes, ropes, clothes, stockings, hair combs, and rugs. They are also used to reinforce automobiles tires.

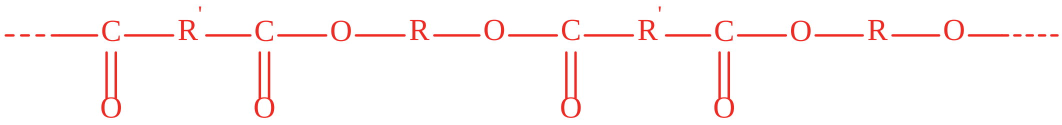
Consider the reaction between an alcohol with two –OH groups, HO–R –OH, and

a dicarboxylic acid, HOOC–R–COOH as represented below. In this case the ester formed still has a reactive group at both ends of the molecule.



$$HO-R-OH + HO-\underset{\underset{O}{\|}}{C}-R-\underset{\underset{O}{\|}}{C}-OH \longrightarrow HO-R-O-\underset{\underset{O}{\|}}{C}-R-\underset{\underset{O}{\|}}{C}-OH + H_2O$$

The general structure of the polyester can be represented as



$$---\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-O-R-O-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-O-R-O----$$

Section of the polyester

Experiment 4.1

Synthesis of Nylon

Objective: To prepare nylon and study its properties.

Apparatus and Chemicals: 250 ml beakers, dropping funnel, glass rod, forceps or copper wire hooks, 0.5 M basic solution of hexamethylenediamine, 0.5 M NaOH solution and adipoyl chloride, 0.5 M HNO_3

Caution: Wear gloves while doing this experiment.

Procedure:

1. Place 5 mL of Solution A in a small beaker. Solution A: Prepare a 0.5 M basic solution of hexamethylenediamine(or 2,6–diaminohexane,$H_2N(CH_2)6(NH_2)$ as follows: weigh 6 g of hexamethylene diamine in a large beaker and dilute to 100 mL with 0.5 M NaOH solution.
2. Place 5 mL of Solution B in a second beaker. Solution B: Weigh 5 g of adipoyl chloride and dissolve in 100 mL of cyclohexane.
3. Slowly add solution B to solution A using dropping funnel, pouring it down the side of the slanted beaker. Do not stirr the mixture of solution A and solution B.
4. Nylon will form at the interface of the two solutions.
5. Draw a thread out of the interface using forceps or a copper wire hook, and draw the thread out of the beaker using glass rod as a pool and slowly windup the thread as you draw it out.
6. After nylon has been collected, wash it thoroughly with water, dry it superficially with towel then let it dry.
   - 6.1 Try to stretch the dried nylon and note its strength
   - 6.2 Heat parcel of the nylon and note its ease of melting
   - 6.3 Take a parcel of the dried nylon and add a drop of nitric acid and observe its reactivity with acids

Observation and discussion

A. Why the two solutions are not able to mix?

B. Why is adipoyl chloride used instead of adipic acid?

C. What did you feel of strength when you stretched the prepared nylon?

D. what happened to the nylon when it was heated?

E. Was nylon resistant to acids?

F. was the nylon dried quikely or slowly?

Exercise 4.2

1. Determine the monomers used to prepare

   a. $\left[- OC - C_6H_4 - COO - (CH_2)_2 - O - \right]_n$

   b. $\left[- NH - CH_2 - CO - N - CH_2 - CO - \right]_n$

2. Decide the type of polymerization reaction taking place between the monomers $H_2NCH_2(CH_2)_4CH_2NH_2$, and $COClCH_2(CH_2)_6CH_2COCl$. Write the structure of the polymer.

3. Consider a polymer made from tetrachloroethylene.
   a. Draw a portion of the polymer chain.
   b. What is the molar mass of the polymer if it contains 3.2 × 103 tetrachloroethylene?
   c. Calculate the percentage of C and Cl in the polymer?

4. Write the structure of the following polymers and also indicate the monomer units involved in the formation of these polymers.
   a. Nylon 66
   b. Dacron

5. Describe the major uses of nylons and polyethylene terephthalate.

4.3 Classification of Polymers

At the end of this section, you will be able to

- *categorize a given polymer based on different criteria*
- *identify natural and synthetic polymers*
- *tell the monomer of natural rubber*
- *list the properties and applications of natural and synthetic polymers;*
- *draw the structures of disaccharides*
- *describe polysaccharides*
- *draw the structure of starch and cellulose*
- *draw the structure of polyethylene, polypropylene, polyvinylchloride, polytetrafluoro ethylene and polymethyl methyl methocrylate*
- *give examples polypropylene, polyvinyl chloride and polyethylene products.*

Activity 4.3

Within your group, discuss the causes of the differences between different types of polymers.

There are a number of methods of classifying polymers. A few of the methods of polymers classification are listed below.

A polymer might be made from identical or different types of monomers. This could be used to classify polymers as homopolymers or copolymers.

Homopolymers

Homopolymers are those made from only one type of monomer. For example, polyethylene is synthesized by the polymerization of one type monomer, ethene (ethylene).

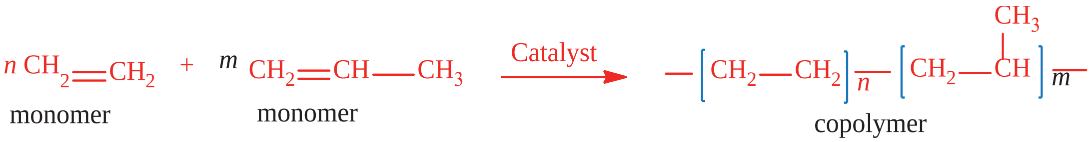
$$\underset{\substack{\text{Ethene (ethylene)}\\ \text{(monomer)}}}{n\ CH_2=CH_2} \xrightarrow{\text{Catalyst}} \underset{\substack{\text{Polyethylene}\\ \text{(homopolymer)}}}{-\left[CH_2-CH_2\right]_n-}$$

Copolymers

Activity 4.4

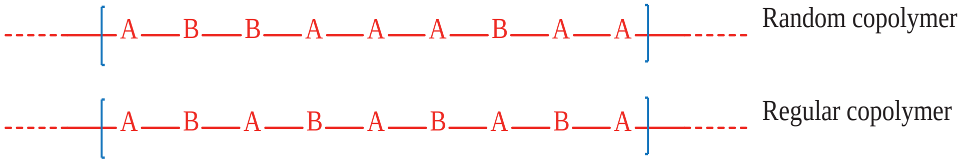
With your discussion group, identify the challenges arise when different types of monomers are used to synthesize a polymer with specific properties such as melting point, density etc.

Copolymers are those prepared by polymerizing more than one kind of monomer unit. For instance, ethene ($H_2C{=}CH_2$) and propene ($H_2C{=}CH{-}CH_3$) can be copolymerized to produce a polymer that has two kinds of repeating units:



$$n\,CH_2{=}CH_2 + m\,CH_2{=}CH{-}CH_3 \xrightarrow{\text{Catalyst}} -\left[CH_2{-}CH_2\right]_n-\left[CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\right]_m-$$

Copolymers are classified as random or regular, based on the way the monomers are arranged along the polymer chain. Random polymers contain repeating units arranged in a random fashion. Regular polymers contain a sequence of monomers in regular alternating repeating units.



Random and Regular copolymers (Where, **A** and **B** represent monomer units).

Another classification system of polymers is based on the nature of the chemical reactions employed in the polymerisation. Here the two major groups are the condensation and the addition polymers.

Condensation polymers are those prepared from monomers where reaction is accompanied by the loss of a small molecule, usually of water, for example polyesters which are formed by the condensation shown in the reaction:

$$n\,HO{-}R{-}OH + n\,HOOC{-}R'{-}COOH \longrightarrow HO\!\left[R{-}COO{-}R'{-}COO\right]_n + (n-1)\,H_2O$$

By contrast, **addition polymers** are those formed by the addition reaction of an unsaturated monomer, such as takes place in the polymerization of vinyl chloride:

$$n\,CH_2 = CHCl \longrightarrow \left[-CH_2 - CHCl - \right]_n$$

Furthermore, polymers can be classified based on whether they are naturally occurring or made by man (synthetic).

Natural polymers

Activity 4.5

Discuss with your friends on:

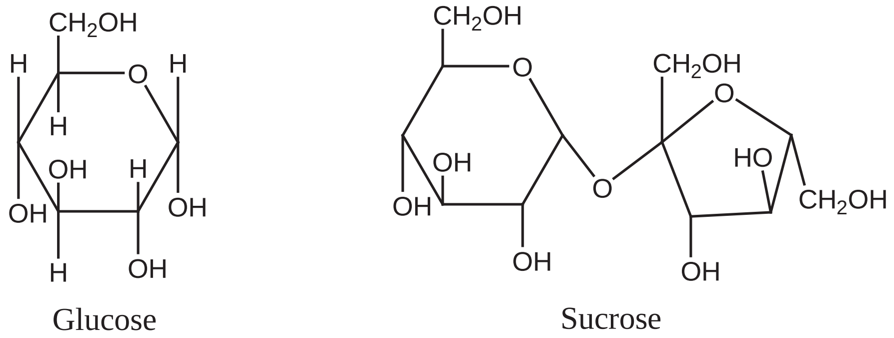
1. the similarity between starch and cellulose
2. the properties of natural rubber
3. similarity between wood and cotton
4. the nature of your genetic material and present your answer to the class.

Natural polymers occur in nature and can be extracted, and often referred to as biopolymers.

Common natural polymers include:

1. Carbohydrates
   a. monosaccharides e.g. glucose, fructose, galactose, and ribose.
   b. diasaccharides e.g. sucrose, lactose and maltose

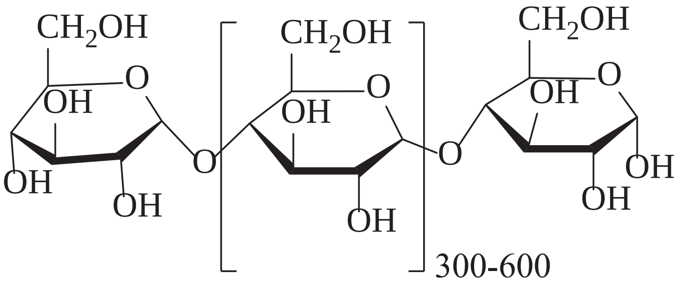
Figure 4.1 (a) and (b) shows the structure of glucose and sucrose respectively



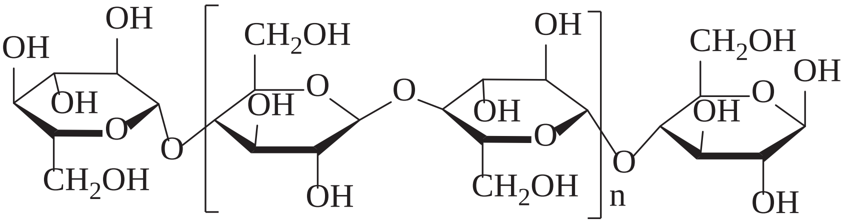
(a) (b)

Figure 4.1(a, b) Structure of monosaccharide (glucose) and diasaccharide (sucrose)

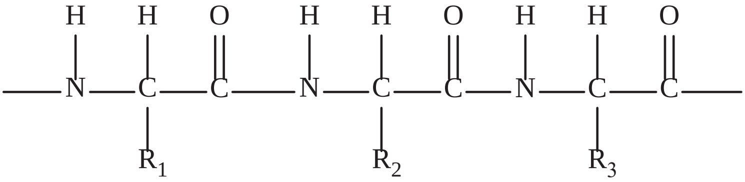
2. Macromolecules such as polysaccharides (e.g., starches, cellulose, gums, etc.), proteins (e.g., enzymes), fibbers (e.g., wool, silk, cotton), polyisoprenes (e.g., natural rubber), and nucleic acids (e.g., RNA, DNA) **(Figure 4.2).**



Starch

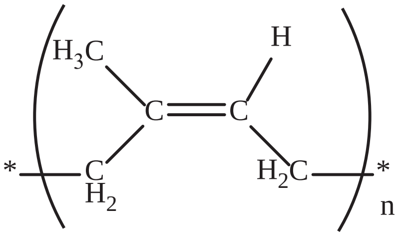


Cellulose (cotton, wood etc)

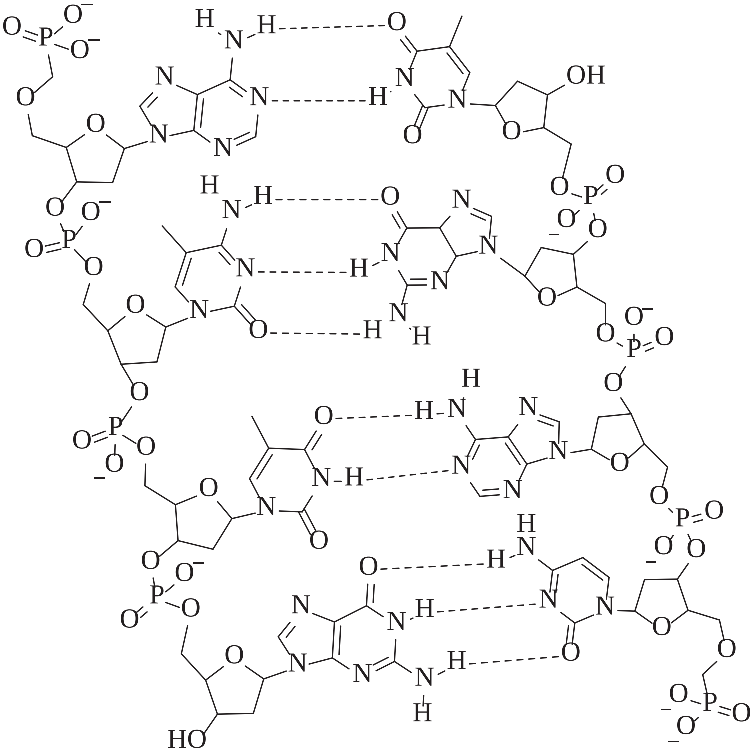


$$-\overset{H}{\overset{|}{N}}-\underset{R_1}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{R_2}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{R_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-$$

Protein (Skin, hair, muscles etc.)



Natural rubber



A portion of Deoxyribose nucleic acid (DNA)

Figures 4.2: Some macromolecule natural polymers

Synthetic polymers

Activity 4.6

Discuss on the following questions in groups and present your answer to the class.

Collect as many synthetic/artificial or manmade materials around you. Classify them as polymers and non-polymers. Give a reason for your classification.

Synthetic polymers are those which are human-made polymers. Synthetic polymers are sometimes referred as "plastics", of which the well-known ones is polyethylene **(Figure 4.3)**. It has no taste or odour and is lightweight, nontoxic and relatively cheap.

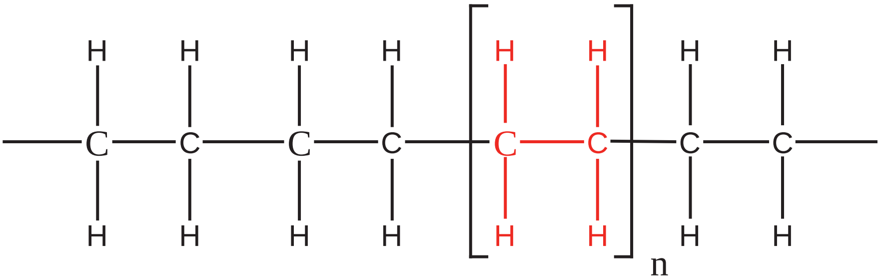


Figure 4.3: Structure of polyethylene (polyethene)

Some of its primarily uses are in making squeeze bottles, plastic wrapping, garment bags, trash bags and electrical insulation **(Figure 4.4).**

Polyethylene trash bags **Squeeze bottle (Wash bottle)** **Polyethylene tube**

Figure 4.4: Some polyethylene materials

Polypropylene

The monomer of polypropylene is propylene (propene) (CH_2=$CHCH_3$). It is produced by the addition polymerization of propylene.

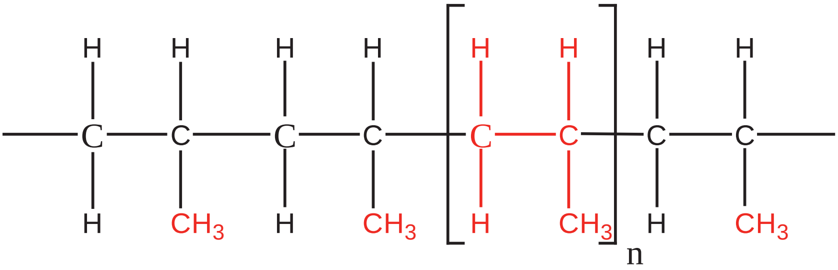


Figure 4.5: Structure of polypropylene

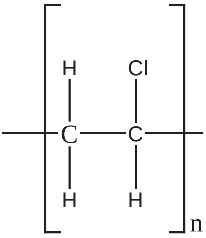
Polypropylene is stronger than polyethylene. It is used for making food containers that can safely be washed in a dishwasher. It can also be used for making ropes; fishing nets, carpets, and bottles (**Figure 4.6**).

Polypropylene rope **Polypropylene carpet** **Polypropylene bottles**

Figure 4.6 Some polypropylene products

Polyvinyl Chloride (PVC)

Polyvinyl chloride is the third most widely produced plastic, after polyethylene and polypropylene. It is prepared by the polymerization of vinyl chloride.



$$-\!\!\left[\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\right]_n\!\!-$$

Figure 4.7: Structure of polyvinyl chloride

It is commonly used for making pipes, leather-like materials, shoes, raincoats, aprons, wallpaper, floor tile, and phonograph records.

PVC pipes PVC floor tile PVC raincoat

Figure 4.8: Some polyvinyl chloride products

Polymethyl methacrylate (Perspex)

Polymethyl methacrylate, PMMA, is sold under the trade name Lucite or plexiglass. It is prepared by the polymerization of methyl methacrylate (CH_2=C (CH_3) $COOCH_3$.

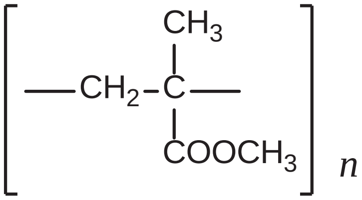


Figure 4.9: Structure of Polymethyl methacrylate

PMMA is a lightweight glass-like polymer used as a glass substitute for example, in airplane windows and streetlights.

Polytetrafluoroethylene, PTFE, Teflon

Teflon is prepared by the addition polymerization of tetrafluoroethylene (CF_2=CF_2). Teflon has good resistance to chemical attack, and it can be used at any temperature between –73 °C and 260 °C with no effect on its properties.

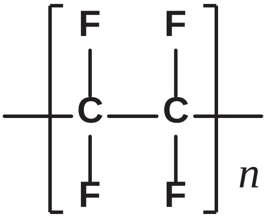


Figure 4.10: Structure of Polytetrafluoroethylene (PTFE)

It also has a very low coefficient of friction, which makes it waxy or slippery to touch. As a result, it is particularly suited to applications in food preparation. For example, bread dough does not stick to a Teflon-coated surface. Teflon is used for coating cooking utensils and for making electrical insulation (**Figure 4.11**).

Teflon coated dish **Teflon tape**

Figure 4.11: Some Teflon materials

One way of classification of polymers is to adopt the approach of using their response to thermal treatment and to divide them into thermoplastics and thermosets.

Thermoplastic polymers

Activity 4.7

Discuss in groups and present your answer to the class.

Collect samples of various polymers (your collection may include: PVC, nylon, polyester, hair, cellulose etc), and heat them one by one with a flame. Observe the impact of heat upon them. Based on your observation, Classify the materials as thermosetting and thermoplastics.

Thermoplastic polymers are those which melt when heated and resolidify when cooled. They are comprised of essentially linear or lightly branched polymer molecules. They can be remelted or reprocessed (recycled).

Examples of thermoplastics include: polyethylene, polypropylene, polyvinyl chloride, teflon, polymethyl methacrylate, nylon and polyester (Dacron), polystyrene (Rubber), and polyamide.

Thermoset polymers

Thermoset polymers are those which do not melt when heated, but at sufficiently high temperatures, decompose irreversibly. They are substantially cross-linked materials, consisting of an extensive three-dimensional network of covalent chemical bonding. They exhibit resistance to heat, corrosion, and mechanical stress. Thermoset materials are no-recyclable.

Examples thermoset polymers include: Bakelite, cyanate esters, epoxy resin, fibber glass (a fibber-reinforced thermoset), polyester resin, Polyurethane, Silicone resin, Vinyl esters, Vulcanized rubber.

Exercise 4.3

1. Define each of the following terms:

    a. monomer
    b. polymer
    c. homopolymer
    d. copolymer
    e. natural polymer
    f. synthetic polyme

2. What are some of the polymers that you encounter every day? Describe their physical properties.
3. Why do different polymers have different properties?
4. Which of the materials listed below may not be made of polymers? leather, computer key board, automobile body, cup, rubber, meat, mirror, plastic chairs
5. Classify each of the following polymers as natural or synthetic

    a. Wool
    b. Dacron
    c. Insulin
    d. Teflon
    e. Cellulose
    f. Polyvinyl chloride
    g. Bakelite
    h. Glycogen
    i. DNA

6. Explain the difference between thermoplastics and thermosetting polymers, using examples.
7. What makes thermoplastic materials recyclable, whereas thermosetting ones are not?
8. List some thermoplastic polymers and describe their properties with the corresponding applications.
9. List some thermoset polymers and describe their properties and applications.

Unit summary

- A polymer is a large molecule built up from numerous smaller molecules. These large molecules may be linear, slightly branched, or highly interconnected.
- The small molecules used as the basic building blocks for these large molecules are known as *monomers*.
- The size of a polymer molecule may be defined either by its mass or by the number of repeat units in the molecule.
- There are a number of methods of classifying polymers. These include
    - based on whether they are naturally occurring or made by man (synthetic).
    - using the types of monomers used to make the polymer to classify as *homopolymers* or *copolymers*.
    - their response to thermal treatment and to divide them into thermoplastics and thermosets
    - based on the nature of the chemical reactions employed in the polymerization and to divide into *condensation* and addition polymers.
- Each of the following polymers are made by addition polymerization. ‹
    - Polyethylene
    - Polypropylene
    - Polyvinyl chloride (PVC)
    - Polymethyl methacrylate (PMMA) ‹
    - Teflon
    - Polystyrene
    - Natural rubber
- Polymers that are synthesized by condensation polymerization are. ‹
    - Nylons
    - Polyesters
    - Bakelite
    - Carbohydrates, and Proteins

- Thermoplastics soften on heating and can be molded into different shapes, and the process of heating and cooling can be repeated several times, but once thermosetting plastics are solidified, they cannot be softened or remolded on heating.
- The uses of polymers include
  - in biology: the construction of structures, energy generation, physiological processing.
  - synthetic fibbers,
  - building materials
  - cooking utensils
  - ropes, carets, bottles, etc.

CHECK LIST

KEY TERMS

- *Addition polymerization*
- *Butyl rubber*
- *Catalyst*
- *Copolymer*
- *Ethylene*
- *Formaldehyde*
- *Homopolymer*
- *Isoprene*
- *Methyl methacrylate*
- *Monomer*
- *Polyethylene*
- *Polymer*
- *Polymerization*
- *Polypropylene*
- *Polystyrene*
- *monosccharide*
- *diasccharide*
- *Polyvinyl chloride (PVC)*
- *Repeating unit*
- *styrene*
- *Tetrafluoroethylene*
- *Thermoplastic*
- *Vinyl chloride*
- *Natural polymer*
- *Natural rubber*
- *Nylon*
- *Polyester*
- *Polymethyl methacrylate (PMMA*
- *propylene*
- *Synthetic polymer*
- *Terepththaleic acid*
- *Thermosetting*

REVIEW EXERCISE FOR UNIT 4

Part I: Multiple Choice Questions

1. Which of the following statement is incorrect about polymers?
    a. They are macromolecules made from smaller units.
    b. They can be prepared by either condensation or addition polymerization.
    c. Most condensation polymers are hompolymers.
    d. Disposing synthetic polymers can pollute the environment.
2. The process by which monomer units combine to form polymers, is:
    a. Condensation
    b. Thermosetting
    c. Thermoplastic
    d. Evaporation
3. What is the molar mass of a polyethylene sample, [— CH_2 —CH_2—]n , when n = 4600? (Atomic mass, H = 1 and C = 12).
    a. 1.288×10^3 g/mol
    b. 1.288×10^5 g/mol
    c. 1.196×10^3 g/mol
    d. 1.196×10^4 g/mol
4. Which one of the following is not formed by addition polymerization?
    a. Polyethylene
    b. Polyvinyl chloride
    c. Teflon
    d. Dacron
5. Which one of the following polymer-monomer pairs is incorrectly matched?
    a. Teflon-propylene
    b. PVC-chloroethene
    c. Plexiglass-methyl methacrylate
    d. Bakelite-phenol and formaldehyde
6. Which one of the following is not a synthetic polymer?
    a. Nylon
    b. Cotton
    c. Teflon
    d. Dacron
7. Polyethylene is not used for making:
    a. Squeeze bottles
    b. Trash bags
    c. Electrical insulation
    d. Airplane windows
8. Dacron is made by the polymerization of ____________ and ________________.
    a. Terephthalic acid, ethylene
    b. Adipic acid, ethylene glycol
    c. Terephthalic acid, ethylene glycol
    d. Adipic acid, hexamethylene diamine
9. Which one of the following is a thermosetting plastic?
    a. Polyethylene
    b. Polypropylene
    c. Dacron
    d. Bakelite

10. Which of the following structures represents the monomer of

$$-\!\!\left[CH_2-CH=CH-CH_2 \right]_n\!\!- \ ?$$

a. $CH_3CH=CHCH_3$
b. $CH_2=CH—CH=CH_2$
c. $CH_2=CH—CH_2—CH_3$
d. None of the above

11. A disaccharide made from two glucose units that are linked by α-1,4 glycosidic bond is:

a. Cellulose
b. Maltose
c. Lactose
d. Sucrose

12. Which one of the following disaccharide is prepared from two different monosaccharide units?

a. Cellulose
b. Maltose
c. Lactose
d. Fructos

Part II: Short Answer Questions

1. Define each of the following terms and give an example for each:

a. Monomer
b. Polymer
c. Carbohydrate
d. Amino acid

2. Classify each of the following polymers as natural or synthetic.

a. Polyethylene
b. Polypropylene
c. Cellulose
d. Dacron
e. Deoxyribonucleic acid
f. Polytetrafluoroethylene
g. Polystyrene
h. Nylons
i. Cotton
j. Polyvinyl chloride

3. Classify each polymer in Question 2 as an addition polymer or a condensation polymer.

4. What functional groups are involved in the addition and condensation polymerization processes?

5. Mention major uses of each of the following synthetic polymers.

a. Polypropylene
b. Polyvinyl chloride
c. Teflon
d. Polystyrene
e. Bakelite
f. Nylon

6. Why are olefins (alkenes) good monomers for polymerization reactions?

7. How does the molecular-level structure of these polymers influence their physical properties?

8. Besides the extent of branching, can you think of any other structural parameters that might lead to the differences in physical properties?
9. What kind of structural changes accompany bond-breaking and bond-forming in olefin polymerization?
10. Draw the structure of the copolymer of:
    a. $HO–CH_2CH_2–OH$ and $HOOC–CH_2CH_2–COOH$.
11. What is the role of a catalyst?
12. Does ethylene polymerize under mild conditions in the absence of a catalyst (initiator)?
13. Teflon" is the polymer that results from the polymerization of tetrafluoroethylene. Write a chemical formula for this reaction. What are some of the properties of Teflon?
14. A polymer's structure influences its physical properties. Describe two structural variations that are possible for polypropylene but not for polyethylene.
15. Consider the polymerization of vinylidene chloride, $CH_2{=}CCl_2$. What structural variations are possible in poly (vinylidene chloride)?
16. Consider the polymerization of 1,2-dichloroethylene, H(Cl)C=C(Cl)H. What structural variations are possible in poly(1,2-dichloroethylene)

UNIT 5

INTRODUCTION TO ENVIRONMENTAL CHEMISTRY

Unit outcomes

At the end of this unit, you will be able ro

- ☞ *define environmental chemistry*
- ☞ *describe the components that make the environment*
- ☞ *explain environmental pollution*
- ☞ *identify the three types of environmental pollution and names of the pollutants*
- ☞ *discuss the causes and effects of air, water and land pollution*
- ☞ *discuss air, water and soil pollution*
- ☞ *describe the main methods to reduce air, water and land pollution*
- ☞ *describe pollutants of the environment*
- ☞ *list greenhouse gases and describe their effect*
- ☞ *discuss about global warming and climate change*
- ☞ *apply pollution control mechanisms for controlling, air, water and land pollution*
- ☞ *describe principle of Green chemistry and cleaner production*
- ☞ *apply the principle of Green chemistry and cleaner production in doing experiments*
- ☞ *design chemical reactions that go hand in hand with principles of Green chemistry and cleaner production*
- ☞ *develop inquiry skills along this unit: observing, predicting, classifying, communicating, and inferring.*

Start-up Activity

When we see the word "Environmental Chemistry", several meanings and questions come into our mind.

- What do you understand from the term environmental chemistry?
- Why is it important to know about environmental chemistry?

Discuss in groups and present your opinion to the class.

5.1 Introduction

At the end of this subsection, you will be able to

- *define environmental chemistry*
- *define terms related to environmental chemistry such as pollutant, contaminate, sink, biological oxygen demand and Threshold Limit Value*
- *list the components of the environment*
- *describe the components of the environment*
- *write the important reaction in each components of the environment*
- *explain how the important reaction take place in each component of the environment*
- *describe the cycle of hydrological, carbon, nitrogen, oxygen, sulfur and phosphorus*
- *explain how the cycle of hydrological, carbon, nitrogen, oxygen, sulfur and phosphorus occurred in the environment.*

Activity 5.1

Discuss the following questions in groups and present your opinion to the class.

1. Why environmental chemistry is seen as a multidisciplinary?
2. Take CO_2 as an example of a typical pollutant, and describe its interaction with ecosystem and eventually its fate in the environment.

Environmental chemistry is a branch of chemical science that deals with the production, transport, reactions, effects, and fates of chemical species in the water, air, terrestrial, and biological environment and the effects of human activities thereon.

A common pollutant species is used to illustrate the definition of environmental chemistry. Sulfur in coal is oxidized to sulfur dioxide gas, which is then released into the atmosphere. Sulfur dioxide gas can be oxidized to sulfur trioxide and eventually converted to sulfuric acid in the atmospheric, then fall back to earth as acid rain, affect a receptor like plants, and end up in a "sink" like a body of water or soil. **Figure 5.1** shows a simplified schematic diagram that shown fate of pollutant species in the environment.

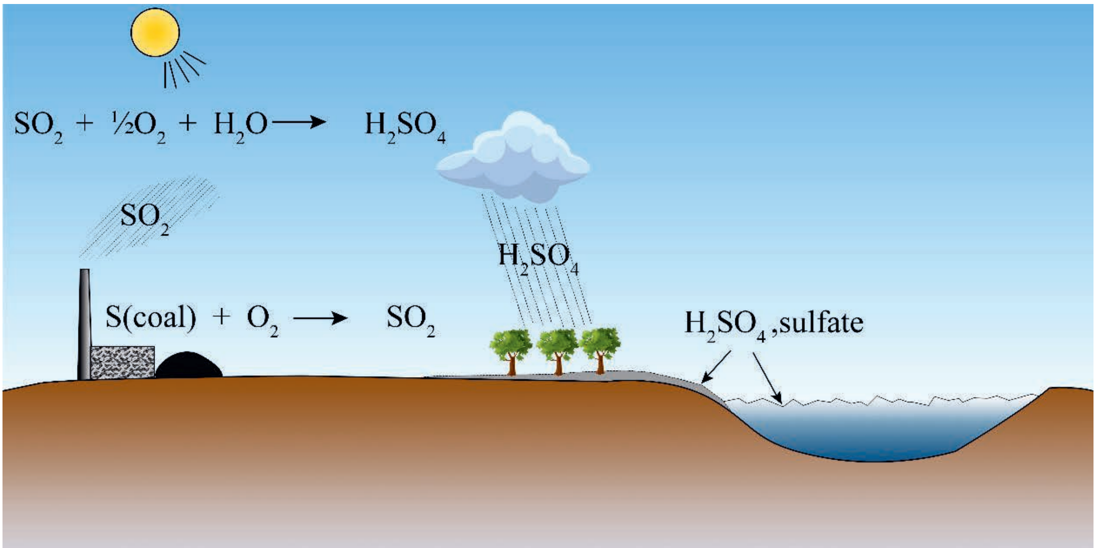


Figure 5.1: Simplified schematic diagram that shown fate of pollutant species in the environment.

5.1.1 Components of the Environment

Activity 5.2

Discuss the following question in groups and present your answer to the class.

What portion of the environment's component is included in the hydrosphere?

The environment consists of various compartments, including: atmosphere, hydrosphere, lithosphere and biosphere. Figure 5.2 shows the four componenets of the environment.

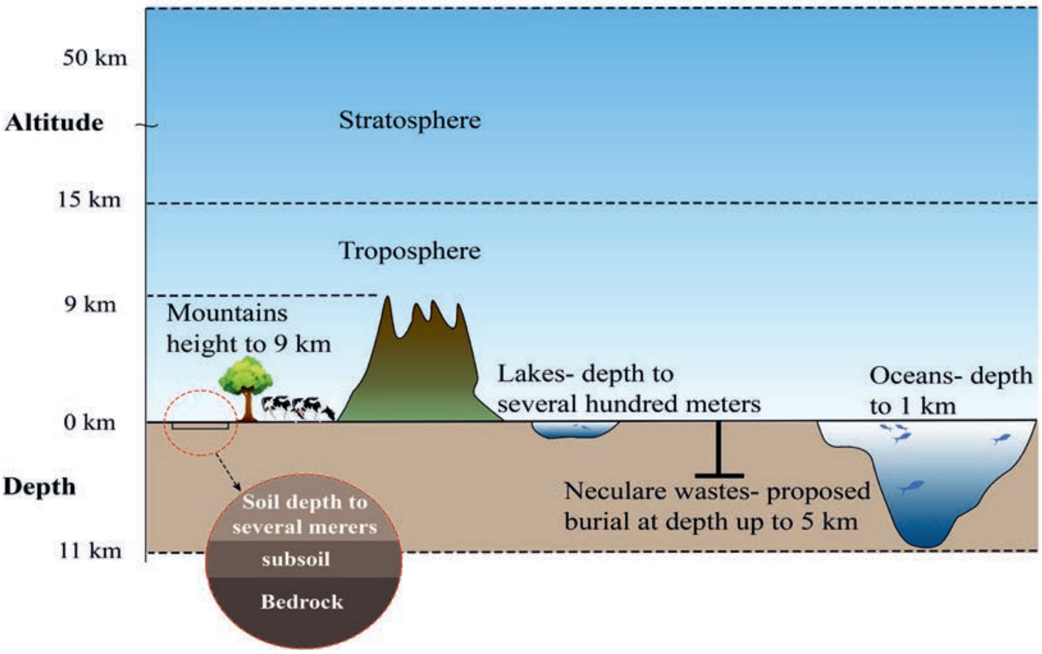


Figure 5.2: Components of the environment (atmosphere, hydrosphere, lithosphere & Biosphere)

The Atmosphere

One of the main components of Earth’s interdependent physical systems is the atmosphere. An atmosphere is the layers of gases surrounding a planet or other celestial body. Earth’s atmosphere is composed of about 78% nitrogen, 21% oxygen, and one percent other gases.

In general, the atmosphere provides many benefits to earth's living organism including human being: such as protective blanket of gas surrounding the earth (0–50km), absorbs infrared (IR) radiation emitted by the sun and re-emitted from the earth, controls temperature of the earth, allows transmission of significant amounts of radiation from near UV (300 nm) to near IR (2500 nm) and blocks transmission of damaging UV radiation.

For example, the following important reactions occurred in the atmosphere:

I. Nitric oxide is oxidized by oxygen to nitrogen dioxide in the presence of ultraviolet light.

$$2NO(g) + O_2(g) \xrightarrow{\text{ultraviolet}} 2NO_2(g)$$

SO_2, SO_3 and NO_2 react with rainwater and form sulphurous acid (H_2SO_3), sulphuric acid (H_2SO_4) and nitric acid (HNO_3), respectively and cause acid rain.

II. Chlorofluorocarbons are used as refrigerants, solvents and plastic foam-blowing agents. When entering the atmosphere, they penetrate into the upper layers and interact with ultraviolet radiation as follows.

$$CF_2Cl_2 + UV \longrightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$

The free chlorine $Cl\bullet$ reacts with ozone to form chlorine monoxide and oxygen.

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

The Hydrosphere

"The hydrosphere is the combined mass of water found on, under, and above the surface of the earth". The hydrosphere includes water that is on the surface of the planet, underground, and in the air. And it is collective term for all different forms of water, including oceans, seas, rivers, lakes, streams, reservoirs, glaciers, and ground waters. Only ~1% of global water supply is fresh water. Whereas, the greatest source of water on the planet is the ocean, which constitutes all salt water and at the same time, is the greatest source of water vapor. In the ocean, there are at least 77 important elements such as sodium and chlorine, magnesium and bromine, which are commercially exploited from seawater.

Some examples of chemical reaction in hydrosphere:

I. Ammonia (NH_3)/Ammonium (NH_4^+) that discharged from agriculture, aquaculture, industry and urban area into large water bodies result in toxicity to fish or aquatic ecosystem.

- For example, the biological oxidation of NH_4^+ to nitrite and then nitrate is a key part of the complex nitrogen cycle and a fundamental process in aquatic environments, having a profound influence on ecosystem stability and functionality.

Nitrate (NO_3^-)/Nitrite (NO_2^-) that discharged from agriculture, industry, aquaculture and sewage into water bodies result in accelerating aquatic plant growth leading to eutrophication.

- For example**,** the organic form of nitrogen, ammonia, has been converted into an inorganic form of nitrogen, nitrate that plants can use. The chemical equation:

$$2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O$$

The equation summarizes the entire nitrification process.

The Lithosphere

The lithosphere consists of earth's crust and upper mantle in which the crust part is the Earth's outer skin that is accessible to humans being. This part of the earth i.e. the crust consists of rocks and soil (most important part to humans and the environment). Some examples of important reaction in lithosphere are:

I. Different bacteria (mainly autotrophic, i.e., not dependent on organic material for their carbon supply) can effect oxidation or reductions of minerals.

$$2FeCO_3 + \frac{1}{2}O_2 + 3H_2O \xrightarrow{\text{Ferrobacilha}} 2Fe(OH)_3 + 2CO_2$$

II. Chemical weathering of rocks:

$$Fe_2O_3 + 3H_2O \rightarrow Fe_2O_3{\bullet}3H_2O \text{ (Hydration of rocks)}$$

The Biosphere

It refers to the realm of living organisms and their interactions with the environment (i.e., other compartments). This compartment divided into smaller units called ecosystems. Each ecosystem contains dynamic interrelationships between living forms and their physical environment. These interrelations manifest as natural cycles, such as hydrologic, oxygen, nitrogen, phosphorous and sulfur. The natural cycles operate in a balanced manner providing a continuous circulation of essential constituents. Examples of some important reaction in the biosphere:

I. Photosynthesis:

$$6CO_2 + 6H_2O \xrightarrow{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$

II. Respiration:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Heat\,energy$$

5.1.2 Natural Cycles in the Environment

Activity 5.3

Discuss the following in your groups and present into the class

1. In the oxygen cycle, what is the role of photosynthesis from the environment perspective?
2. What is the Nitrogen Cycle and why is it Key to Life?

Within the environment, natural cycles serve to continuously circulate constituents essential to life and other processes on earth. Among the common natural cycles: hydrologic cycle, oxygen cycle, nitrogen cycle, phosphorous cycle, sulfur cycle and carbon cycle are the important ones.

The Hydrologic Cycle

Hydrologic cycle is arguably the most important natural cycle. In this cycle there is the continuous exchange of water between environmental compartments. 10% of evaporative losses from oceans precipitate on land (groundwater). Groundwater percolates by capillary action to surface soil.

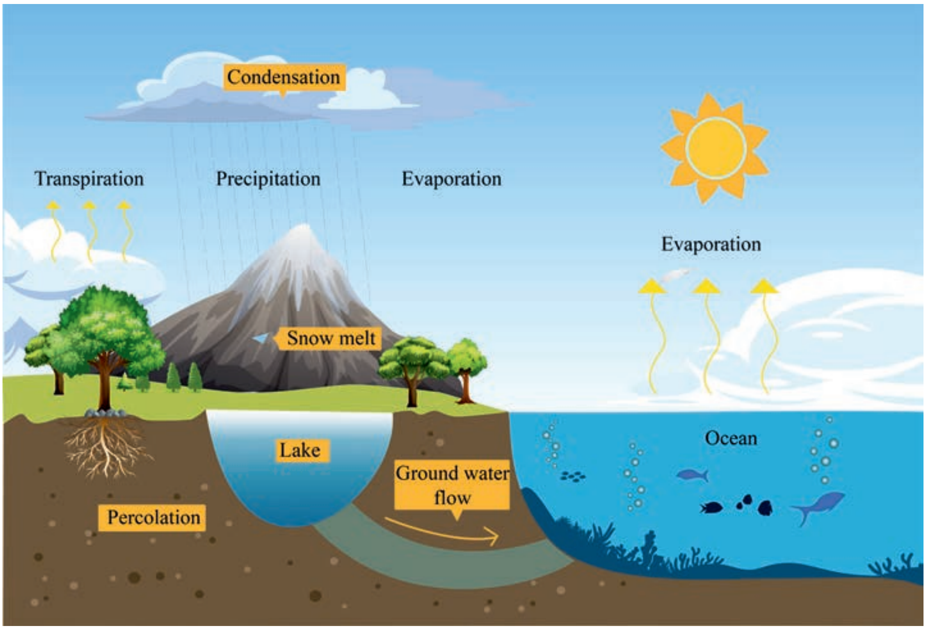


Figure 5.3: The hydrological cycle (water cycle)

The Oxygen Cycle

The oxygen cycle is the important cycle in the environment. Important to atmospheric chemistry, geochemical transformation and life processes. The following reactions show the importance of the oxygen cycle in the environment. For:

- Energy production

$$CH_4 + 2O_2 \xrightarrow{\text{Yields}} CO_2 + 2H_2O + \text{Heat energy}$$

- Degradation of organic material (Example glucose)

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

- Weathering of minerals

$$4FeO + O_2 \xrightarrow{\text{Yields}} 2FeO_3$$

- Photosynthesis

$$6CO_2 + 6H_2O \xrightarrow{\textit{sun light}} C_6H_{12}O_6 + 6O_2$$

- Sun screen (O_3)

$$'O' + O_2 \longrightarrow O_3$$

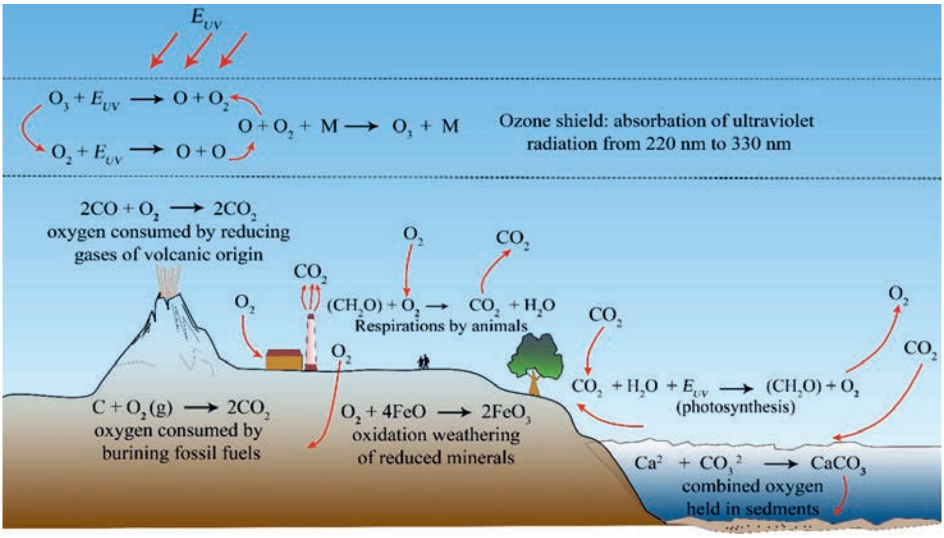


Figure 5.4: The oxygen cycle

The Nitrogen Cycle

The nitrogen cycle is arguably the second most important cycle, after the carbon cycle, to living organisms. Nitrogen is essential to plant growth, and therefore is a significant contributor to the human food chain, but its presence in the environment is strongly influenced by anthropogenic activities. The following are the important reaction of nitrogen cycle in the environment:

- Fixation by bacteria and algae :

$$2N_2 + 3CH_2O + 3H_2O + 4H^+ \longrightarrow 3CO_2 + 4NH_4^+$$

- Nitrification by nitrosomas and nitrobacteria :

$$2O_2 + 3NH_4^+ \longrightarrow NO_3^- + 2H^+ + H_2O$$

- Nitrate reduction by microbial action :

$$2NO_3^- + CH_2O \longrightarrow 2NO_2^- + H_2O + CO_2$$

$$2NO_2^- + 3(CH_2O) + 4H^+ \longrightarrow 2NH_4^+ + H_2O + 3CO_2$$

- Denitrification returns N to the atmosphere:

$$2NO_3^- + 5(CH_2O) + 4H^+ \longrightarrow 2N_2 + 7H_2O + 5CO_2$$

- Perturbed by anthropogenic activity:

$$N_2 + O_2 + \ldots \longrightarrow (\text{combustion})\, NO_X + \ldots$$

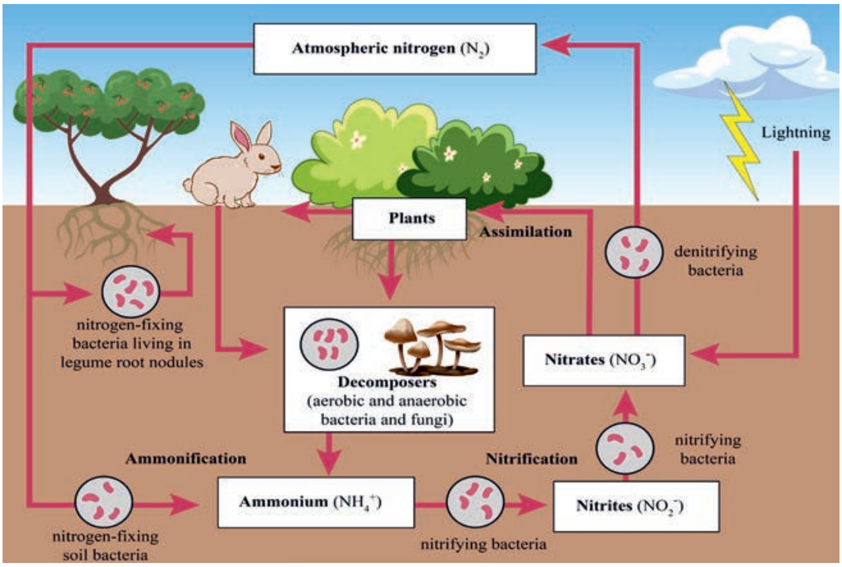


Figure 5.5: The Nitrogen cycle

The Phosphorous cycle

The phosphorus cycle is responsible for increasing the availability of phosphorus in the soil for plant growth and soil fertility. Understanding the mechanism of the phosphorus cycle helps to understand the physiology of different microorganisms involved in the process.

1. Central to many processes, including
   a. Cell division involving production of DNA and RNA
   b. Growth/maintenance of animal bones and teeth
2. Sources include
   a. Inorganic phosphorous, such as soluble $H_2PO_4^-$, HPO_4^{-2} and insoluble $Ca_5(OH)(PO_4)_3$ and $Fe_3(PO_4)_2.8H_2O$
   b. Terrestrial plants convert inorganic phosphate salts to organic phosphate
3. Animals obtain phosphate by eating plants
4. Upon death, phosphorus is returned to soil
5. Soil microorganisms convert returned phosphate into soluble inorganic phosphate (mineralization)
6. In water, P solubility is controlled by availability of Fe and Al (under acidic conditions) and Ca (under basic conditions

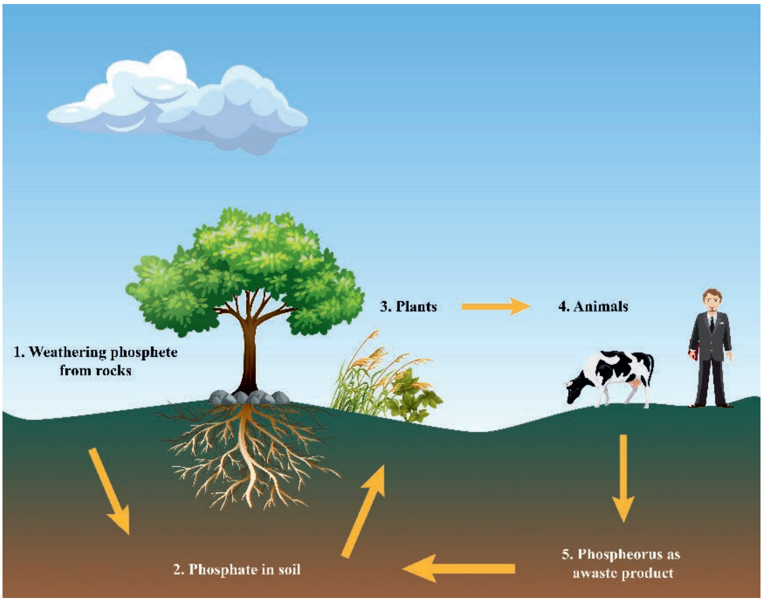


Figure 5.6 : The phosphorus Cycle

The Sulphur Cycle

The sulphur cycle is essential as it balances the concentration of sulphur in different reservoirs so as to make the Earth a hospitable place for life. Sulphur cycle show the circulation of sulfur in various forms through nature. Sulphur occurs in all living matter as a component of certain amino acids. It is abundant in the soil in proteins and, through a series of microbial transformations, ends up as sulfates usable by plants. The following are importance of sulphur cycle in the environment.

- Atmospheric oxidation produces higher charge states
- In hydrosphere and soil, S is present in many inorganic and organic forms with oxidation states from -2 to +6
- Most common forms of S include
    a. Sulfate (SO_4^{2-}), produced via a variety of pathways (e.g., bacterial):

    $$2H_2S + 4O_2 \rightarrow 4H^+ + 2SO_4^{2-}$$

    b. Sulfide (S^{2-}), produced by reduction of sulfate in organic rich reducing aqueous environments:

    $$SO_4^{2-} + 2CH_2O + H^+ \rightarrow H_2S + 2H_2O + 2CO_2$$

The Carbon Cycle

The Earth's atmosphere contains 0.035% carbon dioxide (CO_2), and the biological environment depends upon plants to convert carbon dioxide into sugars, proteins and fats. As shown in **Figure 5.7**, green plants convert atmospheric carbon dioxide and water into glucose and oxygen in a process called photosynthesis.

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O2(g); \Delta H = +2803 \text{ kJ mol}^{-1}$$

Photosynthesis is an endothermic reaction. Solar energy from the sun provides the necessary energy for the above reaction to proceed. Animals (including humans) eat plants, or eat other animals that have eaten plants, and incorporate the plants' carbon atoms into their cells.

Carbon returns to the physical environment in a number of ways. Both plants and animals respire, and they release carbon dioxide during respiration.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l); \Delta H = -2803 \text{ kJ mol}^{-1}$$

Respiration is an exothermic reaction, releasing 2803 kJ/mol of energy. The process of decomposition of organic matter also releases carbon dioxide back into the atmosphere.

Over a very long period of time, dead organisms under high pressure and in the absence of air can be converted into fossil fuels such as coal, oil and gas. Human's combust these fossil fuels as energy sources which releases carbon dioxide back into the atmosphere. The complete combustion of coal, oil, or natural gas results in the formation of carbon dioxide gas:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

The combustion of fossil fuels is exothermic, and therefore, releases energy in the form of heat.

According to law of conservation of mass, the total number of carbon atoms (in the atmosphere) is always constant; but there is a growing concern over the amount of carbon that exists as carbon dioxide, because carbon dioxide is a greenhouse gas and is a major contributor to global warming.

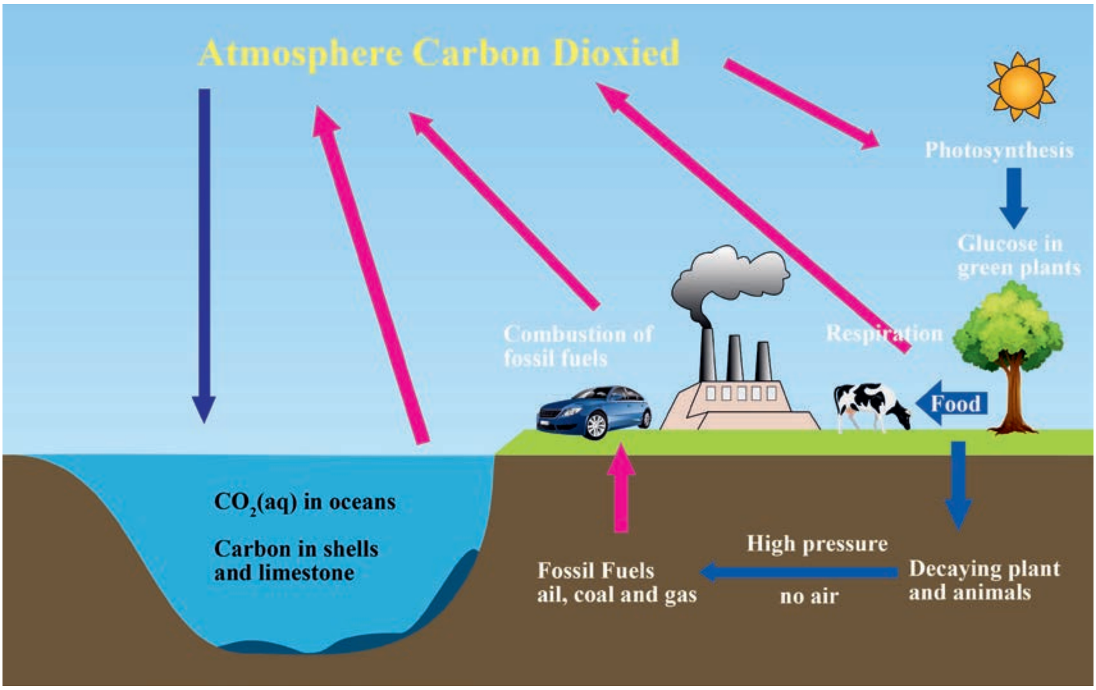


Figure 5.7: Carbon cycle

5.1.3 Concepts Related to Environmental Chemistry

Activity 5.4

Discuss the relationship between pollutant and Environmental pollution? And what criteria should be considered to level the environment is polluted ?

Pollutant:- A substance whose concentration has increased due to human activity, ultimately having detrimental effects on the environment. Examples include sulfur dioxide (SO_2), carbon dioxide ($CO_{2)}$, ozone (O_3), Pb, Hg, excess heat, light and sound.

Contaminant:- A substance that does not occur in nature, but it is introduced into the environment through human activity. A contaminant is called a pollutant when it exerts detrimental effects on human health receptor. Examples include bodies of water, humans, trees, animals and fish.

Sink: - The medium that interacts and retains pollutants or converts them chemically

Dissolved Oxygen (DO): - Oxygen dissolved in water. It is vital for aquatic life. The optimum levels of DO in good quality water are 4 – 8 mg L^{-1}. Whereas water with levels < 4 mg L^{-1} is considered polluted and unfit for human or animal consumption.

Biological Oxygen Demand (BOD): - Indicates the capacity of the DOM (dissolved organic matter) in a sample of water to consume oxygen. Determined experimentally by measuring DO at beginning and end of a 5-day period in a sealed sample. It also gives the measure of oxygen utilized as a result of oxidation of DOM present in the water sample.

Threshold Limit Value (TLV): - Indicates the permissible level of a toxic pollutant in the atmosphere to which a healthy individual can be exposed during an 8-hour day without adverse effects. TLV is found by experimentation on animals, medical knowledge and environmental studies

Exercise 5.1

1. What part of environment does the hydrosphere components include? Give examples.
2. Chlorofluorocarbons are used as refrigerants, solvents and plastic foam-blowing agents. Have a chance to enter in the atmosphere and penetrate into the upper layers and interact with ultraviolet radiation. Please write a chemical reaction equation which shows how the ClFCs deplete the ozone layer.
3. In oxygen cycle the two important reactions are degradation of organic material and photosynthesis could express these two important reactions in terms of chemical equation.
4. Write the equation that express nitrogen fixation by bacteria and algae?
5. Define pollutant and give examples of pollutants.
6. What is Threshold Limit Value (TLV)?
7. Describe the hydrological cycle.
8. What is BOD and how is it measured experimentally?

5.2 Environmental Pollution

At the end of this section, you will be able to

- *explain environmental pollution*
- *describe air, water and soil pollution*
- *describe pollutants of air, water and land*
- *describe the effects of air, water and land pollutants*
- *describe some of the main methods used to reduce air pollution*
- *discuss the causes of air, water and land pollution*
- *explain the effects of air, water and land pollution*
- *describe some of the methods used to reduce air, water and land pollution*
- *carry out a project on the effects of an industry on environment*
- *propose safe method of disposing non-biodegradable wastes and*
- *recommend method of preventing pollution caused by over use of fertilizers.*

Activity 5.5

Discuss the following questions in groups and present your opinion to the class.

1. Ethiopia's 2015 Climate Commitment Sets a High Bar for National Climate Action. What was this climate commitment to be taken by Ethiopia?
2. The Copenhagen summit was a popular international climate change summit. What was the role played by Ethiopia? What were the major issues of the summit?
3. Mention any activity in your area to bring awareness of air pollution and global warming. Discuss in your group and present to the class.

Pollution is any discharge of a solid, liquid or gaseous substance or radiation (energy) into an environment that causes unwanted changes. Pollution causes short-term or long-term harm that affects the earth's ecological balance and lowers the quality of life in the environment. A pollutant is any substance that changes air, water or any other natural resource in a way that impairs the use of the resource. Pollutants are discharged into the environment as a result of natural events (like a volcanic eruption) and as a result of human activities (such as the operation of chemical industries, agriculture, etc.). Pollutants can be classified by the type of pollution they cause: air pollution, water pollution, and land pollution.

5.2.1 Air Pollution

Activity 5.6

1. Based on the situation of your locality, discuss the following issues in groups and present the findings to the class:
    a. Explore some human activities which contribute to air pollution.
    b. How do these activities contribute to air pollution?
    c. What solutions do you recommend to overcome these problems?
    d. What could be your contribution to reduce air pollutions?
2. Give your suggestions on the statement, 'Air pollution anywhere is a potential threat elsewhere.'

Atmosphere is considered as solution. Several different gases make up our atmosphere (Table 5.1). Because N_2 (g) is a molecule present in greatest amount in the atmosphere, N_2 is the "solvent" in our atmospheric "solution". The solute present in largest amount is O_2 (g), but certainly there are many others.

Table 5.1: Gases

Name	Percent by volume
Nitrogen	78%
Oxygen	20.95 %
Argon	0.93%
Gaseous water	0 .08 %
Carbon dioxide	0.04% and increasing

Air pollution is caused by the presence of contaminant gaseous substances in the air that affect the lives of plants and animals on earth. Some common air pollutants are sulphur dioxide, nitrogen oxides, carbon monoxide, ozone, hydrocarbons, particulates, chlorofluorocarbons (CFCs), and lead compounds.

Sulphur dioxide (SO_2): - This enters the atmospheric air from the combustion of coal and petroleum, and during extraction of metals from their sulphide ores. It causes coughing, chest pains and shortness of breath. It is thought to be a cause for bronchitis and lung diseases. It slowly oxidizes to SO_3 by reacting with the oxygen in the air.

Oxides of nitrogen: - These can be formed in the atmosphere by natural processes like thunderstorms. Combustion of fossil fuel containing nitrogen compounds as impurities and exhaust gases from furnaces and engines increase the amount of nitric oxide, NO, and nitrogen dioxide, NO_2, in the atmosphere. Nitric oxide, NO, catalyzes the decomposition of ozone in the upper layer of the atmosphere to oxygen, thus decreasing the ozone layer:

$$2O_3(g) \xrightarrow{NO} 3O_2(g)$$

Nitric oxide is oxidized by oxygen to nitrogen dioxide in the presence of ultraviolet light:

$$2NO(g)+O_2(g) \rightarrow 2NO_2(g)$$

SO_2, SO_3 and NO_2 react with rainwater and form sulphurous acid (H_2SO_3), sulphuric acid (H_2SO_4) and nitric acid (HNO_3), respectively and cause acid rain. Acid rain accelerates corrosion and the deterioration of metals, buildings, statues and also causes tree defoliation, release of heavy metal ions from soil into water courses and drop in the pH of water in rivers and lakes.

Hydrocarbons and ozone are responsible for photochemical smog. It is characterized by a reddish-brown haze containing substances irritating to the eye, nose, and lungs, and causes extensive damage to vegetation. Considerable amounts of hydrocarbons are released into the atmosphere by the evaporation of gasoline as un burnt hydrocarbons in auto exhaust. These substances react with ozone to give compounds that contribute to the oxidizing nature of photochemical smog.

Carbon monoxide: - Most of the carbon monoxide escapes into the atmosphere due to the incomplete combustion of fuel. Prolonged exposure to carbon monoxide impairs vision, produces headaches, and exerts strain on the heart. It also reduces the oxygen-carrying capacity of the blood by reacting with hemoglobin.

Particulates: - Dust storms, forest fires, volcanic eruptions and human activities such as mining and burning coal and oil increase the amount of solid particles in the air. Industrial areas contain particles of limestone, fertilizers, coal, stones, cement and silica. These particulates irritate the lungs and deleteriously affect breathing.

Chlorofluorocarbons (CFCs): - Chlorofluorocarbons are used as refrigerants, solvents and plastic foam-blowing agents. When entering the atmosphere, they penetrate into the upper layers and interact with ultraviolet radiation as follows:

$$CF_2Cl_2 \xrightarrow{UV} CF_2Cl\bullet + Cl\bullet$$

The free chlorine, Cl, reacts with ozone to form chlorine monoxide and oxygen:

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$

These reactions result in the conversion of ozone to molecular oxygen and contribute to depletion of the ozone layer. This situation in the upper atmosphere allows dangerous ultraviolet radiation to reach the earth’s surface. This radiation causes skin cancer in human beings.

Volatile Organic Compounds (VOCs): - These are compounds that can easily become gas or vapor. They are mostly released from the burning of gasoline, wood, natural gas, and coal. Other sources of VOCs include thinners and paints, cigarettes, solvents, wood preservatives, air fresheners, furnishings, copy machines and printers, cleaners, pesticides, and disinfectants.

PCBs (polychlorinated biphenyls): - These are organic chlorine compounds that were at one point extensively used as coolant fluids and dielectric in electrical gadgets, in heat transfer fluids, and in carbonless copy papers.

Excess carbon dioxide: - The combustion of coal and petroleum to generate electricity, move our vehicles, heat our homes and supply power to our industrial machinery causes a significant increase in the concentration of carbon dioxide in the atmosphere. Combustion of these fuels releases about 20 billion tonnes of CO_2 annually. The increase in the concentration of CO_2 in the atmosphere has resulted in a rise in the average global temperature, owing to the greenhouse effect. Carbon dioxide and water vapour absorb infrared radiation, re-radiated from the earth, behaving like the glass in a greenhouse. Since CO_2 and water vapor absorb heat, they are called green-house gases. Due to the absorption of heat by the greenhouse gases in the atmosphere, the overall effect is global warming (an increase in the average temperature of our planet). This rise in global temperature causes melting of polar ice and thus additional water flowing into the oceans. This situation, in turn, results in the rising of the levels of seas and oceans, flooding of coastlines and lowland areas, which can submerge these areas.

Heavy metals: Lead contamination in the atmosphere is a result of vehicle engines that use fuels containing tetraethyl lead which is added to the fuel to reduce engine knocking. The use of lead paints also contributes towards lead contamination. High levels of lead cause damage to the brain, kidneys and liver.

What are the potential air pollutants in and around your home?

Methods of Reducing Air Pollution

Activity 5.7

Discuss in groups and present your ideas to the class.

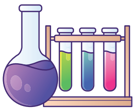
1. Name the major air pollutants.
2. What methods do you recommend to reduce air pollution other than the methods listed below?

The following are some of the ways to reduce air pollution:

- Using public transports
- Turn off the lights when not in use
- Recycle and reuse

- Not to use plastic bags
- Reduction of forest fires and smoking
- Use of fans instead of air conditioner
- Use filters for chimneys
- Implement afforestation
- Avoid using of products with chemicals
- Avoid usage of crackers

5.2.2 Water Pollution



Activity 5.8

1. In your community,
   a. What are the major sources of drinking water?
   b. What are the principal sources of contamination of surface water and ground water?
   c. What could be done to reduce these problems?

   Discuss in groups and present your answer to the class.

Water pollution is the degradation of the quality of water brought by the discharge of untreated sewage, industrial and agricultural waste, and oil spillage. In general, water is said to be polluted if it contains matter that affects the health of living things or causes damage to property. The major water pollutants are nitrate and phosphate fertilizers washed out of the soil, phosphate detergents, untreated sewage, insecticides and herbicides, and the heavy metal ion, acidic and/or basic residues released by industrial processes. Phosphate and nitrate fertilizers washed out of the soil and phosphate detergents from untreated water, enter natural water systems, such as streams, rivers, lakes, and seas. These dissolved minerals are valuable nutrients for plants, and their discharge into the water systems accelerates the growth of surface-water plants, such as algae.As a result, less light reaches the bottom-living plants, which reduces the photosynthesis they need to live, and they die. When these aquatic plants die, they rot under the action of bacteria which multiply greatly and consume the oxygen dissolved in the water at a rate faster than natural aeration or photosynthesis can replenish.

Thus, the amount of oxygen in the water decreases. This depletion of oxygen kills aquatic animals like fish. This sequence of events is called eutrophication. Examples of some of the water pollutant and their descriptions: -

Domestic sewage: Domestic sewage is also a major source of plant nutrients, mainly nitrates and phosphates. Excess nitrates and phosphates in water promote the growth of algae, sometimes causing unusually dense and rapid growths known as algal blooms. When the algae die, oxygen dissolved in the water declines because microorganisms use oxygen to digest algae during the process of decomposition.

Solid waste: The improper disposal of solid waste is a major source of water pollution. Solid waste includes garbage, rubbish, electronic waste, trash, and construction and demolition waste, all of which are generated by individual, residential, commercial, institutional, and industrial activities.

Fertilizers: causes water pollution from excessive amounts of nitrates and phosphate washed out from food and animal waste as well as inorganic fertilizers.

Insecticides (pesticides) and herbicides: Insecticides (pesticides) and herbicides are applied in agriculture may also be washed into lakes, rivers, streams and seas. Some of the insecticides and herbicides do not decompose easily and are persistent in the environment.

Lead: - This is a dangerous toxin found across the world, in fact, in all states. The element readily dissolves in water and upon uptake leads to devastating health problems.

Methods of Reducing Water Pollution

- Treatment of water before discharge into rivers and lakes.
- To avoid unnatural temperature changes in natural water systems, industries should not discharge heat-ladened water into them.
- Recycling industrial and agricultural wastes.
- Using moderate amounts of agricultural chemicals and increasing the use of organic fertilizers and biological methods to control pests.

5.2.3 Land Pollution

Activity 5.9

Discuss the following issues and present your answer to your class.

1. Explain causes of land pollution in your environment?
2. What are the three major things you believe elected officials should take to decrease soil erosion in the region you live?
3. What should be your responsibility in solving the land pollution problems?

Land pollution is caused by things we put into it. It results from the spillage of oil, leaching of harmful chemicals and heavy metal ions, and dumping of non-biodegradable wastes such as plastics.

Causes of Land Pollution

- Spillages of oil from leaking pipelines.
- Harmful heavy metal ions from buried waste leaching into water systems.
- Leaching of harmful chemicals from corroded metal drums which have been buried underground.
- Dumping of non-biodegradable (do not decompose by the action of bacteria) wastes like plastics which remain unchanged in the soil for decades or hundreds of years. Their accumulation in the soil hinders air and water movement and affects the growth of plants.
- Excessive use of synthetic fertilizers in agricultural activities also contributes towards land pollution.

What are the contributions of commercial inorganic fertilizers to land pollution?

Some of the pollutants that cause land pollution and their description:

Garbage: This is one of the significant land pollution causes. In every household, we will find garbage. Tons and tons of garbage are produced by typical and domestic households annually. When that massive amount gets generated, the disposal of it falls short. Consequently, all this garbage gets dumped onto the land. This land of disposal is known as a landfill.

Plastic: - This is one of the most common environmental pollutants and bears one of the greatest impacts. The abundance of plastics in the world even led to the coining of the term “plastic pollution.”

Mercury: - This element is released into the environment due to mining activities, poor disposal of certain items that are either made of mercury or had mercury in them. Batteries are the main source of mercury, which is why it is essential to dispose of them carefully.

Methods of Reducing Land Pollution

Activity 5.10

Discuss in groups and present your opinion to the class.

1. What methods should be practiced in Ethiopian context to reduce land pollution?
2. Propose the potential safe methods of disposing non-biodegradable wastes?

When we deal about methods of reducing land pollution we deal especially with reducing non-biodegradable wastes. This is because non-biodegradable wastes cannot be broken down by decomposers as a result their disposal poses a big problem. Non-biodegradable waste is a major source of soil, air, and water pollution. Besides, it’s cited as the primary cause of serious diseases such as cancer. The following are examples of non-biodegradable waste: glass, medical waste, Plastic, man-made synthetic materials, electronic components, cans, nuclear waste, man-made polymer and artificial rubber.

Project 5.1

Develop a waste water treatment plan for your school and submit it to your teacher.

Exercise 5.2

1. Describe the main agents of:
   a. air pollution b. water pollution c. land pollution
2. What are the impacts/effects of?
   a. air pollution b. water pollution c. land pollution
3. What are the main methods of reducing:
   a. air pollution b. water pollution c. land pollution
4. Describe the potential method of preventing pollution caused by over use of fertilizers
5. How acid rain is formed. Write the reaction that shows formation of acid rain
6. Are pollutants of land can cause air pollution and water pollution? Take one example and show its interdependence?

5.3 Global Warming and Climate Change

At the end of this section, you will be able to

☞ *describe global warming and climate change from the perspective of chemistry*

☞ *list the common greenhouse gases*

☞ *describe greenhouse gases and greenhouse effect*

☞ *discuss about the chemistry of greenhouse gases related to global warming*

☞ *classify greenhouse gases.*

In this sub section, we will discuss the role of several chemical reaction that occur in the atmosphere, as well as direct emissions of some greenhouse gases into the atmosphere which cause to global warming. In general, the relationship between chemistry and climate change will be explored under two headings: global warming and climate change from the standpoint of chemistry, and greenhouse gas chemistry and its impacts on climate change.

5.3.1 Global Warming and Climate Change

Activity 5.11

Discuss in group and present your opinion to your class mates.

1. The role of industrial byproducts to global warming.
2. Types of activities which are carried out in your surrounding that contribute to global warming.
3. In recent years in Ethiopia, the Green legacy has been practiced in the country. What is the relationship between the Green legacy, Global warming and climate change. What other methods used to capture CO_2 from the atmosphere.

Why chemistry is so important in the fight against climate change?

Any human activity has a definite impact on the environment. In this context, climate change is one of the main current concerns and challenges for mankind. Data in our hands reveals the existence of a global warming process and urgent actions are needed before dramatic and irreversible (on a human scale) climate changes could take place. The emission of certain substances to the atmosphere produces a greenhouse effect contributing to the global warming. Even if their origin is diverse, many of these emitted gases or substances resulted from:

Certain type of chemical reaction mainly from combustion of fuel:

$$C_XH_Y + O_2 \rightarrow CO_2 + H_2O + heat\,energy$$

Where X and Y are carbon and hydrogen number of hydrocarbon compound.

- Some of them may be manufactured products like ClFCs, solvents and volatile organic compounds.
- Some of them have a natural origin, as it is the case of methane generated by living organisms, in particular in the oceans.
- In other cases, however, they are associated with human activities. The most well-known is carbon dioxide (CO_2) and its increasing content in the atmosphere is mainly associated with the combustion of fossil fuels.

According to data from the US Department of Energy, global emissions of carbon dioxide resulting from combustion of fossil fuels increased by larger than 10 factor since 1900. A variety of other gases contributes to the greenhouse effect, including solvents, chlorofluorocarbons and other volatile organic compounds (VOCs), or nitrogen and sulphur oxides. Some of them can have, intrinsically, an even greater greenhouse effect than CO_2 but, in general, are released to the atmosphere in amounts significantly lower. Besides, some of them, like nitrogen oxides, are generated concomitantly to CO_2 in combustion.

5.3.2 Chemistry of Greenhouse Gasses and Their Effects on Climate Change

Activity 5.12

Discuss the following questions in group and present your opinion to your class mates.

1. Mechanism in which the greenhouse gases increase average earth's temperature.
2. Reactions of gases occurred in the atmosphere that contributes for global warming?

Greenhouse Effect

The greenhouse effect happens when certain gases, which are known as greenhouse gases, accumulate in Earth's atmosphere. Greenhouse gases include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3), water vapor (H_2O) and fluorinated gases. These gases warm our planet by absorbing infrared (IR) light radiation that would otherwise escape into space. Without this warming effect (called the greenhouse effect), the average temperature on Earth would be a chilly 255 K (that's -18 ^oC, or the temperature on an extremely cold winter day). Because these greenhouse gases in our atmosphere absorb IR light, Earth's average temperature is 288 K (that's 15 ^oC, about the temperature on a slightly cool spring day). Thus, Earth is 33 K warmer than what would be expected if there was no the greenhouse effect.

For example, CO_2 (g) and H_2O (g) do absorb IR light and upon doing so gain energy which is transferred to the rest of the Earth. Even though these gases are present in small amounts, they are very good at absorbing infrared light. Thus, these atmospheric gases are the main contributors to the greenhouse effect. On the other hand, both N_2(g) and O_2 (g) are present in very large amounts in the atmosphere, these gases do not absorb IR light and therefore do not contribute to the greenhouse effect.

Contribution of Greenhouses Gases for Global warming

Do you know which greenhouse gases that human produce have the most impact on global warming?

Not all have the same effect, nor do they come from the same sources, and in the same way each lasts for a different time in the atmosphere. Other variables such as the formation of water of anthropogenic origin and black carbon in snow for their lesser effect are excluded. There are five gases of human origin that contribute most – together up to 95% of the total – to the increase in global warming. Here you will discover the source of their emission, the time they spend in the atmosphere and what percentage they contribute to the greenhouse effect in the following table.

Table 5.2: Sources, atmospheric life time and percentage of contribution of greenhouse gases

Greenhouse gas	The sources of their emission	Time spent in atmosphere	% stage of contribution to global warming
Carbon dioxide	Result of processes such as fuel use, deforestation and production of cement and other materials.	80% lasts for 200 years and the other 20% can take up to 30,000 years to disappear	52.92 %
Methane	Generated by activities such as livestock production, agriculture, sewage treatment, natural gas and oil distribution, coal mining, fuel use and is also given off from waste tips	It lasts an average of 12 years in the atmosphere	14.88 %
Halogenated compounds (CFCs)& HCFCs	Results from the production of chemicals by diverse sectors such as refrigeration and air conditioning, electrical and electronic equipment, medicine, metallurgy, and so on	Depending on the type of compound, their duration in the atmosphere varies from a few months to tens of thousands of years	10.78 %

Tropospheric ozone	This is a product of the reaction between the gases carbon monoxide (CO), nitrogen dioxide (NO_2) and VOCs (Volatile Organic Compounds), given off during the burning of fuels	These gases don't last as long in the atmosphere as others, a matter of months at the most.	10.72 %
nitrous oxide	It comes mainly from the use of fertilizers, fuel use, chemical production and sewage treatment	Lasts longer in the atmosphere, up to 114 years.	10.70 %

Exercise 5.3

1. Write the general chemical reaction equation that express combustion of fuel and result in increasing of global warming.
2. List an example of greenhouse gases that contribute for Global warming from anthropogenic and natural sources.
3. Describe the composition of the atmosphere.
4. Describe the mechanism how greenhouse gases increase global warming.

5.4 Green Chemistry and Cleaner Production

At the end of this section, you will be able to

- *define the terms green chemistry and cleaner production*
- *discuss on the major principles of green chemistry and cleaner production*
- *list the importance of cleaner production*
- *explain atom economy*
- *calculate the atom economy based on the given chemical reaction*
- *apply green chemistry principles while doing laboratory activities*
- *apply atom economy principle during designing chemical reactions*

Activity 5.13

Discuss the following issues in group and present your opinion to the class.

1. What do you do to “green” your day? How does this suggestion reduce your ecological footprint?
2. Brainstorm the criteria for a “green” product.

What does it mean when you say **“**Green chemistry and cleaner production”? Have you looked around?

Think about all of the different substances that you deal with on a daily basis. Consider your notebook or the materials that help to deliver power to your calculator. How was the cover of your notebook made? What will happen to it when you throw it away? What materials were used to make the batteries or the solar cells in your calculator? What will happen to these materials once they no longer work properly?

We are surrounded by a huge variety of materials with a wide range of chemical and physical properties. We are continually developing processes to create products with desired properties. Our ability to manufacture materials provides many conveniences, but also some drawbacks. We are using raw materials at an alarming rate. We are also discarding hazardous chemicals into our landfills or incinerating them and releasing chemicals into our atmosphere.

We are starting to understand more about the hazards of chemical processes. Industries in many countries are now paying attention to the fuels and raw materials they use and the by-products they release along with their intended products. Sometimes manufacturers simplify processes to fewer steps. This has many benefits, including reducing waste. Processes are burning less fuel, using fewer toxic reactants, and releasing fewer unwanted by-products. Industry is attempting to become “greener.”

In this sub section the principles of green chemistry and cleaner production will be discussed in detail.

5.4.1 Principle of Green Chemistry

Activity 5.14

Discuss in groups and present your opinion to the class.

1. How does green chemistry differ from cleaning up pollution?
2. Use of renewable feedstock is one of the principles of green chemistry, and can be accomplished by increasing awareness of sustainability in our modern society that led to switch to the use of biomass as a feedstock and an energy source. What are other examples of renewable feedstock in your surroundings? and an energy source. What are other examples of renewable feedstock’s in your surroundings?

“Green chemistry” is a movement to make industries that involve chemicals more environmental friendly and sustainable. Green chemistry asks the question: “Why generate pollution if there is a greener alternative?”

Developing a green alternative begins with considering the hazards of the required chemicals as well as their properties. Chemists then develop a manufacturing process so that every stage of product development is environmentally safe—from the raw materials to what happens to the product at the end of its useful life. In other words, the process is “benign by design.”

A green chemistry solution may involve using safer chemicals. Liquid carbon dioxide, for example, is starting to replace toxic organic solvents used in dry cleaning. Greening a chemical process can also involve making a process more efficient. For example, the original makers of ibuprofen, an important pain reliever, found a way to make the drug in half the number of steps. The result is a process that generates less waste, uses less energy, and is more profitable! The “12” principle of green chemistry which are listed below directly or indirectly involves both modern methods of pollution control mechanism and cleaner production.

The “12” Principles of Green Chemistry

1. Prevention

The proper definition says that it is better to prevent waste than to treat or clean up waste after it has been generated. Generally, it describes the ability to update chemical transformations in order to limit the generation of hazardous waste as a significant advancement towards contamination or pollution avoidance.

By preventing waste generation, the risks associated with waste storage, transportation, and treatment could be limited. A solid example can be the pulp and paper industry, usage of chlorine compounds in processes produce toxic chlorinated organic waste. Green chemistry developed a method to convert wood pulp into paper using oxygen, water, and polyoxometalate salts while producing only water and carbon dioxide as by-products. Isn’t that great?

Simply, “Less Waste is directly proportional to Less Pollution”.

2. Atom Economy

The Atom economy is a primary criterion for green chemistry. The idea of the atom economy is to improve chemical processes, by avoiding the waste of atoms from reactants to products. Atom economy can be assessed easily by calculating the number of atoms in the Chemical Reaction. Atom Economy is the ratio of “the mass of the desired product” by “the total mass of the products”, and can be expressed in percentage as illustrated in the formula below.

Assume for a reaction:

$A + B \rightarrow C + D, where\ ‘C’\ is\ the\ desired\ product$ and ‘D’ is the by-product

The Atom Economy can be calculated as,

$$Atom\,economy = \left[\left(Mass\,of\ C\right) / \left(Mass\,of\ C + D\right)\right] * 100$$

For an optimal process, the atom economy should be near or equal to 100%.

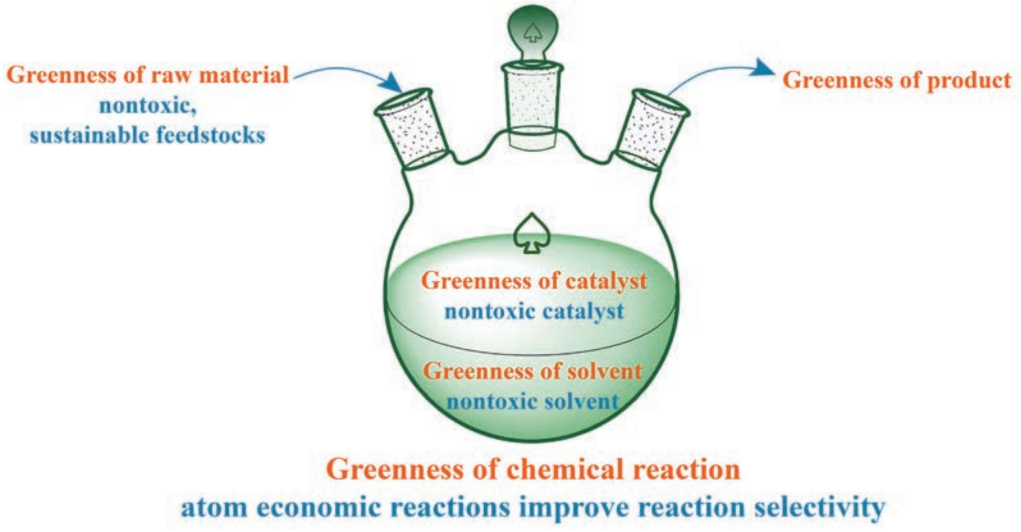


Figure 5.8: simple diagrams which shows atom economic reaction

Atom economy beneficial to promote the atom economy as it helps in: minimizes the waste, and reduces the cost associated with waste management and treatment; simplifies storage and transportation; minimizes potential pollution problems and prevents companies from illegal pursuits and reduces emissions, etc.

3. Less Hazardous Chemical Synthesis

- Wherever practicable, synthetic methods should be designed to use or generate chemicals that pose little or no toxicity to the environment and human health.
- The goal should be to avoid reactions that give hazardous by-products.

4. Design of Safer Chemicals

The design of safer chemicals deals with the rendering of chemicals which fulfill their intended purpose and yet are benign and harmless to the ecosystems. This modification should be reflected up to the molecular level of the chemical’s design.

5. Safer Solvent and Auxiliaries

Most of the industries from polymer to pharmaceutical industries and other chemical allied industries use solvents at some point in their manufacturing. In general, the use of solvents should be avoided, but that is not possible in all cases. So we can possibly replace toxic, non-recyclable solvents with safer and innocuous solvents.

6. Design for Energy Efficiency

Recognition of the energy requirements, their impact on the environment and economy, and its minimization to the extent possible will pave way for a greener process. Processes should be carried out at ambient conditions that means run chemical reactions at room temperature and pressure whenever possible. Some ways in which this can be achieved are well-maintained equipment in plants, recovery of waste heat, and removal of solvents, proper utilization of catalysts, and combined heat and power (CHP).

7. Use of Renewable Feedstock

Use starting materials (also known as feedstock's) that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products or the wastes of other processes; the source of depletable feedstock's is often fossil fuels (petroleum, natural gas, or coal) or mining operations.

8. Reduce Derivatives

In this principle, "the reaction takes place at a particular functional group blocking unnecessary waste generation "by reducing the process steps with the use of enzymes, catalysts, or solvent, therefore, reducing demand for feedstock and utilities required for down-streaming hence increasing overall economy and efficiency of the process.

For example, the synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (see Figure 5.9). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

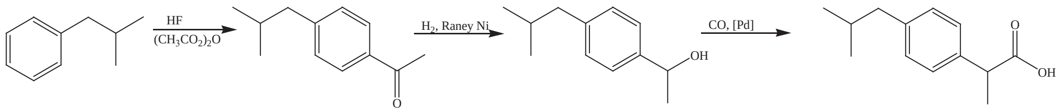


Figure 5.9: The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy

9. Catalysis

Catalysis is one of the most important pillars of Green Chemistry. “Stoichiometric” technologies are the primary source of waste; on the other hand, “Catalytic Processes” are achieving the goals of environmental protection and economic benefit.

Catalysts provide many benefits from lower energy consumption to increase selectivity of the reaction and allow a decreased use of harmful and toxic chemical agents.

Zeolites, Clays are promising and benign catalysts used in Heterogeneous Catalysis, which can replace the use of harmful catalysts. Enzymes are Biocatalysts which are natural substances derived from biological sources, are renewable and Biodegradable. Catalysis can help us build a more sustainable world and can play a major role to mitigate the global environmental impacts of unsustainable chemical processes.

10. Design for Degradation

This principle stands for, “Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment”. That means during the usage of chemicals it should be stable and do not persist the environment but after usage, it should be degraded into small molecules that are not harmful to the environment and humans.

Figure 5.10: Simple illustration of biodegradable product

11. Real-time Analysis for Pollution Prevention

Just like watching the live news telecast i.e., in real-time makes it better to understand and act best according to the situation. Real-time analysis in Chemical and allied industries are essential for production, transportation, and especially in the case of pollution prevention. Pollution in the industrial premises could become a potential threat to various probable hazards. The real-time analysis opens the scope of online process control and prevents any possible threats hence increasing overall profit to the industry as well as ensures safety to the environment. It Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Inherently Safer Chemistry for Accident Prevention

It involves choosing a safe or safer chemical to mitigate the chances of occurrence of an accident. It benefits the industry as well as the environment as it acts as a safeguard against calamitous industrial or laboratory accidents. Avoidance of hazard is the key.

5.4.2 Cleaner Production in Chemistry

Activity 5.15

Consider any chemical reaction do think that one gram of reactants produces one gram of a product/s? If not why? Discuss in groups and present your opinion to the class.

An ideal chemical reaction should have a number of attributes such as safety, simplicity , selectively, high yield, energy efficiency, use of renewable or recyclable raw materials and reagents, and absence of hazardous byproducts or at least minimizing or containing them.

In practice, it is impossible to achieve all these attributes simultaneously. Indeed it is a challenge for chemists and engineers to identify environmentally preferable reaction pathways that optimize the balance of all the desirable attributes.

Goals of Green Chemistry from the perspective of cleaner production

The goals of "green chemistry" from cleaner perspective include the following:

1. to reduce adverse environmental impacts by appropriate and innovative choice of materials and their chemical transformation
2. to develop processes based on renewable (plan-based) rather than non-renewable (fossil carbon –derived) raw materials
3. to develop products that are less toxic or which require less toxic raw materials/feedstock's
4. To develop products that degrades more readily /rapidly in the environment than the current products.
5. to reduces the requirement for hazardous or environmentally persistent solvents and extraction in chemical processes
6. to improve energy efficiency by developing low temperature and low pressure processes by using new/improved catalysts
7. to minimize byproducts in chemical transformation through redesign of reactions and reaction sequences. In other words, to achieve better" Atom economy"

$$\text{\% of atom economy} = \left(\frac{\text{Formula weight of the product}}{\text{sum of formula weights of all the reactants}} \right) * 100$$

Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment. It is better to see atom economy in detail with illustrative example below:

Atom economy: The atom economy (a measure of atom utilization or efficiency) is a measure of the amount of starting materials that end up as useful products. It is important for sustainable development and for good economic reasons to use reactions with high atom economy. A chemical reaction may give, and often does, more than one product, but of the mixture of products, perhaps only one of them is the desired useful product. The percentage atom economy of a reaction is readily calculated using the balanced equation for the reaction expressed in reacting masses.

The atom economy of a reaction is a theoretical percentage measure of the amount of starting materials that ends up as the 'desired' useful reaction products. It's sometimes referred to as atom utilization.

$$\text{Atom economy} = 100 * \frac{\text{Mass of desired or useful product}}{\text{Total mass of all reactants or products}}$$

In atom economy calculations you can say reactants or products because of the law of conservation of mass. The greater the % atom economy of a reaction, the more 'efficient' or 'economic' it is likely to be. Many reactions give more than one product, and not all of them are useful, so it is useful to calculate what % of the products is theoretically useful, and we call this the atom economy of the reaction. The reactions that only give one product, have the maximum atom economy of 100% and these are the most economic reactions e.g. synthesis of ammonia and reacting ethene with water to make ethanol.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \text{ and } CH_2 = CH_2 + H_2O \rightarrow CH_3CH_2OH$$

Example

Example of calculation of atom economy:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

Using the atomic masses of Fe = 56, C = 12, O = 16, we can calculate the atom economy for extracting iron based on the above reaction.

Solution:

[(2 x 56) + (3 x 16)] + [3 x (12 + 16)] → [2 x 56] + [3 x (12 + 16 + 16)]

[160 of Fe_2O_3] + [84 of CO] → [112 of Fe] + [132 of CO_2]

so, there are a total of 112 mass units of the useful/desired product iron, Fe, out of a total mass of reactants or products of 160 + 84 = 112 + 132 = 244.

Therefore, the atom economy = 100 x 112 / 244 = 45.9%

Note**:** It doesn’t matter whether you use the total mass of reactants or the total mass products in the calculations; they are the same due to the law of conservation of mass.

Why the reaction with only one product will always give the highest atom economy?

Exercise 5.4

1. Give examples of a green chemistry solution that involve safer chemicals.
2. Explain what cleaner production means?
3. Which principle of green chemistry best explained in cleaner production?
4. Which one is the aim of green chemistry?
    a. Design chemical products and process that maximize profits
    b. Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances
    c. Design chemical products and processes that work most efficiently
    d. Utilize non-renewable energy
5. Which of the following is a challenge for green chemists?
    a. Awareness of the benefits of green chemistry
    b. Developing chemicals that are recyclable
    c. Training for cleaning up chemical spills
    d. Knowing when to reduce and eliminate hazardous waste
6. Environmental benefits of green chemistry include?
    a. Fewer raw materials and natural resources used
    b. Cleaner production technologies & reduced emissions
    c. Smaller quantities of hazardous waste to be treated and disposed of
    d. All of the above
7. Calculate the atom economy of the fermentation of sugar to make ethanol ('alcohol')

$$\underset{\text{Ethene}}{H_2C{=}CH_2\ (g)} + H_2O\ (g) \xrightarrow[573\ \text{k/60 atm}]{H_3PO_4} \underset{\text{Ethanol}}{CH_3CH_2OH\ (g)}$$

Unit Summary

- Environmental chemistry encompasses a number of fields of chemistry and chemical processes that take place in soil, water, air, and in living systems.
- Environmental chemistry is the branch of chemical science that deals with the production, transport, reactions, effects, and fates of chemical species in the water, air, terrestrial, and biological environment and the effects of human activities thereon.
- The environment consists of various compartments, including: atmosphere, hydrosphere, lithosphere and biosphere
- Examples of some important reaction in the biosphere:
- Photosynthesis: $6CO_2 + 6H_2O \xrightarrow{sunlight} C_6H_{12}O_6 + 6O_2$ and
- Respiration: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Heat\,energy$
- Pollutant: A substance whose concentration has increased due to human activity, ultimately having detrimental effects on the environment
- Pollution is any discharge of a solid, liquid or gaseous substance or radiation (energy) into an environment that causes unwanted changes.
- Pollutants can be classified by the type of pollution they cause: air pollution, water pollution, and land pollution.
- Air pollution is caused by the presence of contaminant gaseous substances in the air that affect the lives of plants and animals on earth
- Some common air pollutants are sulphur dioxide, nitrogen oxides, carbon monoxide, ozone, hydrocarbons, particulates, chlorofluorocarbons (CFCs), and lead compounds.
- Water pollution is the degradation of the quality of water brought about by the discharge into it of untreated sewage, industrial and agricultural waste, and oil spillage.

- The major water pollutants are nitrate and phosphate fertilizers washed out of the soil, phosphate detergents, untreated sewage, insecticides and herbicides, and the heavy metal ion, acidic and/or basic residues released by industrial processes
- Land pollution is caused by things we put into it. It results from the spillage of oil, leaching of harmful chemicals and heavy metal ions, and dumping of non-biodegradable wastes such as plastics.
- The emission of certain substances to the atmosphere produces a greenhouse effect contributing to the global warming. The greenhouse effect happens when certain gases, which are known as greenhouse gases, accumulate in Earth's atmosphere.
- Greenhouse gases include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3), and fluorinated gases.
- Because N_2 (g) is the compound present in greatest amount in the atmosphere, N_2 is the "solvent" in our atmospheric "solution". The solute present in largest amount is O_2 (g), but certainly there are many others.
- "Green chemistry" is a movement to make industries that involve chemicals more environmentally friendly and sustainable.
- Developing a green alternative begins with considering the hazards of the required chemicals as well as their properties
- A green chemistry solution may involve using safer chemicals.
- One of the principles of green chemistry, chemists should develop a manufacturing process so that every stage of product development is environmentally safe—from the raw materials to what happens to the product at the end of its useful life.

$$\text{\% of atom economy} = \left(\frac{\text{Formula weight of the product}}{\text{sum of formula weights of all the reactants}}\right) * 100$$

- Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment)

CHECK LIST

KEY TERMS

- *Key terms of the Unit*
- *Agents of land pollutant*
- *Agents of water pollutant*
- *Air pollutant*
- *Air Pollution*
- *Atom Economy*
- *cleaner production*
- *Climate Change*
- *Climate Change*
- *Components of environment*
- *Contaminate*
- *Environmental chemistry*
- *Environmental Pollution*
- *Global Warming*
- *Green Chemistry*
- *Greenhouse effect*
- *Greenhouses Gasses*
- *Land Pollution*
- *Pollutant*
- *Principle of Green chemistry*
- *Safer solvent*
- *Sink*

REVIEW EXERCISE FOR UNIT 5

Part I: Write True if the statement is true and false if the statement is false

1. Green chemistry can provide green technology solutions for a sustainable future?
2. Bio-catalysis has become very useful in green chemistry manufacturing?
3. Green chemistry is more expensive than traditional chemistry?
4. Pollutant is a substance, whose concentration has increased due to natural activity.
5. It is better to prevent waste than to treat or clean up waste after it has been generated is one of the important principles of green chemistry.

Part II: Choose the best answer for the following questions among the given alternatives

1. Green chemists reduce risk by?
   a. Reducing the hazard inherent in a chemical product or process
   b. Minimizing the use of all chemicals
   c. Inventing technologies that will clean up toxic sites
   d. Developing recycled products
2. The first listed of the 12 Principles of Green Chemistry is?
   a. Prevent waste
   c. Atom economy
   b. Catalysis
   d. Benign solvents
3. Which of the following is the greenest solvent?
   a. Formaldehyde
   c. Ethanol
   b. Benzene
   d. Water
4. _________ is an excellent 'green' solvent as well as a greenhouse gas?
   a. Methanol
   c. Carbon monoxide
   b. CFCs
   d. Carbon Dioxide
5. Benzene, a ________ substance, is an important industrial solvent used in the production of pharmaceuticals, plastics, and dyes?
   a. Odorless
   c. Biodegradable
   b. Non-flammable
   d. Carcinogenic

6. The gases that contribute to the greenhouse effect on Earth are, in order of greatest to smallest in importance

   a. CO_2, H_2O, CH_4
   c. CH_4, CO_2 , H_2O
   b. H_2O, CO_2, CH_4
   d. H_2O, CH_4 , CO_2

7. Which of the following is an example of impact of development activities on the hydrosphere?

   a. Air pollution
   c. Soil erosion
   b. Soil pollution
   d. Water pollution

8. What is the source of carbon monoxide?

   a. Incomplete burning of wood
   c. Exhaust fumes of motor vehicles
   b. Fuels
   d. All of above

9. What is the source of sulfur dioxide?

   a. PowerStation's and industries using fossil fuels
   b. Exhaust fumes of motor vehicles
   c. Incomplete burning of wood
   d. None of above

10. Which of the following will not cause any atmospheric pollution?

    a. Hydrogen
    c. Carbon dioxide
    b. Sulphur Dioxide
    d. Carbon monoxide

11. Photochemical smog is related to the pollution

    a. Soil
    b. Water
    c. Noise
    d. Air

12. The largest reservoir of nitrogen in our planet is:

    a. Ocean
    c. Biosphere
    b. Atmosphere
    d. Fossil fuels

13. Most important causative pollutant of the soil/land

    a. Plastics
    c. Detergents
    b. Iron junks
    d. Glass junks

14. Depletion of ozone layer is due to oxide of

    a. Carbon
    b. Phosphorus
    c. Nitrogen
    d. None

15. Greenhouse effect is caused
    a. Those gases which absorb the infrared light reflecting from earth
    b. CH_4, SO_2 and NO_2
    c. CO_2 only
    d. None of the above
16. The result of ozone hole is
    a. Acid rain
    b. Global warming
    c. The UV radiations the earth
    d. Greenhouse effect
17. Which of the following gases contribute to the global warming?
    a. Carbon monoxide
    b. Sulphur dioxide
    c. Carbon dioxide
    d. Nitrogen dioxide
18. Which of the Following Greenhouse Gases Is Present in Very High Quantities?
    a. Carbon dioxide
    b. Ethane
    c. Propane
    d. Methane
19. Burning of Fossil Fuels Results In
    a. Increased oxygen level
    b. Decreases greenhouse gases
    c. Increased greenhouse gases
    d. Increased ethane level
20. One of the following is Naturally Occurring Greenhouse Gas?
    a. Nitrous oxide
    b. Methane
    c. Carbon dioxide
    d. Ethane
21. $$N_2 + O_2 \rightarrow 2NO$$
    $$2NO + O_2 \rightarrow 2NO_2$$
    $$NO_2 \rightarrow NO + O$$
    $$O + O_2 \rightarrow O_3$$
    The above reactions describe the chemical process that forms:
    a. Photochemical smog
    b. Industrial smog'
    c. Acid precipitation
    d. Ozone
22. One of the following is not true about the role of catalyst in cleaner production?
    a. Allows a decreased use of harmful and toxic chemical agents
    b. Enzymes are Biocatalysts are not renewable and Biodegradable
    c. Increased selectivity of the reactions
    d. Lower energy consumption

Part III: Give Short Answer for the following Questions

1. Why is it called the “greenhouse” effect?
2. Do all greenhouse gases have the same effect?
3. Carbon monoxide is more dangerous than carbon dioxide. Why?
4. List common water, air and soil pollutant?
5. Describe the mechanism to reduce, water, air and soil.
6. What is greenhouse effect? Which gas is mainly responsible for global warming?
7. What is atom economy? What implies that the reaction has good atom economy?
8. Write at least 5 Green chemistry principle most commonly practiced in your surrounding?

Part IV. Do the following problems.

1. Write a brief note about “What does “Green chemistry and cleaner production mean?”
2. Write a brief note on adverse effects of specific metal pollutants.
3. Consider the following three reactions “A”, “B” and “C”:

   Reaction A: converting ethanol to ethene
   Reaction B: ethene + water ===> ethanol
   Reaction C: fermentation of sugar to make ethanol (‘alcohol’)

   Calculate the atom economy of the above reaction A, B and C. Both reaction B and C are gives the same desired product ethanol, which is more environmental friendly? And give your reason?