Republic of Iraq
Ministry of Education
General Directorate of Curricula

Chemistry

Sixth Scientific Grade

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Fourth Translated Edition 2025 / 1447

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Translated from 8th Arabic Edition

Introduction

The chemistry textbook - for the sixth scientific grade represents the final stage in the series of chemistry books for the secondary level - at its intermediate and preparatory level. The committee in charge of writing this book made an effort to implement the objectives and terms stipulated in the following:

the content of the book have a direct and close link between the chemistry curricula at the secondary level and its counterparts at the undergraduate level in all branches. The book includes modern theories and principles, and practical and mathematical applications for most of them.

This book includes an introduction to mathematical relations in chemistry that students used in previous years. It includes eight chapters. The first chapter deals with the chemistry of the thermodynamic and its three laws related to energy, equilibrium, and thermodynamic functions. The second chapter explains the topic of chemical equilibrium, which introduces the topic of ionic equilibrium covered by the third chapter. As for the fourth chapter, it dealt with the topic of oxidation, reduction, and electrochemistry, where a full explanation of electrochemical cells, their types, and Faraday's laws were presented. The fifth chapter deals with the topic of harmonic chemistry. As it explains the principles of this topic from the harmonic complexes, their nomenclature and theories. The sixth chapter deals with the methods of qualitative and quantitative chemical analysis and their ramifications from the gravimetric and volumetric analysis processes. The last two chapters dealt with the topics of organic chemistry of substitution compounds and biochemistry. The book's chapters covered the different branches of chemistry, analytical, inorganic, physical, organic, and life, to qualify students for entry to the undergraduate level. And they have a solid scientific base in which to complete their scientific career.

The committee appreciates the efforts of the scientific experts, Dr. Fadel Salim Matta and Dr. Taqi Al-Din Hadi Hamdan.

The committee also thanks Mrs. Kholoud Mahdi Salem for her assistance in carrying out this work. Likewise, the committee sincerely hopes to provide the General Directorate of Curricula on its website with everything serious contribution to raising the scientific level of chemistry for our dear students ...

Allah is the Grantor of success

Authors

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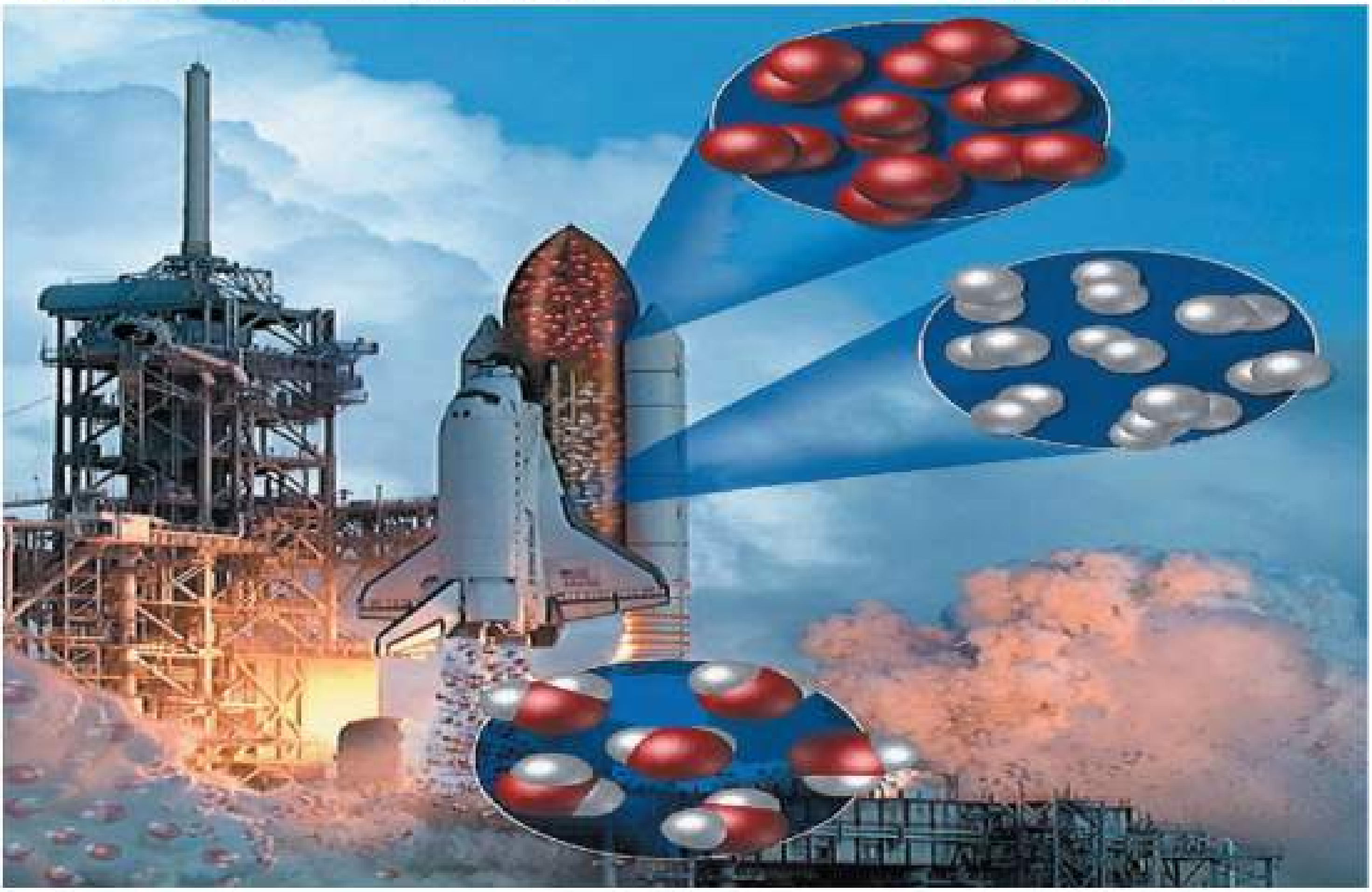
THERMODYNAMICS

CHAPTER-1



ACHIEVEMENTS

After completing this chapter, the student is expected to :

* Define thermodynamics, energy, units of energy, system, environment, universe, types of systems, dynamics, heat, heat capacity, and specific heat concepts. They try to define the heat of reaction measured at constant pressure.

* Learn what enthalpy means and its relationship with heat of reaction and also units of enthalpy.

* Decide whether the reaction is endothermic (heat absorbing) or exothermic (heat releasing) with respect to the sign of enthalpy.

* Write the heat equation with respect to rules and tell its difference from chemical equation.

* Differentiate standard enthalpy of reaction, standard enthalpy of formation and standard enthalpy of combustion concepts.

* Learn the methods to calculate enthalpy of reaction.

* Learn entropy and free energy concepts.

* Define absolute entropy, standard entropy of formation and learn how to calculate Gibbs free energy.

* Understand Gibbs free energy equation and decide the direction of reaction depending on enthalpy and entropy values.

Chapter - 1

1-1-PREFACE

During our studies, we have encountered a few types of energy. For example, heat energy, electric energy, mechanical energy, light energy, nuclear energy, chemical energy, etc. These different types of energy are stored inside all matter and they are released when the matter changes form. Although types of energy are different, a type of energy isn't independent of another. Under certain conditions, a type of energy can be transformed into another.

Thermodynamics is the branch of science which studies energy and its transformation. For example, it studies the transformation of heat energy from combustion of fuel into mechanical energy which runs the engines. Thermodynamics explains many phenomena. The most significant of those are:

1-The reason of occurrence of chemical reactions

2-Estimates the chemical and physical changes that one or more substances undergo under certain conditions

3-The reason why some reactions occur spontaneously while some don't under the same conditions.

4-The reason why the energy accompanying reactions is sometimes given to reaction while sometimes it is released as a result of the reaction.

On the other hand, thermodynamics isn't interested in time factor in which reactions occur. It only studies if a certain reaction (or more generally, if any change will occur) will occur or not. The rate of change is in the field of kinetics.

We can generally divide energy into two. One is potential energy, the other is kinetic energy. Potential energy includes chemical energy stored in all substances and fuels. Kinetic energy is the energy which molecules, moving water, cars, planes, missiles and others have due to their movement. For example, the potential energy in water is transformed into kinetic energy if its movement starts from the top of a fall. Resulting energy can move blades of a turbine to produce electric energy. Therefore, the first law of thermodynamics states the following: "Energy can be neither created nor destroyed, from scratch but can change form."

1-2-UNITS OF ENERGY AND TEMPERATURE

According to International System of Units (SI), the unit which defines energy, joule (its symbol J) is shown as follows:

$1J = 1\ kg.m^2/s^2$

Kg is kilogram, m is meter, s is second.

In thermodynamics, unit of temperature is Kelvin (K). This unit is converted from centigrade (°C) according to the following equation:

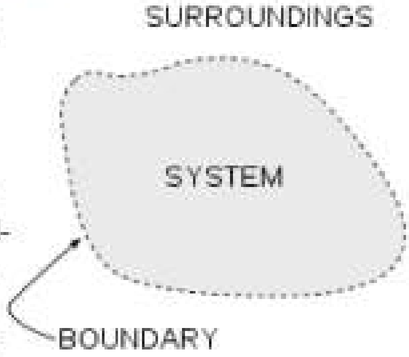
$T(K) = t(°C) + 273$

1-3-SOME THERMODYNAMICS TERMS

The most important thermodynamics term is thermodynamic system. This is a part of the universe we are studying. System consists of substance or substances which participate in limited physical and chemical changes within certain boundaries. The area outside these boundaries is called as surroundings. System and its surroundings are called as universe. Here we will use the term cluster.

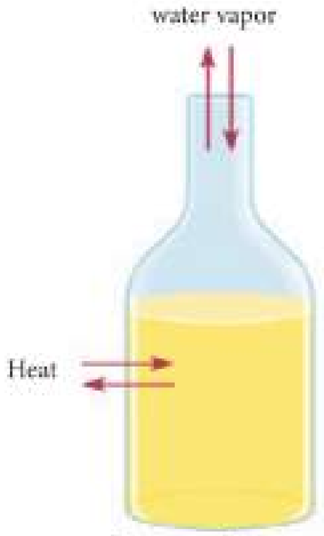
Cluster = System + Surroundings

We can divide system into three according to the relationship between system and surroundings. These are:



1-Open System

If the boundaries allow matter and energy interchange between system and surroundings, system is called as an **open system.** For example, boiling water in a metal container. Water is distributed around surroundings as vapor. Besides, heat of water is also released. That means there is an interaction of matter and energy.



Energy and matter interchange occur

2-Closed System

If boundaries allow only energy interchange but doesnt change the amount of matter, it is a **closed system.**
A metal container which is tightly closed is a good example. In this case, although heat of water is released through surroundings, the amount of water remains unchanged.

Only energy interchange occur

3-Isolated System

If system boundaries allow neither energy nor matter interchange with its surroundings, it is called as an **isolated system.** Thermoses are good examples as they prevent heat and amount of matter being released from system.

No energy and matter interchange occur

Physical states of matter as number of moles of substances in the system, physical variables of system which can be observed and measured, volume, pressure and temperature are called as system properties.

1-4-HEAT

Heat is one of the common energy types in our daily lives. We show heat with (q). Heat is the energy change between two objects with different degrees of temperature. Temperature is a measurement of heat energy. Lost or gained heat energy of any object is directly proportional to change in degrees of temperature. Change is shown with (Δ).

$\Delta T = T_f - T_i$

T_f is final temperature. T_i is initial temperature. The relationship between heat and temperature can be written as follows:

(1) $q \propto \Delta T$

In order to convert this ratio to an equation, ΔT is multiplied with a ratio constant called as heat capacity (C).

(2) $q = C \times \Delta T$

Heat capacity is the amount of heat necessary to increase the temperature of m gram m(g) of substance by 1 °C. Its unit is (J/°C). Heat capacity is related to specific heat (ς)* with the following relationship:

* latinic letter (ς) read (zeta)

(3) $C = \varsigma \times m$

Specific heat is the amount of heat necessary to increase the temperature of 1 gram of substance by 1 °C. Its unit is (J/g.°C). By inserting value of C in Equation 3 into equation 2, we get the following relationship.

$q\ (J) = \varsigma\ (J/g.°C) \times m\ (g) \times \Delta T\ (°C)$

Table 1-1

Specific Heat values of some substances at 25 °C

Substances	Specific Heat
Water(liquid)	4.18
Ethyl alcohol	2.44
Water (solid)	2.01
Water (gas)	2.03
Beryllium	1.83
Magnesium	1.023
Aluminum	0.90
Calcium	0.65
Iron	0.45
Strontium	0.30
Silver	0.24
Barium	0.20
Lead	0.13
Gold	0.13

Example 1-1

What is the amount of heat in (KJ) unit necessary to increase the temperature of 870 g of piece of iron from 5 °C to 95 °C? (specific heat of iron 0.45 J/g.°C)

Solution:

Change in degree of temperature:

$\Delta T = (T_f - T_i)\ °C = (95 - 5)\ °C = 90\ °C$

Heat q is calculated using the following equation.

$q\ (J) = \varsigma\ (J/g.°C) \times m\ (g) \times \Delta T\ (°C)$

$q\ (J) = 0.45\ (J/g.°C) \times 870\ (g) \times 90\ (°C) = 35235\ J$

The amount of heat consumed by piece of iron is calculated as kJ:

$$q(kJ) = q\ (J) \times \frac{1(kJ)}{1000\ (J)}$$

$$q(kJ) = 35235\ (J) \times \frac{1(kJ)}{1000\ (J)} = \mathbf{35.2\ kJ}$$

Exercise 1-1

205 J of heat was given to 10 g of magnesium metal. The temperature was raised from 25°C to 45°C. Calculate the specific heat of magnesium.

Answer: 1.03 J/g.°C

1-5-ENTHALPY CHANGE

Most of the chemical reactions occur under constant pressure. Few reactions occur at constant volume. Therefore, constant pressure is preferred to constant volume while measuring heat accompanying chemical reaction. Under constant pressure, the change in heat of reaction is called as enthalpy of reaction is shown with (H) and enthalpy change is shown with ΔH. This value is equal to the heat of reaction under constant pressure. In other words

$\Delta H = q_p$

q_p shows measured heat under constant pressure.

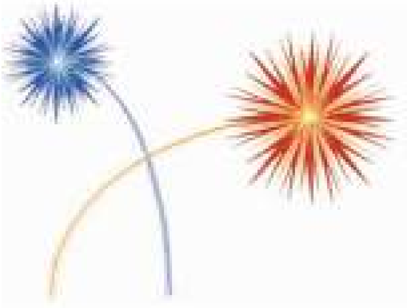
When a chemical reaction is considered as a system, enthalpy change shows if the reaction is endothermic (heat absorbing) or exothermic (heat releasing). If enthalpy of reaction is shown with ΔH_r, we can express the following:

-If ΔH_r is less than zero ($\Delta H_r < 0$) or ($\Delta H_r = -$), the reaction is exothermic.

-If ΔH_r is greater than zero ($\Delta H_r > 0$) or ($\Delta H_r = +$), the reaction is endothermic.

It seems that change in enthalpy of reaction is equal to the following equation:

$\Delta H_r = \Delta H \text{ (Products)} - \Delta H \text{ (Reactants)}$



The reaction occurring during explosion of fireworks is exothermic.

1-6-STATE FUNCTION

Without considering the path followed, the property or amount which depends on the difference between initial state of system before change and final state of system after change is called as **state function.** As an example for state function, enthalpy can be given. Later we will see other functions as entropy, free Gibbs energy, etc. (Figure 1-1)

Figure 1-1

State function depends only on the initial and final states of the system. It doesn't depend on the path the system follows. In the picture, The increase in potential energy that occurs when a mountain climber climbs from base to the top does not depend on the path taken.

Values of heat or work change with respect to the conditions of experiment change. Therefore it isn't accepted as a state function. Heat and work is related to the path followed and steps during change occurs. It is impossible to measure their state functions. But the amount of change (Δ) of these functions can be measured. For example, we can't measure absolute value of enthalpy but we can only measure enthalpy change. Thus:

$\Delta H = \Delta H_f - \Delta H_i$

f means final and i means initial.

1-7-GENERAL PROPERTIES OF SUBSTANCES

General properties of substances are divided into two:

1-Extensive Properties:

It includes all properties related to amount of substance in the system as mass, volume, heat capacity, enthalpy, entropy, free energy, etc.

2-Intensive Properties:

It includes all properties which are independent of amount of substance in the system as pressure, degree of temperature, density, specific heat, etc.

It is understood from above that enthalpy is a state function. It is an extensive property as it depends on amount of substance. Thus, the enthalpy change of 2 moles of a substance is twice the enthalpy change of 1 mole of the same substance.

1-8-THERMOCHEMISTRY

Thermochemistry is the branch of science which studies energy change (absorbed heat or evolved heat) that results from physical and chemical changes. In simpler words, thermochemistry deals with calculation of enthalpies of chemical reactions and physical changes. As we have mentioned before, if the value of ΔH_r are negative, reaction is exothermic; if the value of ΔH_r are positive, reaction is endothermic. If we assume a reaction as a system, an exothermic reaction releases its energy from system to surroundings. This is shown in the following chemical reaction and physical change.

Attention:

When the word (Energy) is writen at the reactant side, the reaction will be endothermic, but if it writen at the product side the reaction will be Exothermic.

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} + \text{Energy}$ Chemical Reaction

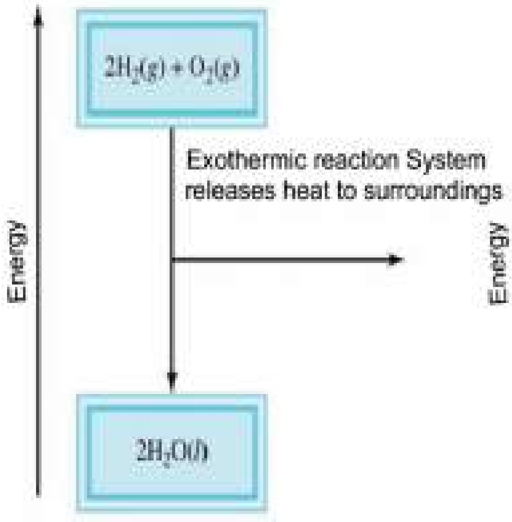
$H_2O_{(g)} \rightarrow H_2O_{(l)} + \text{Energy}$ Physical Change

In an endothermic reaction, system absorbs energy from surroundings. The following chemical reaction and physical change can be given as examples.

$2HgO_{(s)} + \text{Energy} \rightarrow 2Hg_{(l)} + O_{2(g)}$ Chemical Reaction

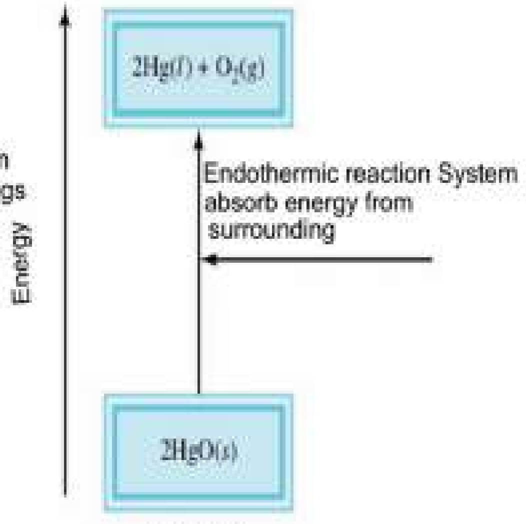
$H_2O_{(s)} + \text{Energy} \rightarrow H_2O_{(l)}$ Physical Change

If we write the word "energy" beside reactants, reaction is endothermic; if we write it beside products, reaction is exothermic.



$\Delta H < 0$

$\Delta H = -$



$\Delta H > 0$

$\Delta H = +$

1-9-MEASUREMENT OF ENTHALPY OF REACTION

In a chemical reaction and physical change under constant pressure, an instrument called as calorimeter is used in order to measure the heat of reaction (enthalpy of reaction) which is absorbed or released. There are many types of calorimeters

In this container, enough amounts of substances to react are placed.

A calorimeter is a container which contains water with a known mass.

Water is placed in a very well isolated container. Figure 1-2 shows one of calorimeters which measures enthalpies of reaction. As the released heat increases the temperature of water and calorimeter, if the heat capacity and content of calorimeter is known, heat can be measured through increase in temperature.

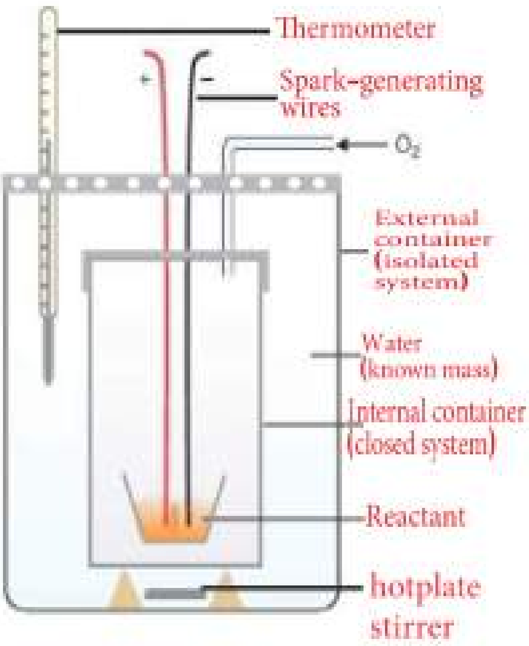


Figure 1-2

Calorimeter vessel which is used to measure enthalpies of reaction.

Example 1-2

3 g of glucose $C_6H_{12}O_6$ was placed inside a calorimeter. Then interaction vessel was filled with oxygen gas. This vessel was placed in the isolated container. Isolated container was filled with 1200 g of water.

Initial temperature was 21°C. After burning the mixture, the temperature of the calorimeter and its content was raised to 25.5 °C at the end of the reaction. Calculate the amount of heat released as a result of burning 1 mole of glucose in kJ /mol unit. (Heat capacity of the calorimeter can be neglected).

(Molecular mass of glucose is 180 g/mol) (Specific heat of water is 4.2 J/g.°C)

Exercise 1-2

When 3 g of hydrazine (N_2H_4) was burnt in a calorimeter containing 1000 g of water, the temperature was raised from 24.6°C to 28.2°C. By neglecting the heat capacity, calculate the released heat from burning of 1 mole of hydrazine in kJ/mol unit.(Molar mass of N_2H_4 = 32 g/mol) (Specific heat of water = 4.2 J/g.°C)

Answer: -161 kJ/mol

Solution:

Difference in degrees of temperature

$\Delta T = (T_f - T_i)\ °C = (25.5 - 21)\ °C = 4.5\ °C$

As heat capacity of calorimeter was neglected, the amount of heat can be calculated using the following relationship.

$q\ (J) = \varsigma\ (J/g.°C) \times m\ (g) \times \Delta T\ (°C)$

$q\ (J) = 4.2\ (J/g.°C) \times 1200\ (g) \times 4.5\ (°C) = 22680\ J$

As we would like to calculate the amount of released heat, this must have a negative sign. That is equal to (-22680 J). This is the amount of heat released through burning 3 g of glucose. To find out the amount of heat released from burning of 1 mole of glucose, we use the following relationship between number of moles (n) and mass (m).

$$n\ (mol) = \frac{m\ (g)}{M\ (g/mol)} = \frac{3\ (g)}{180\ (g/mol)} = 0.017\ mol$$

Therefore, the amount of heat released from burning of 1 mole of glucose is:

$$q = \frac{-22680\ J}{0.017\ mol} = -1334118\ J/mol$$

As this heat was measured in a calorimeter under constant pressure, it shows the enthalpy of reaction.

$\Delta H = q_p = -1334118\ J/mol$

The unit of enthalpy is J/mol. In order to find out the value of enthalpy in kJ unit, it is converted as follows:

$$\Delta H(kJ/mol) = \Delta H(J/mol) \times \frac{1(kJ)}{1000\ (J)}$$

$$\Delta H(kJ/mol) = -1334118\ (J/mol) \times \frac{1(kJ)}{1000\ (J)}$$

$$= -1334\ kJ/mol$$

Therefore, the amount of heat which was released through burning of 1 mole of glucose : **-1334 kJ/mol**

1-10-THERMOCHEMICAL EQUATION

Writing of a thermochemical equation (which defines a chemical reaction and a physical change) is different from writing other chemical equations. The following rules must be followed while writing a thermochemical equation:

1-The sign of change in enthalpy which accompanies a chemical reaction or a physical change must be written. The positive sign of enthalpy shows that reaction or change is endothermic. For example, the melting process of ice is shown as follows:

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H = 6$ kJ/mol

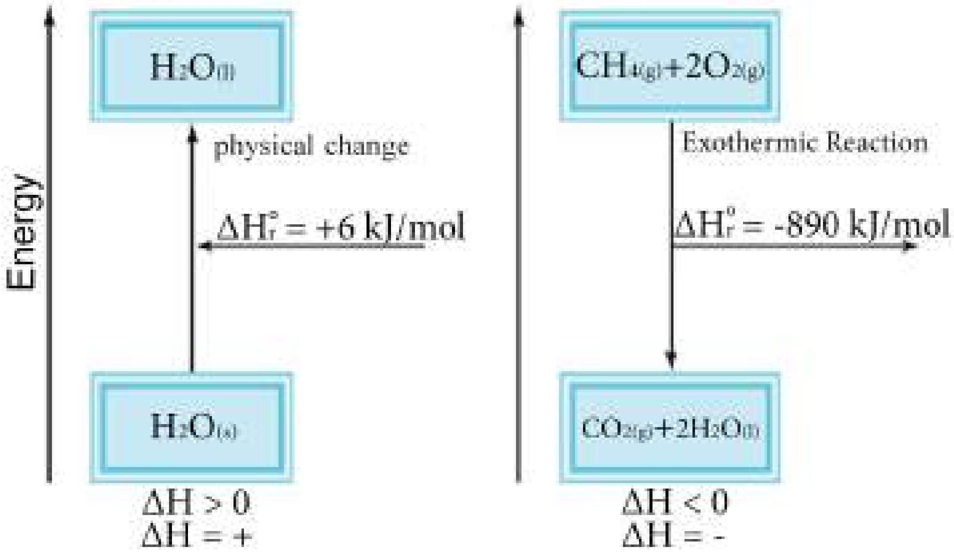
That means to melt 1 mole of ice under 1 atm pressure and 25°C, 6 kJ/mol of heat is absorbed. Absorbed heat can be written along with reactants (left hand side of the reaction) and inserted into the thermochemical equation:

$H_2O_{(s)} + 6\ \text{kJ/mol} \rightarrow H_2O_{(l)}$

If the sign of enthalpy is negative, it shows the reaction is exothermic. The following reaction is an example:

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H = -890$ kJ/mol

That means when 1 mole of methane gas is burnt at 25°C and under 1 atm pressure, 890 kJ/mol heat is released. Released heat can be written along with products if it is released during thermal reaction. Therefore, the reaction above can be rewritten as follows:



Melting of ice is endothermic phenomenon, whereas burning of methane gas is an exothermic reaction

2- Physical states of reactants and products need to be written. For this purpose, some letters are used. These are: s (solid), l (liquid), g (gas), aq (aqueous). The reason for this is that absorbed or released heat can change with physical states of reactants and products. The following example shows this clearly:

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H = -286$ kJ/mol

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -242$ kJ/mol

3- If the reaction (chemical reaction or physical change) is written reversely, the sign of enthalpy of reaction changes (from negative to positive or vice versa).

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H = 6$ kJ/mol

$H_2O_{(l)} \rightarrow H_2O_{(s)}$ $\Delta H = -6$ kJ/mol

Attention: Item 3 is one of applications of Laplace's Law.

For any chemical reaction or physical change. the amount of heat released is equal to the amount of heat absorbed. but with opposite signal.

4- If two sides of the reaction are multiplied or divided with a certain coefficient, the same process needs to be done with the value of enthalpy.

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H = 6$ kJ/mol

$2H_2O_{(s)} \rightarrow 2H_2O_{(l)}$ $\Delta H = 2 \times 6$ kJ/mol $= 12$ kJ/mol

1-11-STANDARD ENTHALPY OF REACTION

The value found under standard conditions which are 25°C and 1atm pressure is called as standard enthalpy of reaction and shown with ΔH_r° symbol. These conditions are different from standard conditions (STP) which is 0°C and 1 atm pressure while dealing with gases.

Let's write a thermal reaction which includes all properties mentioned above.

$C_5H_{12(l)} + 8O_{2(g)} \rightarrow 5CO_{2(g)} + 6H_2O_{(l)}$ $\Delta H_r^\circ = -3523$ kJ/mol

We can read this as follows:

1 mole of liquid pentane (C_5H_{12}) was burnt with 8 moles of oxygen gas. As a result of the burning process, 5 moles of carbon dioxide gas, 6 moles of liquid water and 3523 kJ of heat were released under standard conditions, 25°C and 1atm pressure.

1-12-TYPES OF ENTHALPY

1-12-1-Standard Enthalpy of Formation

The heat which is necessary (absorbed or emitted) to form 1 mole of compound from its components under standard conditions is called as standard enthalpy of formation. It is shown with ΔH_f° symbol. Here, the most stable forms of elements under standard conditions are taken. According to this, the most stable form of hydrogen is gas, whereas mercury in liquid and magnesium in solid forms. These are measured at 25°C and 1atm pressure (standard conditions).

For example, carbon element can be found in graphite and diamond forms. But graphite is its most stable form. Sulfur is found two stable forms: rhombic sulfur ($S_{rhombic}$) and orthorhombic sulfur ($S_{orthorhombic}$). But rhombic sulfur is the most stable form.

According to IUPAC system, standard enthalpy of formation of all elements is equal to 0 kJ/mol in their standard forms (the most stable form of an element).

ΔH_f° (Element) = 0 kJ/mol

Oxygen in gas form is the most stable. In this case, the following relationship can be written.

$\Delta H_f^\circ (O_2) = 0$ kJ/mol

In the same manner, if graphite is more stable than diamond, the following relationship will be correct.

$\Delta H_f^\circ (C_{graphite}) = 0$ kJ/mol

The formation equations of some substances are given below:

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} \qquad \Delta H_f^\circ(H_2O_{(l)}) = -286 \text{ kJ/mol}$$

$$\frac{3}{2} H_{2(g)} + 2O_{2(g)} + \frac{1}{4} P_{4(s)} \rightarrow H_3PO_{4(s)} \qquad \Delta H_f^\circ(H_3PO_{4(s)}) = -1279 \text{ kJ/mol}$$

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} \qquad \Delta H_f^\circ(MgCl_{2(s)}) = -642 \text{ kJ/mol}$$

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_f^\circ(CO_{2(g)}) = -394 \text{ kJ/mol}$$

Table 1-2 shows ΔH_f° values of some compounds. While writing thermal equations, rational numbers are used to show formation of 1 mole of sought compound. Therefore, we change the mole numbers of reacting substances.

ΔH_f° is the enthalpy of 1 mole of compound by taking most stable forms of elements under standard conditions. But ΔH_r° standard heat of reaction of any compound might not be equal to ΔH_f° standard enthalpy of formation. For example, ΔH_r° of the following reaction is equal to -72 kJ.

$$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)} \qquad \Delta H_r^\circ = -72 \text{ kJ}$$

If we consider this equation, 2 moles of HBr was formed at the end of the reaction. Therefore, the half of this heat -36 kJ is the heat released when 1 mole of HBr is formed from its most stable elements. The standard enthalpy of formation of HBr compound is as follows:

$$\Delta H_f^\circ(HBr) = \frac{1}{2} \Delta H_r^\circ = \frac{-72}{2} \text{ kJ/mol} = -36 \text{ kJ/mol}$$

This is obtained by dividing the both sides of equation by two.

$$\frac{1}{2} H_{2(g)} + \frac{1}{2} Br_{2(g)} \rightarrow HBr_{(g)}$$

Example 1-3

As the standard enthalpy of formation of benzene $\Delta H_f^0(C_6H_6)$= 49 kJ/mol, write down the thermochemical equation to make $\Delta H_r^0 = \Delta H_f^0(C_6H_6)$

Solution:

1 mole of (C_6H_6) must be formed from the most stable form of its elements at 25°C and 1 atm pressure.

$$6C_{(graphite)} + 3H_{2(g)} \rightarrow C_6H_{6(l)} \qquad \Delta H_r^\circ = \Delta H_f^\circ (C_6H_6) = \mathbf{49\ kJ/mol}$$

Table 1-2
Standard Enthalpies formation of Some compounds

Compound	ΔH_f° (kJ / mol)
$Ag_2S_{(s)}$	- 32
$BaCO_{3(s)}$	–1219
$CaCl_{2(s)}$	–795
$CH_{4(g)}$	- 75
$CH_3OH_{(l)}$	–239
$CO_{2(g)}$	–394
$C_2H_{2(g)}$	+227
$C_4H_{10(g)}$	–125
$CuSO_{4(s)}$	–770
$KClO_{3(s)}$	-391
$MgSO_{4(l)}$	–1278
$H_2O_{(l)}$	- 286
$H_2O_{(g)}$	- 242
$HNO_{3(l)}$	–173
$HBr_{(g)}$	-36
$HI_{(g)}$	+26

Exercise 1-3

As standard enthalpy of formation ΔH_f° of sulfuric acid (H_2SO_4) is (-814 kJ/mol), write down the thermochemical equation to make $\Delta H_r^\circ = \Delta H_f^\circ(H_2SO_4)$.

Exercise 1-4

As standard enthalpy of formation of hydrogen fluoride (HF) is $\Delta H_f^\circ(HF) = -271$ kJ/mol, calculate standard enthalpy of reaction ΔH_r° of the following reaction.

$H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$

Answer: -542 kJ

Example 1-4

Which of the following reactions has a standard enthalpy of reaction ΔH_r° which is equal to standard enthalpy of formation ΔH_f° of formed compounds?

1) $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$ $\Delta H_r^\circ = -1625$ kJ

2) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_r^\circ = -394$ kJ

3) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_r^\circ = -283$ kJ

Solution:

Reaction 1: Standard enthalpy of reaction isn't equal to standard enthalpy of formation of Fe_2O_3 compound, because 2 moles of substance have been formed at the end.

Reaction 2: Standard enthalpy of reaction of CO_2 compound is equal to its standard enthalpy of formation. Because 1 mole of CO_2 has been formed from the most stable form of its elements.

Reaction 3: ΔH_r° isn't equal to ΔH_f° CO_2, because the reactants aren't in the most stable form.

Answer: is reaction (2)

1-12-2-Standard Enthalpy of Combustion

Combustion reactions include reactions of substances (fuels) with oxygen. In biological systems, food is accepted as fuel. When food is decomposed (combusted) in body, carbohydrates are transformed to glucose sugar. One of the methods of heating houses or cooking is via combustion of butane gas. Combustion of 1 mole of butane gas yields -2873 kJ of energy according to the following equation:

$$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)} \qquad \Delta H_c^\circ = -2873 \text{ kJ/mol}$$

Most cars run via combustion of gasoline in their engines. Gasoline is usually shown as octane (C_8H_{18}). As a result of combustion of 1 mole of octane, 5471 kJ of energy is released.

$$C_8H_{18(l)} + \frac{25}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(l)} \qquad \Delta H_c^\circ = -5471 \text{ kJ/mol}$$

Another example of combustion reactions is the reaction between hydrogen and oxygen.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad \Delta H_c^\circ = -286 \text{ kJ/mol}$$

Combustion of hydrogen supplies energy to space shuttles.

Standard enthalpy of combustion is shown with ΔH_c° symbol. Standard combustion is defined as the heat released through combustion of 1 mole of any substance under standard conditions (25°C temperature, 1 atm pressure). In Table 1-3, standard enthalpy of combustion values for some elements and compounds are shown.

Elements oxides are formed from combustion of elements with oxygen. Through combustion of organic substances, carbon dioxide gas, liquid water and heat is released. For example, combustion of glucose ($C_6H_{12}O_6$) in body supplies necessary energy for biological functions of body.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} \qquad \Delta H_r^\circ = -2808 \text{ kJ/mol}$$

The main condition to make sure that standard enthalpy of reaction ΔH_r° become equal to standard enthalpy of combustion ΔH_c° is combustion of 1 mole of substance with enough oxygen. **Most of combustion reactions are exothermic reactions.**

Example 1-5

Write down the chemical reaction of combustion of liquid ethyl alcohol (C_2H_5OH) using the following data. $\Delta H_c^\circ (C_2H_5OH_{(l)}) = -1367$ kJ/mol

Solution:

To yield -1367 kJ/mol of heat, 1 mole of liquid ethyl alcohol (C_2H_5OH) is combusted with enough O_2.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$$
$$\Delta H_c^\circ (C_2H_5OH_{(l)}) = -1367 \text{ kJ/mol}$$

1-12-3-Enthalpy of Physical Changes

Matter is in a cycle of changing states. The process of transformation from liquid to gas form is called as vaporization. The heat necessary for vaporization of 1 mole of any substance is called as enthalpy of vaporization. It is shown with ΔH_{vap} symbol. For example, 1 mole of liquid water absorbs 44 kJ of heat while transformed into water vapor. The equation for the reaction is given below:

$$H_2O_{(l)} \xrightarrow{\text{vaporization}} H_2O_{(g)} \quad \Delta H_{vap} = 44 \text{ kJ/mol}$$

The opposite of this reaction that is the transformation of water vapor to liquid water is called as condensation. The symbol of enthalpy of condensation is ΔH_{cond}. As vaporization is the reverse of condensation, the value of ΔH_{cond} is the same as ΔH_{vap} and with an opposite sign.

$$H_2O_{(g)} \xrightarrow{\text{condensation}} H_2O_{(l)} \quad \Delta H_{cond} = -44 \text{ kJ/mol}$$

One of the physical changes is the transformation of substances from solid to liquid. This is called as fusion. The heat necessary to transform 1 mole of solid substance to liquid is called as enthalpy of fusion and shown with ΔH_{fus}.

For example, the process of transformation of 1 mole of ice to water occurs through absorption of 6 kJ/mol heat.

$$H_2O_{(s)} \xrightarrow{\text{fusion}} H_2O_{(l)} \quad \Delta H_{fus} = 6 \text{ kJ/mol}$$

The opposite of fusion is crystallization. The enthalpy of crystallization is shown with ΔH_{cryst} symbol. Transformation of 1 mole of water from liquid to solid is shown in the following equation.

Table 1-3 Standard enthalpy of combustion values ΔH_c° for some elements and compounds.

Substances	kJ / mol
$C_{12}H_{22}O_{11(s)}$	-5644
$C_8H_{18(l)}$	-5471
$C_6H_{12}O_{6(s)}$	-2808
$C_3H_{8(g)}$	-2219
$CH_{4(g)}$	-891
$C_{(graphite)}$	-394
$H_{2(g)}$	-286
$C_2H_5OH_{(l)}$	-1367
$C_2H_{4(g)}$	-1411
$S_{(rhombic)}$	-298
$NH_{3(g)}$	-383

Exercise 1-5

As $\Delta H_c^\circ (C_3H_8) = -2219$ kJ/mol, write down the combustion reaction of propane gas (C_3H_8).

$$H_2O_{(l)} \xrightarrow{\text{crystallization}} H_2O_{(s)} \qquad \Delta H_{cryst} = -6 \text{ kJ/mol}$$

As a summary of what is mentioned above can be given in the following relationship:

$$\Delta H_{vap} = -\Delta H_{cond} \text{ and } \Delta H_{fus} = -\Delta H_{cryst}$$

The sign of enthalpies of vaporization and fusion is positive. In other words, heat is absorbed (endothermic) to realize these reactions. The sign of enthalpies of condensation and crystallization is negative. That means heat is released (exothermic) during these reactions.

Example 1-6

As enthalpy of vaporization of liquid ammonia is 23 kJ/mol, what is the value of enthalpy of condensation?

Solution:

The vaporization equation of ammonia is as follows:

$$NH_{3(l)} \xrightarrow{\text{vap.}} NH_{3(g)} \quad \Delta H_{vap} = 23 \text{ kJ/mol}$$

As condensation is reverse of vaporization:

$$NH_{3(g)} \xrightarrow{\text{cond.}} NH_{3(l)}$$

$$\Delta H_{cond} = -\Delta H_{vap} = \mathbf{-23\ kJ/mol}$$

Exercise 1-6

As enthalpy of fusion of solid acetic acid (CH_3COOH) is 5.11 kJ/mol, calculate the enthalpy of crystallization of this acid?

Answer: -5.11 kJ/mol

1-13- METHODS OF CALCULATING STANDARD ENTHALPY OF REACTION

1-13-1-Hess's Law

It isn't possible to form some compounds from their elements directly, because either the reaction occurs so slowly or some unwanted side products are formed. Therefore, the values of ΔH_r° of this kind of reactions are measured indirectly. This method depends on Hess's Law . According to this law,

the total enthalpy of chemical reaction is the same whether the reaction is made up in one or several steps (equal the sum of enthalpies of intermediate reaction).

In other words, if we can divide the reaction into a series of reactions, the value of ΔH_r° of the main reaction can be calculated. Because ΔH_r° depends on the initial and final states of the system. It doesn't depend on the path the reaction follows. Hess's law is similar to the ascension of an elevator in an apartment building from the 1st floor to the 6th floor either directly or stopping at each floor. The result is the same in both situations.

For example, in the reaction of carbon (graphite) and oxygen and forming carbon monoxide, the released heat can't be measured directly.

$$C_{(graphite)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_r^\circ = ?$$

The reason is that the formation of CO_2 can't be prevented. But the heat released during full combustion of carbon (graphite) with oxygen and the heat released during combustion of CO and forming CO_2 can be calculated as shown in the following equations.

1) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_r° = -393.5$ kJ/mol

2) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_r° = -283$ kJ/mol

The formation of CO from graphite C and O_2 doesn't contain CO_2. Therefore, we need to eliminate CO_2. For this, we can reverse Equation 2.

3) $CO_{2(g)} \rightarrow CO_{(g)} + \frac{1}{2} O_{2(g)}$ $\Delta H_r° = +283$ kJ/mol

As chemical equations and values of enthalpies can be summed just as algebraic equations, we can get the following by summing (1) and (3)

1) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_r° = -393.5$ kJ/mol

3) $CO_{2(g)} \rightarrow CO_{(g)} + \frac{1}{2} O_{2(g)}$ $\Delta H_r° = +283$ kJ/mol

---

4) $C_{(graphite)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H_r° = -110.5$ kJ/mol

This equation is the same as the reaction equation between $C_{(graphite)}$ and $O_{2(g)}$ whose $\Delta H_f°$ value is wanted. That means this reaction occurs along with 110.5 kJ/mol of heat release. Figure 1-3 shows what has been told above.

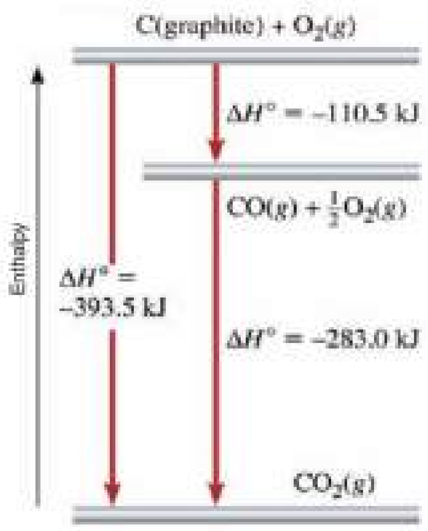


Figure 1-3

We can divide the enthalpy of formation reaction of 1 mole of CO from the reaction between $C_{graphite}$ and O_2 (gas) into two according to Hess Law.

Example 1-7

Calculate standard enthalpy of formation of main elements of $CS_{2(l)}$ compound from its most stable forms.

$C_{(graphite)} + 2S_{(rhombic)} \rightarrow CS_{2(l)}$ $\Delta H_f°(CS_{2(l)}) = ?$ kJ/mol

Thermal equations and values of enthalpies are given below.

1) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_r° = -394$ kJ/mol

2) $S_{(rhombic)} + O_{2(g)} \rightarrow SO_{2(g)}$ $\Delta H_r° = -296$ kJ/mol

3) $CS_{2(l)} + 3O_{2(g)} \rightarrow CO_{2(g)} + 2SO_{2(g)}$ $\Delta H_r° = -1072$ kJ/mol

Solution:

If we examine the equation which we want to find out the value of $\Delta H_f°(CS_2)$, $CS_{2(l)}$ is on the products' side. But in Equation 3 it is on the reactants' side. Therefore, we reverse Equation 3.

4) $CO_{2(g)} + 2SO_{2(g)} \rightarrow CS_{2(l)} + 3O_{2(g)}$ $\Delta H_r° = +1072$ kJ/mol

The equation in which the value of $\Delta H_f°(CS_2)$ is wanted, it contains 2 moles of S. Therefore, we need to multiply Eq. 2 by 2.

5) $2S_{(rhombic)} + 2O_{2(g)} \rightarrow 2SO_{2(g)}$ $\Delta H_r° = 2 \times -296$ kJ/mol $= -592$ kJ

Exercise 1-7

Calculate the standard enthalpy of formation of the reaction in which acetylene ($C_2H_{2(g)}$) is formed from its main elements.

$2C_{(graphite)} + H_{2(g)} \rightarrow C_2H_{2(g)}$

$\Delta H_f^\circ \ (C_2H_{2(g)}) = ?$ kJ

The following thermal equations are given:

1) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta H_r^\circ = -394$ kJ/mol

2) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$

$\Delta H_r^\circ = -286$ kJ/mol

3) $2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(l)}$

$\Delta H_r^\circ = -2599$ kJ/mol

Answer: 225.5 kJ/mol

Exercise 1-8

When benzene (C_6H_6) is burnt in air, it yields carbon dioxide gas and liquid water. Calculate the ΔH_r° value of this reaction according to the following.

$\Delta H_f^\circ \ (C_6H_{6(l)}) = 49$ kJ/mol ,

$\Delta H_f^\circ \ (CO_{2(g)}) = -394$ kJ/mol ,

$\Delta H_f^\circ \ (H_2O_{(l)}) = -286$ kJ/mol ,

Answer: -3271 kJ/mol

If we add Equation 4 and 5 with Equation 1:

1) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H_r^\circ = -394$ kJ/mol

4) $CO_{2(g)} + 2SO_{2(g)} \rightarrow CS_{2(l)} + 3O_{2(g)}$ $\quad \Delta H_r^\circ = +1072$ kJ/mol

5) $2S_{(rhombic)} + 2O_{2(g)} \rightarrow 2SO_{2(g)}$ $\quad \Delta H_r^\circ = -592$ kJ/mol

---

$C_{(graphite)} + 2S_{(rhombic)} \rightarrow CS_{2(l)}$ $\quad \Delta H_f^\circ(CS_{2(l)}) = ?$ kJ/mol

This equation is the same as the equation which we want to find out the value of $\Delta H_f^\circ(CS_{2(l)})$. Therefore:

$\Delta H_f^\circ(CS_{2(l)}) = -394$ kJ $+ 1072$ kJ $+ (-592$ kJ$) =$ **86 kJ**

1-13-2-Using The Values of Standard Enthalpy of Formation

In order to calculate (ΔH_r°) enthalpy of reaction, the ΔH_f° values of compounds can be used.

$$\mathbf{aA + bB \longrightarrow gG + hH}$$

We use the following relationship to calculate the ΔH_r° value of this reaction.

$$\Delta H_r^\circ = \Sigma\, n\, \Delta H_f^\circ(\text{Products}) - \Sigma\, n\, \Delta H_f^\circ(\text{Reactants})$$

n is number of moles of reactants and products. Σ means total. The calculation of ΔH_r° value of the thermal reaction above can be done as follows:

$$\Delta H_r^\circ = [g\Delta H_f^\circ(G) + h\Delta H_f^\circ(H)] - [a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)]$$

Here what we will pay attention is that the enthalpy of formation ΔH_f° of the most stable form of any element is equal to zero. As mentioned before,

$\mathbf{\Delta H_f^\circ(Element) = 0\ kJ/mol}$

Example 1-8

The reaction of aluminum and iron (III) oxide compounds occurs as follows:

$2Al_{(s)} + Fe_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(s)}$ $\quad \Delta H_r^\circ = ?$ kJ

Calculate the standard enthalpy of reaction using the following.

$\Delta H_f^\circ \ (Al_2O_{3(s)}) = -1670$ kJ/mol

$\Delta H_f^\circ \ (Fe_2O_{3(s)}) = -822$ kJ/mol

Solution:

The following can be written using the relationship above.

$\Delta H_r^\circ = \Sigma\, n\, \Delta H_f^\circ(\text{Products}) - \Sigma\, n\, \Delta H_f^\circ(\text{Reactants})$

$\Delta H_r^\circ = [\Delta H_f^\circ (Al_2O_{3(s)}) + 2\Delta H_f^\circ (Fe_{(s)})] - [2\Delta H_f^\circ (Al_{(s)}) + \Delta H_f^\circ (Fe_2O_{3(s)})]$

$\Delta H_f^o (Al_{(s)}) = 0$ because the most stable form of aluminum is the solid form. However, under standard conditions, iron is in solid form,
Therefore, $\Delta H_f^\circ (Fe_{(s)})$ is zero.

$\Delta H_r^\circ = [(-1670) + 2\ (0)]kJ/mol - [2\ (0) + (-822)]kJ/mol$

$= \mathbf{-848\ kJ/mol}$

1-14-SPONTANEOUS PROCESSES

These are physical and chemical reactions occurring by themselves without any outside factor under certain conditions. The reactions occurring autonomously at a certain temperature, pressure or concentration are called as spontaneous reactions.

The following can be given as examples for physical and chemical spontaneous processes.

-Water drops from a fall downward but the opposite is impossible.

-Flow of heat from a hot object to a cold one, the opposite doesn't occur.

-Lump of sugar dissolves in coffee spontaneously, but dissolved sugar can't solidify by itself.

-Freezing of water at 0°C spontaneously, melting of ice at 0°C and 1 atm.

-Rusting of iron spontaneously when objected to oxygen and moisture; but rust of iron can't transform into iron.

-While a piece of Na forms NaOH and hydrogen by reacting with water, H_2 and NaOH can't form water and sodium by reacting.

-While gas in a vacuumed container expands spontaneously, gas molecules can't accumulate in a container spontaneously. Figure 1-4

As seen in these examples, while some processes occur spontaneously in a direction, they can't occur spontaneously in the opposite direction.

Why do some processes occur spontaneously?

One of the most suitable answers which can be given for this question is that along with spontaneous processes, a decrease occurs in the energy of all system (less energy means more stability). In other words, final energy of system is less than the initial energy. This case explains the fact that heat flows from a hot object to a cold one and water drops from top of a fall.

Most reactions which cause decrease in energy are exothermic reactions. For example, combustion of methane under standard conditions:

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H_r^\circ = -890\ kJ$

Acid-Base Neutralization Reactions:

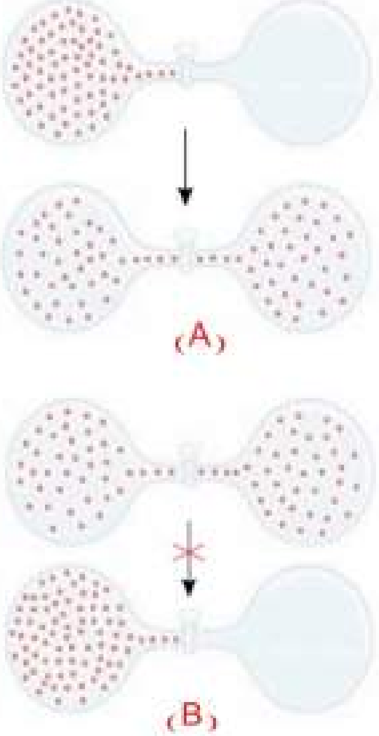
$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \qquad \Delta H_r^\circ = -56\ kJ$

With respect to given examples, can it be said that spontaneous processes are always exothermic reactions?

Answer:

It isn't possible to generalize this hypothesis for a very simple reason, because there are some spontaneous physical and chemical changes despite being endothermic.

Spontaneous and Non- Spontaneous Processes



A) Self- Expansion of gas in a vacuumed container

B) All gas Molecules can not accumulate in a container.

Figure 1-4

For example:

Dissolution of ammonium chloride (NH_4Cl) in water is an endothermic process and it occurs spontaneously.

$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$ $\Delta H_r^\circ = +14$ kJ

Decomposition of mercury oxide (HgO) occurs spontaneously and it is endothermic.

$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)}$ $\Delta H_r^\circ = 91$ kJ

Melting of ice is an endothermic process but it occurs spontaneously.

$H_2O_{(s)} \longrightarrow H_2O_{(l)}$ $\Delta H_{fus} = 6$ kJ/mol

Vaporization of water is an endothermic process and it is spontaneous.

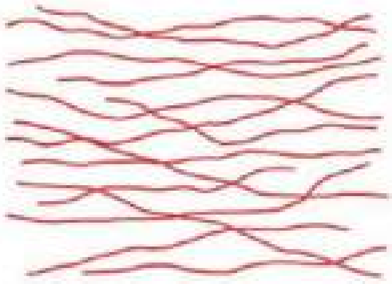
$H_2O_{(l)} \longrightarrow H_2O_{(g)}$ $\Delta H_{vap} = 44$ kJ/mol

With respect to examples above, we can say that an endothermic process can be spontaneous. But we can't generalize this statement, because there are many reactions despite being endothermic they don't occur spontaneously.
In other words, we can't decide if a reaction occurs spontaneously or not by just looking at it being endothermic or exothermic. To decide this, we need a new thermodynamic function called as entropy.

1-15-ENTROPY

Entropy is a thermodynamic function .which is defined as a measure of the vandomness or irregularity of a system Its symbol is (S). The disorder in all reactions-whether spontaneous or not-is called as entropy.

It shows to which extent the disorder of system has reached. As the disorder increases in the system, the value of entropy increases. As the system becomes more ordered (disorder decreases), the value of entropy decreases.



Order ↑ S ↓

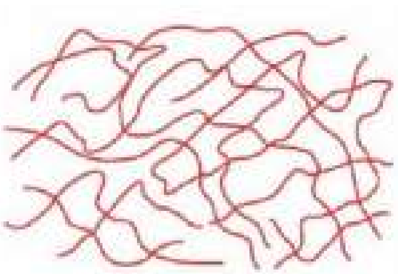
Entropy is a thermodynamic function which is similar to enthalpy and its only change in entropy can be measured.

$\Delta S = S_f - S_i$

Here, S_f is final entropy and S_i is initial entropy.

In all spontaneous reactions and physical processes, disorder increases. For example, ammonium chloride dissolves in water spontaneously.

$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$ $\Delta H_r^\circ = +14$ kJ



Disorder ↑ S ↑

In this dissolution reaction, the salt decomposes to its ions. These ions are more disordered than ammonium chloride molecules. When liquid water vaporizes, vapor molecules become more disordered than liquid water molecules. Liquid water molecules are also more disordered than ice molecules. Generally, the entropy of gas state is always bigger than the entropy of liquid state. The entropy of liquid state has a bigger value than the entropy of solid state. Fig. 1-5

The increase in the entropy of system occurs with an increase in distribution of energy. A change in physical states of the system changes its entropy.

In solid state, molecules are ordered and closely packed. When fusion starts, these atoms or molecules start moving and they get out of crystal lattice and disorder increases. Thus, a shift from order to disorder occurs. As a result, entropy increases too. Similarly, entropy of system increases in vaporization.

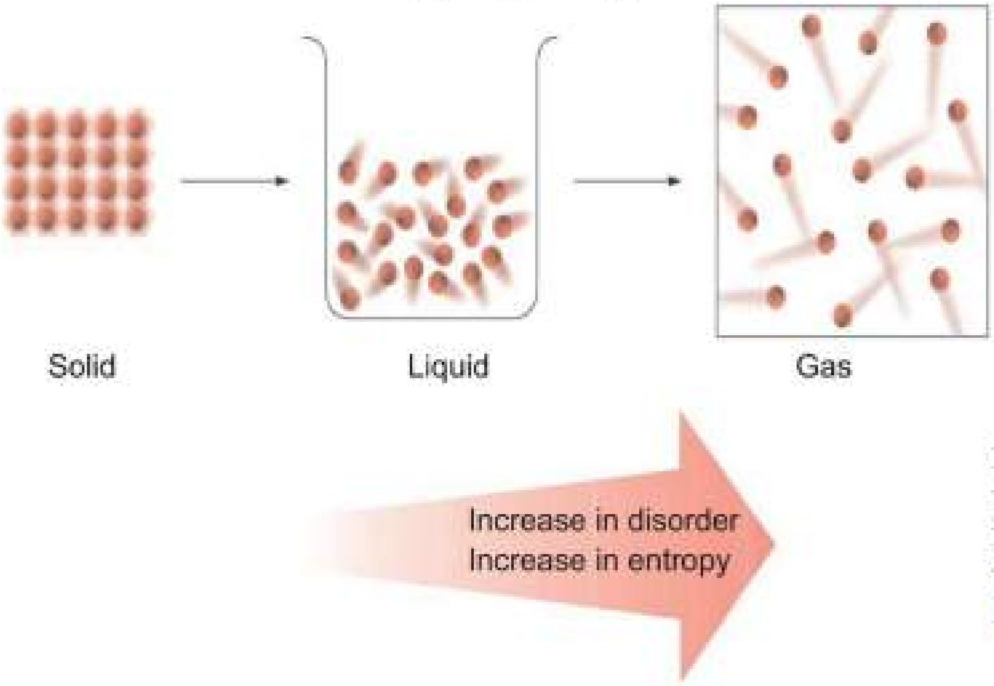
This increase is greater than that of melting process. The reason is that atoms and molecules in gas state distribute more to fill all the space they are inside. Frequently entropy increases in reactions occurring in solutions. For example, when sugar crystals are dissolved in water, the ordered structure of sugar is disrupted. Therefore, disorder of solution is greater than that of pure solvent and pure solute. When an ionic solid as sodium chloride is dissolved, the increase in entropy depends on two factors. These are:

A- Preparation of solution (Mixing solute and solvent)

B- Ionization of solid compound

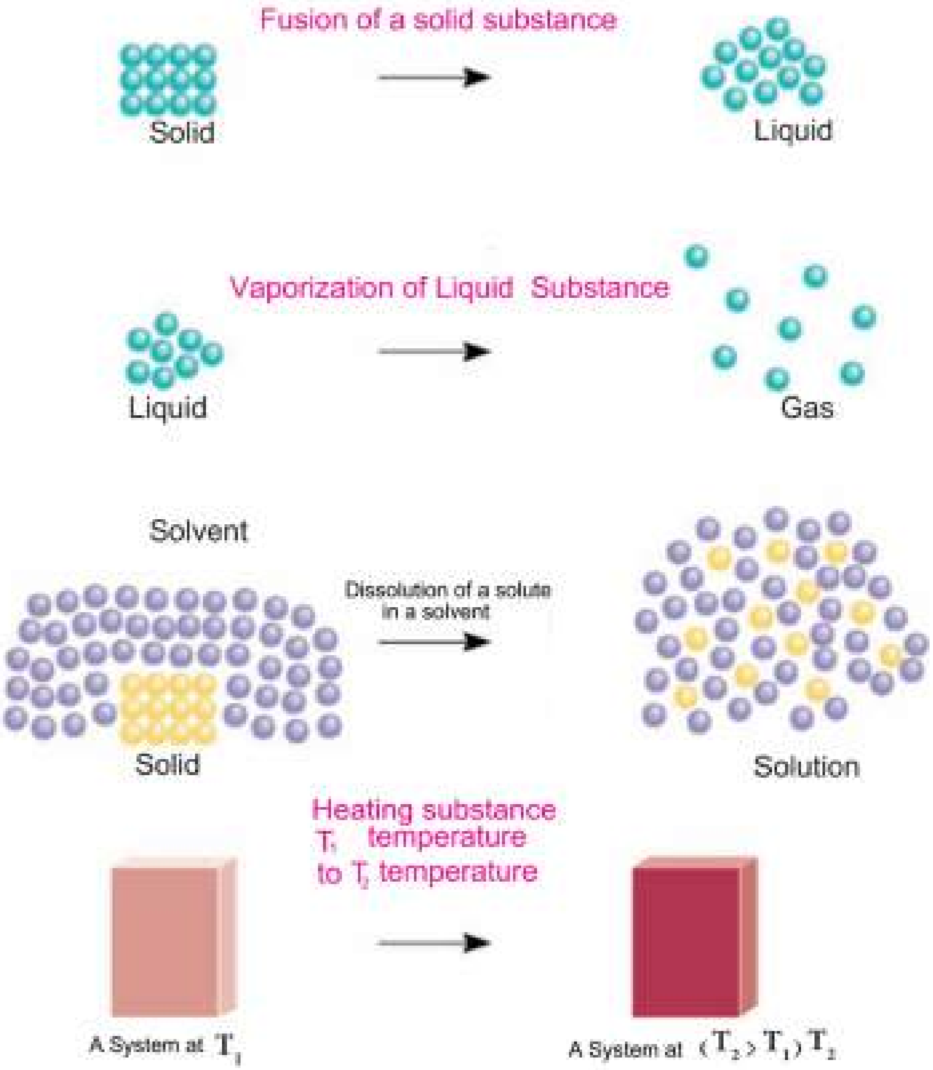
Heating increases entropy of system. Because heating does not only increase displacement motion of molecules but also increases rotational motion and vibration. Besides, with temperature increase, all energy types which depend on molecular motion also increase. Therefore, heating increases disorder of system and its entropy.

$$\Delta S_{(g)} > \Delta S_{(l)} > \Delta S_{(s)}$$



Entropy of gases is greater than that of liquids. Similarly, entropy of liquids is greater than that of solid substance.

Figure 1-5



Some reactions in which entropy increases.

Figure 1-6

Example 1-9

For the following processes, estimate if change in entropy (ΔS) is greater or smaller than zero.

A- Freezing of ethyl alcohol

B- Vaporization of liquid bromine

C- Dissolution of glucose in water

D- Cooling of nitrogen gas from 80°C to 20°C

Solution:

A- Freezing means transformation of liquid ethyl alcohol to solid ethyl alcohol. As molecules are more ordered in solid than liquid, change in entropy is smaller than zero ($\Delta S<0$).

B- While liquid bromide is transformed to bromide vapor, the disorder of molecules increases. Therefore, change in entropy is greater than zero ($\Delta S>0$).

Exercise 1-9

How do the entropies of the following systems change?

A- Condensation of water vapor

B- Formation of sugar crystals in supersaturated solution

C- Heating H_2 gas from 20°C to 80°C

D- Sublimation of solid iodine

C- Because solid glucose molecules distribute in water, disorder increases. That means change in entropy is greater than zero($\Delta S>0$).

D- Cooling of nitrogen gas from 80°C to 20°C decreases disorder of nitrogen molecules. As a result, entropy decreases and change of entropy is smaller than zero ($\Delta S<0$).

1-15-1-Calculation of Standard Entropy in Chemical Reactions

Thermodynamics allows calculation of value of standard entropy (S°) in all chemical elements and compounds. Using this value, we can measure change of standard entropy of reaction (ΔS_r°) in a chemical reaction. We use the following relationship for this:

$$\Delta S_r^\circ = \Sigma\, n\, S^\circ(\text{Products}) - \Sigma\, n\, S^\circ(\text{Reactants})$$

n means number of moles of reactants and products, Σ means total.

For the following general chemical reaction:

$$aA + bB \longrightarrow gG + hH$$

The change of standard entropy of this reaction (ΔS_r°) can be written using the relationship above as follows:

$$\Delta S_r^\circ = [g\, S^\circ(G) + h\, S^\circ(H)] - [a\, S^\circ(A) + b\, S^\circ(B)]$$

Table 1-4 shows standard entropy values for some elements and chemical compounds. According to International System of Units, unit of entropy is J/K.mol.

Example 1-10

Calculate change of standard entropy of reaction (ΔS_r°) of the following reaction at 25°C and 1 atm standard conditions.

$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$

$S^\circ(CO)$ = 198 J/K.mol, $S^\circ(CO_2)$ = 214 J/K.mol,

$S^\circ(O_2)$ = 205 J/K.mol

Solution:

$$\Delta S_r^\circ = \Sigma\, n\, S^\circ(\text{Products}) - \Sigma\, n\, S^\circ(\text{Reactants})$$

$$\Delta S_r^\circ = [2S^\circ(CO_2)] - [2S^\circ(CO) + S^\circ(O_2)]$$

$$\Delta S_r^\circ = [2 \times 214\ \text{J/K.mol}] - [(2\times198 + 205)\ \text{J/K.mol}]$$

$$\Delta S_r^\circ = \mathbf{-173\ J/K.mol}$$

1-16-GIBBS FREE ENERGY

In 1800, a scientist named Gibbs developed a relationship between enthalpy (H) and entropy (S). This relationship enables us to estimate whether a reaction occurs spontaneously or not simpler than relying on using enthalpy or entropy values separatlely. Gibbs proposed a new thermodynamic function which is called as "Gibbs free energy."

Table 1-4

standard entropy values for some elements and compounds

Substances	S°(J/K.mol)
$H_2O_{(l)}$	70
$H_2O_{(g)}$	189
$Br_{2(l)}$	152
$Fe_{(s)}$	27
$C_{(diamond)}$	2
$C_{(graphite)}$	6
$CH_{4(g)}$	186
$C_2H_{6(g)}$	230
$Ag_{(s)}$	43
$Ba_{(s)}$	67
$O_{2(g)}$	205
$Cl_{2(g)}$	223
$CO_{2(g)}$	214
$Fe_2O_{3(s)}$	87
$C_2H_{2(g)}$	201
$C_2H_{4(g)}$	220
$CuSO_{4(s)}$	66

Exercise 1-10

Calculate change of standard entropy of reaction (ΔS_r°) of the following reaction at 25°C and 1 atm standard conditions.

$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$

According to;

$S^\circ(Fe_2O_3)$ = 87 J/K.mol,

$S^\circ(O_2)$ = 205 J/K.mol,

$S^\circ(Fe)$ = 27 J/K.mol

Answer: -549 J/K.mol

Table 1-5

Values of Standard Free Gibbs Energy of Formation Of some Compounds

ΔG_f° (kJ / mol)	Substance
173	$C_6H_{6(l)}$
-300	$SO_{2(g)}$
-137	$CO_{(g)}$
-394	$CO_{2(g)}$
87	$NO_{(g)}$
52	$NO_{2(g)}$
-348	NaCl
-95	$HCl_{(g)}$
-53	$HBr_{(g)}$
-51	$CH_{4(g)}$
-33	C_2H_6
68	C_2H_4
-1576	$Al_2O_{3(s)}$
-741	Fe_2O_3
-110	AgCl
-318	ZnO
-229	$H_2O_{(g)}$
-237	$H_2O_{(l)}$
-271	$HF_{(g)}$
2	$HI_{(g)}$
-33	$H_2S_{(g)}$
-17	$NH_{3(g)}$
-604	$CaO_{(s)}$

The symbol of this function is G. It defines the maximum energy which can be obtained from measurement of ΔH and ΔS at constant temperature and pressure. Change in Gibbs free energy ΔG is defined as follows:

(at constant temperature and pressure) $\Delta G = \Delta H - T\Delta S$

Free Gibbs Energy (sometimes called as free energy for ease) is a function just like enthalpy and entropy. It is a real function which shows if physical changes or chemical reactions occur spontaneously or not. The sign of Gibbs Free Energy is commented as follows:

-If value of ΔG is negative ($\Delta G<0$), reaction or physical change occurs spontaneously.

-If value of ΔG is positive ($\Delta G > 0$), reaction or physical change doesn't occur spontaneously (the change or reaction occurs spontaneously at opposite direction).

-If value of ΔG is zero ($\Delta G = 0$), reaction or physical change is at equilibrium.

1-16-1-Standard Gibbs Free Energy of Reaction

Standard Gibbs Free Energy of Reaction which is shown with ΔG_r° symbol is the change in value of free energy if a reaction occurs under standard conditions (25°C temperature and 1 atm pressure). In order to calculate ΔG_r° for any reaction, values of Standard Gibbs Free Energy of Formation ΔG_f° are used. Standard Gibbs Free Energy of Formation is the amount of change in free energy when 1 mole of any compound is formed from most stable forms of its elements under standard conditions (25°C temperature and 1 atm pressure.)
It is possible to calculate value of ΔG_r° by a similar equation to standard enthalpy of reaction from standard enthalpy of formation values. It is as follows:

$$\Delta G_r^\circ = \Sigma\ n\ \Delta G_f^\circ(\text{Products}) - \Sigma\ n\ \Delta G_f^\circ(\text{Reactants})$$

n is number of moles of reactants and products and Σ is total.
For the following general reaction:

$$aA + bB \longrightarrow gG + hH$$

The change of standard free Gibbs energy of this reaction is as follows:

$$\Delta G_r^\circ = [g\ \Delta G_f^\circ\ (G) + h\ \Delta G_f^\circ\ (H)] - [a\ \Delta G_f^\circ\ (A) + b\ \Delta G_f^\circ\ (B)]$$

Table 1-5 shows values of standard free Gibbs energy of formation of some compounds. Here what needs attention is that ΔG_f° values of most stable forms of elements are equal to zero.

ΔG_f° **(Element) = 0 kJ/mol**

Unit of standard free energy is (J/mol) according to International System of Units.

Example 1-11

Calculate standard free Gibbs energy of the following reaction under standard conditions, 25°C and 1 atm pressure. Also tell if the reaction occurs spontaneously or not under these conditions.

$2C_6H_{6(l)} + 15O_{2(g)} \rightarrow 12CO_{2(g)} + 6H_2O_{(l)}$

Givens:

$\Delta G_f^\circ(C_6H_{6(l)}) = 173$ kJ/mol, $\Delta G_f^\circ(CO_{2(g)}) = -394$ kJ/mol

$\Delta G_f^\circ(H_2O_{(l)}) = -237$ kJ/mol

Solution:

$\Delta G_r^\circ = \Sigma n\, \Delta G_f^\circ(\text{Products}) - \Sigma n\, \Delta G_f^\circ(\text{Reactants})$

$\Delta G_r^\circ = [12\, \Delta G_f^\circ\, (CO_2) + 6\, \Delta G_f^\circ\, (H_2O)] - [2\, \Delta G_f^\circ\, (C_6H_6) + 15\, \Delta G_f^\circ\, (O_2)]$

$$\Delta G_r^\circ = [12 \times (-394\text{ kJ/mol}) + 6 \times (-237\text{ kJ/mol})] - [2 \times 173\text{ kJ/mol} + 15 \times 0]$$

$\Delta G_r^\circ =$ **-6496 kJ**

As the result is negative, the reaction occurs spontaneously.

1-16-2-Application of Gibbs Equation and Direction of Chemical Reactions

Gibbs equation is accepted as a very important equation which enables us to understand properties of chemical reactions. The equation is also related to changes which occurs in properties of system.

$$\Delta G = \Delta H - T\, \Delta S$$

Because using ΔG values saves us from calculation of changes in enthalpy and entropy. According to Gibbs equation, change in free energy (ΔG) includes two important factors which affect if a chemical reaction can occur spontaneously or not.

First Factor:

Reactions mostly work towards the direction with the lowest energy (enthalpy). If value of ΔH is negative, in other words exothermic, the possibility of spontaneous occurrence of reaction increases.

Second Factor:

Reactions mostly work towards the direction with the highest entropy. If value of ΔS is positive (if disorder increases), the possibility of spontaneous occurrence of reaction increases. Positive value of ΔS causes value of ΔG being negative.

Exercise: 1-11

Calculate standard Gibbs free energy of the following reaction under standard conditions, 25°C and 1 atm pressure. Also tell if the reaction occurs spontaneously or not under these conditions.

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

Givens:

$\Delta G_f^\circ\, (NO) = 87$ kJ/mol,

$\Delta G_f^\circ\, (NO_2) = 52$ kJ/mol

Answer : -70 kJ/mol
Spontaneous

If we put aside temperature, there must be a relationship as follows between two factors mentioned above for a reaction occur spontaneously. ($\Delta H < 0$ and $\Delta S > 0$)

Generally, ΔH and ΔS symbols affect values of ΔG in 4 ways:

1-If ΔH and ΔS have positive values, when TΔS is bigger than ΔH, ΔG will be negative. This condition occurs when T is high.

2-If ΔH is positive and ΔS is negative, value of ΔG will be always positive independent of the effect of temperature T.

3-If value of ΔH is negative and ΔS is positive, value of ΔG will be negative independent of the effect of temperature T.

4-If both values of ΔH and ΔS are negative and if value of TΔS is less than ΔH, value of ΔG will be negative. This condition occurs only when T is low.

The temperature which causes negative ΔG values in Situation 1 and 2 depends on real values of ΔH and ΔS of system. Table 1-6 summarizes possible effects defined below.

Table 1-6 Factors effecting on sign of ΔG in ΔG=ΔH-TΔS

ΔH	ΔS	ΔG	Example
+	+	Reaction occurs spontaneously at high temperature. It occurs spontaneously in the opposite direction at low temperatures.	$2HgO_{(s)} \longrightarrow 2Hg_{(l)} + O_{2(g)}$
+	-	ΔG is always positive. Reaction does not occur spontaneously at all temperature. It occurs Spontaneously in opposite direction.	$3O_{2(g)} \longrightarrow 2O_{3(g)}$
-	+	ΔG is always negative. Reaction occurs spontaneously at all temperature.	$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$
-	-	Reaction occurs spontaneously at low temperatures. It occurs spontaneously in opposite direction at high temperature.	$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$

Under standard conditions 25°C and 1 atm pressure, when ΔH_r° and ΔS_r° are measured, Gibbs equation can be used as follows:

$$\Delta G_r^0 = \Delta H_r^0 - T\Delta S_r^0$$

Example 1-12

Explain the following startn from Gibbs equation.
Self-dissolution of sulfar dixide gas in water with releasing heat.

Solution:

Dissoiving (dissolution) process of sulfur dioy is an exothermic process (releasing heat) so that $\Delta H = (-)$ has a negative value.

Dissoiution process of the gas accompunying with decreasing in the entropy (transformed from disorder to order) so that $\Delta S = (-)$ has a negative value.

From the equation

$\Delta G = \Delta H - T\ \Delta S$

$\Delta G = (-\Delta H) - (-T\ \Delta S)$

$\Delta G = -\Delta H + T\ \Delta S$

$\Delta G = (-)$ as this process is spontaneous.

At the low or normal tempertures, the value of ΔH is greater than $T\Delta S$ so $\Delta G = (-)$, and dissolving spontaneous.
That mean the enthalpy is the determining factor for the spontaneity of this process.

Exercise-1-12

Explain the following startn from Gibbs equation.
Non-decomposition of water to its element under standard conditions.

Exercise-1-13

Calculate the value of $\Delta G_r°$ of the following reaction under standard conditions, 25°C and 1 atm pressure.

$C_5H_{12(l)} + 8O_{2(g)} \rightarrow 5CO_{2(g)} + 6H_2O_{(l)}$

Under standard conditions, the value of enthalpy of reaction $\Delta H_r°$ was calculated and the following result was obtained:

$\Delta H_r° = -3536$ kJ/mol

Besides, $\Delta S_r°$ was calculated and the following result was obtained:

$\Delta S_r° = 374$ J/K.mol

Answer: -3647.5 kJ/mol.

Attention:

While solving this kind of questions, we shouldn't forget that units of $\Delta H_r°$ and $\Delta S_r°$ aren't the same. Therefore, we need to convert unit of entropy from J/K.mol to enthalpy unit kJ/K.mol.

Example 1-13

According to the following data,

$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$

Substance	$\Delta H_f°$ kJ/mol	S° J/K.mol
$C_2H_5OH_{(l)}$	-278	161
$O_{2(g)}$	0	205
$CO_{2(g)}$	-394	214
$H_2O_{(l)}$	-286	70

Calculate the following values for the reaction under standard conditions.

A) $\Delta H_r°$

B) $\Delta S_r°$

C) $\Delta G_r°$

Solution:

A) Calculation of $\Delta H_r°$

$\Delta H_r° = \Sigma\, n\, \Delta H_f°\,(\text{Products}) - \Sigma\, n\, \Delta H_f°\,(\text{Reactants})$

$\Delta H_r° = [2\, \Delta H_f°\,(CO_2) + 3\, \Delta H_f°\,(H_2O)] - [\Delta H_f°\,(C_2H_5OH) + 3\, \Delta H_f°\,(O_2)]$

$\Delta H_r° = [2 \times (-394 \text{ kJ/mol}) + 3 \times (-286 \text{ kJ/mol})] - [-278 \text{ kJ/mol} + 3 \times 0]$

$\Delta H_r° =$ **-1368 kJ/mol**

B) Calculation of $\Delta S_r°$

$\Delta S_r° = \Sigma\, n\, S°\,(\text{Products}) - \Sigma\, n\, S°\,(\text{Reactants})$

$\Delta S_r° = [2S°\,(CO_2) + 3S°\,(H_2O)] - [S°\,(C_2H_5OH) + 3S°\,(O_2)]$

$\Delta S_r° = [2 \times 214 \text{ J/K.mol} + 3 \times 70 \text{ J/K.mol}] - [161 \text{ J/K.mol} + 3 \times 205 \text{ J/K.mol}]$

$\Delta S_r° = -138$ J/K.mol

$$\Delta S_r°(\text{kJ/K.mol}) = \Delta S_r°(\text{J/K.mol}) \times \frac{1(\text{kJ})}{1000\ (\text{J})}$$

$$\Delta S_r°(\text{kJ/K.mol}) = -138(\text{J/K.mol}) \times \frac{1(\text{kJ})}{1000\ (\text{J})}$$

$\Delta S_r°(\text{kJ/K.mol}) =$ **-0.138 kJ/K.mol**

C) Calculation of $\Delta G_r°$

Let's change temperature from centigrade (°C) unit to Kelvin (K) unit.

$T(K) = t(°C) + 273 = 25 + 273 = 298$ K

As the value of $\Delta G_r°$ is negative, the reaction occurs spontaneously at 25 °C and 1 atm pressure.

$\Delta G_r° = \Delta H_r° - T\Delta S_r°$

$\Delta G_r° = -1368$ kJ/mol - 298 K × (-0.138 kJ/K.mol)

$\Delta G_r° =$ **-1327 kJ/mol**

1-17-CALCULATION OF ENTROPIES OF PHYSICAL CHANGES

In the previous chapters, we have defined standard enthalpies of physical changes as enthalpy of vaporization ΔH_{vap} and enthalpy of fusion ΔH_{fus}. Besides, we know that substances change from solid to liquid at melting temperature T_m. Substances change from liquid to gas at boiling temperature T_b. Melting and boiling temperatures are at equilibrium between solid or liquid vapor and atmospheric pressure. That means value of ΔG at these temperatures is equal to zero. Therefore, Gibbs relationship can be written as follows:

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H_{tr} - T_{tr}\Delta S_{tr}$

We get the following from this relationship:

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$$

tr means transition. For example, substances changes from solid to liquid at melting temperature. Therefore, melting equation will be as follows:

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}$$

fus means fusion. Substances change from liquid to gas at boiling temperature. Therefore, the vaporization equation above can be rewritten as follows:

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

vap means vaporization. We need to highlight that these equations are only valid when system is at equilibrium (for example melting, vaporization and sublimation).

Attention:

Here, there is another physical change which isn't mentioned. It is the change of state of substance directly from solid to gas. This is called as sublimation. As enthalpy of sublimation is a state function, it is equal to the sum of enthalpies of melting and vaporization.

Exercise 1-14

Calculate change of entropy in J/K.mol unit for water boiling at 100°C (boiling point).

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$\Delta H_{vap} = 44$ kJ/mol

Answer: 118 J/K.mol

QUESTIONS OF CHAPTER-1

1-1- Define the following terms:

System, surroundings, group, open system, state function, isolated system, joule, closed system, 1st law of thermodynamics

1-2- What are the units of the following according to International System of Units (SI)?

Enthalpy, entropy, free Gibbs energy

1-3- What are the meanings of the following terms?

Thermochemistry, exothermic, endothermic

1-4- What does state function mean? Give two concepts as examples for state function. Give a process which is not a state function but process function.

1-5-Give the reason for the necessity of writing physical state while writing thermal reactions.

1-6- What is the difference between specific heat and heat capacity? Tell the units of each concept.

1-7- What is the difference between intensive and extensive properties? Give examples for each.

1-8- Write about the calorimeter which is used to measure absorbed or released heat where pressure (q_p) that is enthalpy (ΔH) is constant.

1-9- Calculate the specific heat of a piece of silver which has a mass of 360 g and heat capacity of 86 J/°C.

Answer: 0.24 J/g.°C

1-10- 350 g of mercury was cooled from 77°C to 12°C. Calculate the released heat in kJ unit.
Specific heat of mercury = 0.14 J/g.°C

Answer: -3.2 kJ

1-11- The temperature of 34 g of ethanol was raised to 79°C from 25°C. Calculate the amount of absorbed heat. Specific heat of ethanol = 2.44 J/g.°C

Answer: 4479.8 J

1-12- While heating 4.5 g of gold pieces, 276 J of heat was absorbed. If the initial temperature was 25°C, what is the final temperature? Specific heat of gold = 0.13 J/g.°C

Answer: 496.8°C

1-13- Find the value of ΔG_r° in the following reaction:

$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$

Givens:

$\Delta H_f^\circ(CO) = -110.5$ kJ/mol, $\Delta H_f^\circ(CO_2) = -393.5$ kJ/mol,

$S^\circ(O_2) = 205$ J/K.mol, $S^\circ(CO) = 198$ J/K.mol, $S^\circ(CO_2) = 214$ J/K.mol,

Answer : -514.4 kJ

1-14- When 1.5 g of acetic acid (CH_3COOH) was burnt in the calorimeter which had 750 g of water, the temperature of the calorimeter and its content was raised from 24°C to 28°C. Calculate the amount of heat released from combustion of 1 mole of acetic acid by neglecting the heat capacity of the calorimeter. (Molar mass of acid= 60 g/mol) (Specific heat of water= 4.2 J/g.°C)

Answer: -504000 J/mol

1-15- What are the standard reaction conditions in thermochemistry? What are the differences between those and standard conditions used for gases?

1-16- 2.6 g of acetylene C_2H_2 (M= 26 g/mol.) was put in a calorimeter. After burning the substance, 130 kJ heat was released. Calculate the standard enthalpy of formation of acetylene. The following data is given.

$\Delta H_f^\circ(CO_2) = -393.5$ kJ/mol, $\Delta H_f^\circ(H_2O) = -286$ kJ/mol

Answer: 227 kJ/mol

1-17- Calculate the change in standard enthalpy of formation ΔH_f° (Al_2O_3) and standard enthalpy of combustion ΔH_c°(Al) for the following reaction.

$4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)}$ $\Delta H_r^\circ = -3340$ kJ

Answer: -1670 kJ/mol; -835 kJ/mol

1-18- Apply Hess's Law in the following thermal equations at 25°C and 1 atm pressure and tell its use in chemistry.

1) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ $\Delta H_r^\circ = -185$ kJ
2) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ $\Delta H_r^\circ = -484$ kJ

Calculate the ΔH_r° of the following reaction.

$4HCl_{(g)} + O_{2(g)} \rightarrow 2Cl_{2(g)} + 2H_2O_{(g)}$ $\Delta H_r^\circ = ?$ kJ

Answer: -114 kJ

1-19- If the following thermal equations were given at 25°C and 1 atm pressure:

1) $\frac{1}{2} N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)}$ $\Delta H_r^o = 33$ kJ

2) $N_{2(g)} + 2O_{2(g)} \rightarrow N_2O_{4(g)}$ $\Delta H_r^o = 11$ kJ

Calculate ΔH_r^o for the following reaction

$2NO_{2(g)} \rightarrow N_2O_{4(g)}$ $\Delta H_r^o = ?$ kJ

Answer: -55 kJ

1-20- Calcium carbonate decomposes according to the following reaction.

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

Standard enthalpy of formation ΔH_f^o of each of CaO, CO_2, $CaCO_3$ is (-635, -393.5, -1207) kJ/mol respectively. As ΔS_r^o is 160 J/K.mol, Calculate;

1) ΔH_r^o then draw its energy diagram.
2) ΔG_r^o
3) At which temperature does the reaction occur spontaneously?

Answer: 1) 178.5 kJ 2) 130.8 kJ/mol 3) Greater than 1115.6 K

1-21- Find ΔH_f^o for Fe_2O_3 using the following data:

$2Al_2O_3 \rightarrow 4Al + 3O_2$ $\Delta H = 3340$ kJ

$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$ $\Delta H = -848$ kJ

Answer: -822 kJ

1-22- Calculate standard enthalpy of formation of $HPO_{3(s)}$ compound using the following data.

$P_4O_{10(s)} + 4HNO_{3(l)} \rightarrow 4HPO_{3(s)} + 2N_2O_{5(g)}$ $\Delta H_r^o = -180$ kJ

ΔH_f^o values of the compound are following.

ΔH_f° (P_4O_{10}) = -2984 kJ/mol, ΔH_f° (N_2O_5) = -43 kJ/mol
ΔH_f° (HNO_3) = -174 kJ/mol

Answer: -943.5 kJ/mol

1-23- Calculate the ΔS_r° of the following reaction at 25°C and 1 atm pressure;

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

Using the following data.

S° (N_2) = 192 J/K.mol, S° (H_2) = 131 J/ K.mol
S° (NH_3) = 193 J/K.mol

Answer: -199 J/K.mol

1-24- What does spontaneous process mean? Give two examples for spontaneous and non-spontaneous processes.

1-25- Which of the following processes occurs spontaneously? Which not?

A- Dissolution of table salt in water

B- After opening the cap of perfume bottle, spread out of perfume in the room

C- Separating helium and neon gas mixture

1-26- Define entropy. What are the units of entropy according to International System of Units (SI)?

1-27- Calculate value of ΔS_r° in J/K.mol for the following reaction.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

Givens: ΔH_f° (H_2O) = -242 kJ/mol, ΔG_f° (H_2O) = -228 kJ/mol

Answer: -94 J/K.mol

1-28- Calculate ΔS_r° of the following reaction at 25°C and 1 atm pressure;

$$SiH_{4(g)} + 2O_{2(g)} \rightarrow SiO_{2(s)} + 2H_2O_{(l)}$$

Use the following data;

$S^\circ(SiH_4)$ = 206 J/K.mol, $S^\circ(O_2)$ = 205 J/K.mol
$S^\circ(SiO_2)$ = 42 J/K.mol, $S^\circ(H_2O)$ = 70 J/K.mol

Answer: -434 J/K.mol

1-29- As the value of ΔS_r° of the following reaction is 137 J/K.mol at 25°C and 1 atm pressure, and $S^\circ(O_2)$ is 205 J/K.mol, what is the value of S° of (O_3) ozone?

$$2O_{3(g)} \rightarrow 3O_{2(g)}$$

Answer: 239 J/K.mol

1-30- Define standard free Gibbs Energy of formation and tell its units.

1-31- Calculate the ΔH_r° for the following reaction by using Hess's law.

$CO + 2H_2 \rightarrow CH_3OH$

Standard enthalpy of combustion of each of CO, H_2, CH_3OH is (-284, -286, -727) kJ/mol.

Answer: -129 kJ

1-32- If the ΔH and ΔS values of the following reactions are known, find out the temperatures at which those reactions occur spontaneously.

Reaction A: ΔS = +48 J/K.mol and ΔH = +126 kJ/mol

Reaction B: ΔS = -105 J/K.mol and ΔH = -12kJ/mol

Answer: A: Greater than 2625 K

B: Less than 114.3 K

1-33- The following reaction ,

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

is non- spontaneous at normal conditions, calculate in which temperature the reaction will be spontaneous, at **927°C** or **627°C**

Givens : $\Delta H_r^\circ = 178.5$ **KJ** , $\Delta S_r^\circ = 160$ **J/K**

Answer: **927°C**

1-34- Explain the following processes starting from Gibbs equation (ΔG = ΔH - TΔS).

1- At what temperature dose ice melt spontaneously?

2- Calcium carbonate spontaneously decomposes at high temperatures.

3- Decomposition of mercury (II) oxide is always spontaneous at high temperature , not low temperature.

4-The water doesnt freeze spontaneously under normal condition.

CHEMICAL EQUILIBRIUM

CHAPTER-2

ACHIEVEMENTS

After completing this chapter, the student is expected to :

- * Differentiate reversible and irreversible reactions.
- * Understand how a reaction reaches equilibrium state.
- * Discover the relationship between K_c and K_p which are equilibrium constants.
- * Learn the importance of equilibrium constants in order to tell way the reaction goes.
- * Learn the relationship between the equilibrium constants and equation writing method.
- * Learn the result and the importance of the reaction.
- * Understand the Le Chatelier Law, equilibrium state and the factors affecting equilibrium constants and applies all those information to problems.

Chapter - 2

2-1 REVERSIBLE AND IRREVERSIBLE REACTIONS

The interaction of two or more substances yields one or more new substance/s. **differ in their characters** This process is defined as a chemical reaction. Chemical reactions are shown through chemical equations. Chemical equations demonstrate the changes which substances undergo in order to produce new materials via formulas. The arrow sign in the equation shows the way the reaction works.

Chemical reactions are divided into two: Reversible reactions and irreversible reactions. During irreversible reactions one or two of the reactants are **completely consumption** This is shown with a single arrow $\longrightarrow$. For example, when the fuel in a car is fully combusted, carbon dioxide and water are produced. This process is irreversible. Because transformation of carbon dioxide and water into fuel is extremely difficult or in other words impossible. These kinds of changes are called one-way reactions. These kinds of reactions are **complete and** irreversible. Below are some examples for those.

1- The formation of sodium sulfate salt and water by addition of sulfuric acid into sodium hydroxide

$$H_2SO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

2- The formation of carbon dioxide through addition of hydrochloric acid into sodium carbonate.

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

The definition of irreversible reactions: These are chemical reactions in which under certain conditions one or all of the reactants are consumption products under the same conditions cannot change back into the substances forming them.

The other type of reaction is called reversible reaction.

During these reactions, products can reform the reactants while only some of the reactants turn into products. In other words, reversible reactions cannot be completed however long time passes by under suitable conditions. Some reactants always remain in the reaction chamber. This situation is shown by two reverse arrows in the equation $\rightleftharpoons$.

There are many reversible chemical reactions. Respiration is an example. This event occurs by gas change. The blood coming to lungs carry water and carbon dioxide. The blood leaves these substances and loads up oxygen. Then through inner-respiration, it leaves oxygen and reloads water and carbon dioxide. Some other examples are given below.

1- The formation of ethyl acetate and water through the reaction of acetic acid with ethyl alcohol.

$$CH_3COOH_{(l)} + CH_3CH_2OH_{(l)} \rightleftharpoons CH_3COOCH_2CH_{3(l)} + H_2O_{(l)}$$

2- In order to form hydrogen iodide gas in a closed system, the reaction of hydrogen gas and iodine vapor. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

3- In a closed system the decomposition of calcium carbonate salt into calcium oxide and carbon dioxide. $CO_{2(g)}$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

4- Some physical changes like vaporization of water in a closed system.

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

The definition of reversible reactions: These are reactions in which products are changed back into reactants. Products have the capability of reacting in order to reform the substances yielding them.

2-2 REVERSIBLE REACTIONS AND EQUILIBRIUM STATE:

As stated above, most of the reversible reactions continue in opposite ways under the same reaction conditions. For example, H_2 gas reacts with N_2 under suitable conditions and forms ammonia (NH_3) gas. In the beginning, the forward reaction is fast in the way of producing ammonia, having R_f value (R_f is rate of forward reaction.) By the time, under the same conditions, as the concentration of ammonia increases, the forming ammonia decomposes into H_2 and N_2 at R_b rate (R_b is the rate of the backward reaction.) Both reactions continue until the rates of the reactions become equal **($R_f = R_b$)** Thus, the reaction reaches chemical equilibrium.

$$N_{2(g)} + 3H_{2(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2NH_{3(g)}$$

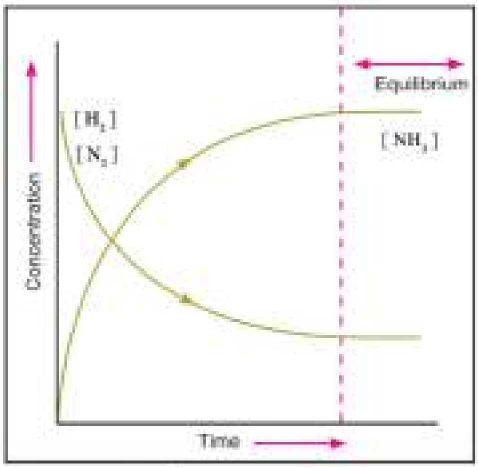


Figure 2-1

Reversible reaction reaches equilibrium after a while.

2-3 HOMOGENEOUS AND HETEROGENEOUS REVERSIBLE REACTIONS:

Reversible homogeneous reactions are reactions in which reactants and products are at the same physical conditions. The examples for those are given below (Keep in mind that all the reactions occur in a closed system)

1- Equilibrium reaction between gases:

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

2- Equilibrium reaction in a solution:

$HCOOH_{(aq)} + CH_3OH_{(aq)} \rightleftharpoons HCOOCH_{3(aq)} + H_2O_{(l)}$

3- Equilibrium reaction between solids:

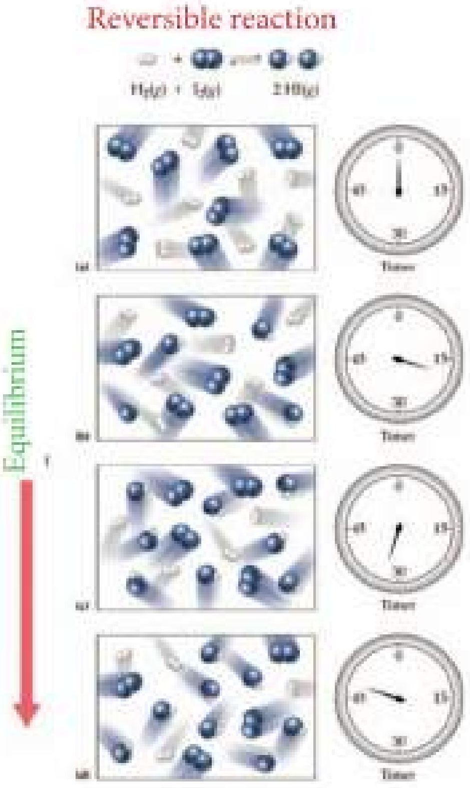
$Zn_{(s)} + S_{(s)} \rightleftharpoons ZnS_{(s)}$

Regarding the reversible heterogeneous reaction are that reactions that include the reactants and the products in more than one phase and their examples in closed system;

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$

$2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$



Reversible reaction reaches equilibrium after a while.

2-4 EQUILIBRIUM STATE AND LAW OF MASS ACTION:

At 445 °C, 2 moles of hydrogen iodide must be formed when a mole of hydrogen gas and a mole of iodine gases are mixed in order to form hydrogen iodide gas.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

But, when this mixture reaches equilibrium, the analysis shows that 78% of HI gas and 11% of iodine gas and 11% of hydrogen gas is found. Similarly, at the same temperature, if pure HI gas is heated, it decomposes into hydrogen and iodine gases. The mixture always contains 78% HI gas and 11% iodine and 11% of hydrogen at equilibrium.

The relationship between chemical reaction rate and reactions of substances is called Law of Mass Action. According to the law, the rate of a chemical reaction is directly proportional to the molar concentrations of the reacting substances. The mole numbers in a balanced equation are used as exponents for these concentrations.

When the law of mass action mentioned above is applied:

$$H_{2(g)} + I_{2(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2HI_{(g)}$$

According to law of mass action, the R_f and R_b rates can be shown mathematically as:

$$R_f = k_f [H_2][I_2]$$

$$R_b = k_b [HI]^2$$

2-5 EQUILIBRIUM CONSTANT:

Consider a reversible equilibrium reaction.

$$aA + bB \rightleftharpoons gG + hH$$

In the equation, A, B, G and H are reactants and products.
a, b, g, h are the mole numbers in the equation.

According to the forward reaction, when we apply the law of mass action, the equation below is acquired.

$$R_f = k_f [A]^a [B]^b \qquad (1)$$

But, according to the backward reaction, when we apply the law of mass action, the equation below is acquired.

$$R_b = k_b [G]^g [H]^h \qquad (2)$$

k_f and k_b is the rate constants for the forward and backward reactions respectively. When the equilibrium is reached, the rate of the forward reaction is equal to the backward reaction rate.

$R_f = R_b$. Figure 2-2. Thus we get:

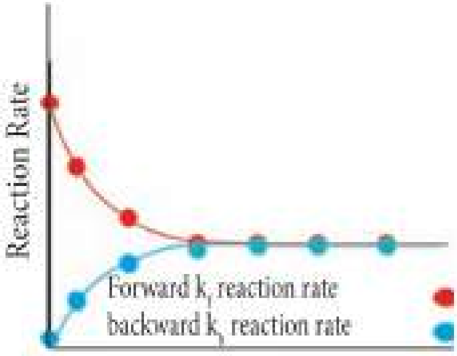


Figure 2-2
The equilibrium state graphics for a gas mixture: It shows formation, decomposition and the rate of reaching equilibrium.

$$k_f [A]^a [B]^b = k_b [G]^g [H]^h \quad (3)$$

If we arrange equation 3, we get the relationship below:

$$\frac{k_f}{k_b} = \frac{[G]^g [H]^h}{[A]^a [B]^b} \quad (4)$$

By the ratio of rate constants of forward and reverse reactions (k_f and k_b), a new equilibrium constant is obtained which is called as equilibrium constant K_{eq}. Therefore, Equation 4 becomes as follows.

$$K_{eq} = \frac{[G]^g [H]^h}{[A]^a [B]^b} \quad (5)$$

Equilibrium is the ratio of rate constant of forward reaction (k_f) to rate constant of reverse reaction (k_b). Therefore, The Equilibrium Constant is obtained by the ratio of molar concentrations of products over reactants for a reaction that is at equilibrium. each is raised to the power of the number of its moles in the balanced reaction equation. This value remains constant as long as the temperature doesn't change.

At equilibrium, when the concentrations of reactants and products are measured as molarity (M), equilibrium constant K_{eq} is shown with K_c. Letter c is taken from the word concentration. Equilibrium constant doesn't have a certain unit. As equation 5 shows the molar concentrations of reactants and products, its equilibrium constant is expressed with K_c insteade of K_{eq} and written as follows:

$$K_c = \frac{[G]^g [H]^h}{[A]^a [B]^b} \quad (6)$$

Example 2-1

Calculate the equilibrium constant K_{eq} for the following reaction.

$$N_{2(g)} + 3H_{2(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2NH_{3(g)}$$

The rate constant of forward reaction k_f is 0.11 and the rate constant of reverse reaction k_b is given as 0.05.

Solution:

$$K_{eq} = \frac{k_f}{k_b} = \frac{0.11}{0.05} = 2.2$$

Exercise 2-1

In an equilibrium reaction, the equilibrium constant K_{eq} is 4.24. As the rate constant of reverse reaction k_b is 0.02, calculate the rate constant of forward reaction.k_f

Answer: 0.0848

If all the reactants and products are in gaseous form, with respect to their molar concentrations, their partial pressures are measured more easily. Therefore, it is more suitable to tell the concentration of a gas using its partial pressure (P). Thus, equilibrium constant K_{eq} is shown as K_p (equilibrium constant in partial pressure form). The amounts of the reacting gases are told as their partial pressures, so in equation 5, the equilibrium constant of the gases is shown as below:

$$K_P = \frac{P_G^g \times P_H^h}{P_A^a \times P_B^b} \qquad (7)$$

The definition of equilibrium constant in terms of partial pressures is the multiplication of partial pressures of products over multiplication of partial pressures of reactants and the coefficients of all gaseous species in the reaction are used as a power. This value does not change at constant temperature. It is constant.

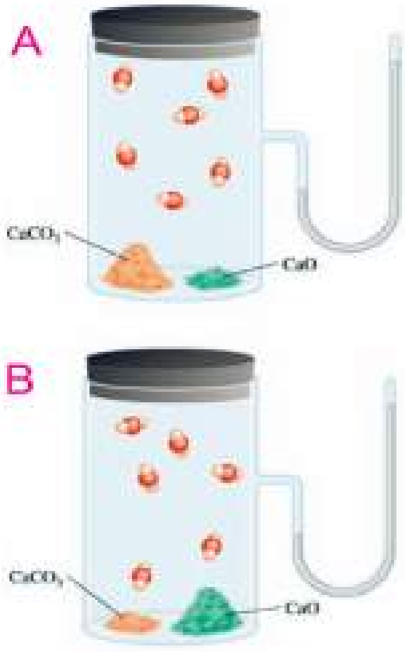


Figure 2-3
In spite of the changes in the amounts of $CaCO_3$ and CaO, the pressure of CO_2 at equilibrium remained Constant at the same temperature.

There is a point here needs some consideration: In homogeneous reactions where all reactants and products are in gaseous state, the equilibrium constant is found through dividing multiplication of partial pressures of products only in gas form to multiplication of partial pressures of reactants only in gas form. (As shown in eq. 7)
In equilibrium reactions which contain substances in different physical states, pure solid and liquid substances are not considered while writing equilibrium constant. e.g as in sodium bicarbonate's thermal decomposition reaction below:

$$2NaHCO_{3(s)} \xrightarrow{\Delta} Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$$

Heterogeneous reactions also reach equilibrium just as homogenous reactions. For example, if sodium bicarbonate is heated in a closed container, the reaction reaches equilibrium at a certain time.

$$2NaHCO_{3(s)} \xrightleftharpoons{\Delta} Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$$

The equilibrium constant for this reaction is written as follows:

$$K_c = \frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]}$$

In equilibrium constant relationship, the concentrations of solid and liquid substances are not written. Therefore, while writing equilibrium constant for heterogeneous reactions, concentrations of pure solids and liquids are not considered. Thus, the equilibrium constant for thermal decomposition of sodium bicarbonate is written as follows:

$$K_c = [CO_2][H_2O]$$

Or the equilibrium constant in partial pressures (K_p) is as below:

$$K_p = P_{CO_2} P_{H_2O}$$

Another example is the equilibrium constant for thermal decomposition of calcium carbonate when the reaction reaches equilibrium:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

The equilibrium constant in terms of molar concentrations is written as follows:

$$K_c = [CO_2]$$

In terms of partial pressures it is written as:

$$K_p = P_{CO_2}$$

The pressure of CO_2 at equilibrium is not affected from the change in the amounts of $CaCO_3$ and CaO and remained constant at the same temperature. figure 2-3.

Example 2-2

For the reactions below, write down the equilibrium constants in terms of molar concentrations K_c :

(1) $2HBr_{(g)} \rightleftharpoons H_{2(g)} + Br_{2(g)}$

(2) $NO^-_{2(aq)} + H_2O_{(l)} \rightleftharpoons HNO_{2(aq)} + OH^-_{(aq)}$

(3) $CaCO_{3(s)} + 2HCl_{(aq)} \rightleftharpoons CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

Solution :

$$K_c = \frac{[H_2][Br_2]}{[HBr]^2}$$

$$K_c = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$$K_c = \frac{[CO_2][CaCl_2]}{[HCl]^2}$$

Example 2-3

For the reactions below, write down the equilibrium constants in terms of partial pressures:

$$(1)\quad 3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$(2)\quad 2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$$

Solution:

$$K_P = \frac{P^2_{NH_3}}{P^3_{H_2}\,P_{N_2}}$$

$$K_P = \frac{1}{P_{O_2}}$$

2-6 CALCULATION OF EQUILIBRIUM CONSTANT K_{eq}:

When the reaction reaches equilibrium, the value of the equilibrium constant can be calculated through the measurement of the concentrations of all reactants and products. These values are inserted in the formula to write the equilibrium constant at a constant temperature. Because at constant temperature, for any reaction at equilibrium state, the value of K_{eq} remains constant independent of the amounts of the reactants and products.

Example 2-4

Assume that the equilibrium reaction at a given temperature is:

$$2CH_{4(g)} \rightleftharpoons C_2H_{2(g)} + 3H_{2(g)}$$

At certain temperature and at equilibrium, the concentrations are given below. Calculate K_{eq} for the reaction.

$$[CH_4] = 0.02\,M\ ,\ [C_2H_2] = 0.05\,M\ ,\ [H_2] = 0.143\,M$$

Solution:

As the molar concentrations at equilibrium are given, we can write the equilibrium constant relationship K_{eq} in terms of K_c as below:

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} = \frac{(0.05)(0.143)^3}{(0.02)^2} = 0.37$$

Besides that, some questions may be asked in which the initial partial pressures of reactants or concentrations and the equilibrium constants are given. (Here, students should see the difference between the initial concentrations
The table consists of three steps. The first step is the concentrations or partial pressures of reactants before reaction (initial), the second step is the changes occurring in the concentrations or partial pressures of substances during reaction (change) and the final step is the concentrations or partial pressures of substances after the reaction reaches equilibrium (equilibrium).

As show in the following example :

Example 2-5

In a 1 **L** container at 430°C, 0.5 mole of H_2 and 0.5 mole of I_2 reacts. The equilibrium constant is found as $K_c = 5.29$, when the equilibrium is reached. Calculate the concentrations of substances in mixture at equilibrium.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Solution:

The initial concentrations of the reactants are calculated through the relationship below using the volume of the mixture and mole number.

$$[M] = \frac{n\,(mol)}{V\,(L)}$$

$$[H_2] = [I_2] = \frac{0.5\,(mol)}{1\,(L)} = 0.5\ mol/L$$

	$H_{2(g)}$ +	$I_{2(g)} \rightleftharpoons$	$2HI_{(g)}$
Concentrations / M	$[H_2]$	$[I_2]$	$2[HI]$
Initial Concentration	0.5	0.5	0.0
Change in concentration	$-x$	$-x$	$+2x$
Concentration at equilibrium	$0.5-x$	$0.5-x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$5.29 = \frac{[2x]^2}{[0.5-x][0.5-x]}$$

$$5.29 = \frac{[2x]^2}{[0.5-x]^2}$$

Exercise 2-2

When the system reaches equilibrium, the concentrations of reactants are:

$[N_2O_4] = 0.002$ M

$[NO_2] = 0.017$ M

For the reaction below, calculate K_{eq} at 100 °C

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

Answer: 6.92

Taking the square root of the equation, we get the x value.
x = 0.267 mol/L
Therefore, the concentrations at equilibrium are:

$$[H_2] = [I_2] = 0.5 - 0.267 = 0.233 \ \text{mol/L}$$
$$[HI] = 2 \times 0.267 = 0.534 \ \text{mol/L}$$

In some problems, the partial pressures or concentrations of the reactants and after equilibrium, the concentration or partial pressure of one of the reactants' or products' are given. Then the equilibrium constant is asked to be calculated.

Example 2-6

In an experiment, 0.625 moles N_2O_4 gas was decomposed in a 5 liters-container at a given temperature. When the equilibrium is reached, remaining N_2O_4 concentration is observed as 0.025 mol/L. Calculate the K_c value of the reaction. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Solution:

We convert the mole number in 5 liters to the mole number in 1 liter. In other words, we calculate the initial molar concentration of N_2O_4 gas.

$$(\text{mol/L}) = \frac{n(\text{mol})}{V(L)} = \frac{0.625(\text{mol})}{5(L)} = 0.125 \text{mol/L}$$

	$N_2O_{4(g)} \rightleftharpoons$	$2NO_{2(g)}$
Concentration/)(	$[N_2O_4]$	$2[NO_2]$
Initial Concentration	0.125	0.000
Change in concentration	−x	+2x
Concentration at equilibrium	0.125−x	2x

N_2O_4 concentration at equilibrium is equal to 0.025 mol/L. So,

$$0.125 - x = 0.025 \Rightarrow x = 0.10 \text{ mol/L}$$
$$[NO_2] = 2x = 2 \times 0.10 = 0.20 \text{ mol/L}$$

The equilibrium constant relationship,

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.20]^2}{[0.025]} = 1.6$$

Example 2-7

For the gas equilibrium reaction below,

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

In a 1 liter- closed container at a given temperature, the pressure of SO_3 gas before decomposition is 3 atm. After the reaction comes to equilibrium, the total pressure of the gas mixture is found 4 atm. Calculate K_P value of the reaction at equilibrium.

Solution:

	$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$		
Pressure /atm	$2SO_3$	$2SO_2$	O_2
Initial Pressure	3.0	0.0	0.0
Change in Pressure	$-2x$	$+2x$	$+x$
Pressure at equilibrium	$3.0-2x$	$2x$	x

According to Dalton's Law, total pressure is equal to the sum of partial pressures of gases in the mixture. If we assume the total pressure is P_T at equilibrium, pressure is:

$$P_T = P_{SO_3} + P_{SO_2} + P_{O_2}$$

$$4 = (3-2x) + 2x + x$$

$$x = 1 \text{ atm}$$

$$P_{SO_3} = 3.0 - 2x = 3.0 - 2 \times 1 = 1 \text{ atm}$$

$$P_{SO_2} = 2x = 2 \times 1 = 2 \text{ atm}$$

$$P_{O_2} = x = 1 \text{ atm}$$

$$K_p = \frac{P^2_{SO_2} \quad P_{O_2}}{P^2_{SO_3}} = \frac{(2)^2 \quad (1)}{(1)^2} = 4$$

2-7-THE RELATIONSHIP BETWEEN K_P AND K_C EQUILIBRIUM CONSTANTS:

There is a relationship between equilibrium constants in terms of partial pressures K_p and in terms of molar concentrations K_c with respect to two equations below:

$$K_p = K_c (RT)^{\Delta n_g} \quad \text{or} \quad K_c = K_p (RT)^{-\Delta n_g}$$

Exercise 2-3

For the reaction below:

$$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$$

In a 1 liter-container, the reaction began with 0.8 moles CO_2 at a given temperature. When the reaction reached equilibrium, the half of the gas decomposed. Calculate the value of K_c.

Answer: 0.2

Exercise 2-4

As the reaction's equilibrium constant is $K_c = 200$, in the gas reaction below,

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Different amounts of H_2 and N_2 were put in a 1 liter-container. When the reaction reaches equilibrium, 0.3 moles of H_2 was used and 0.2 moles of N_2 remained. What are the mole numbers of H_2 and N_2 before reaction?

Answer:

$[N_2] = 0.3$ mol

$[H_2] = 0.4$ mol

Warning! Δn_g shows the difference between mole numbers of reactants and products only in **gaseous form**. Therefore, g subscript is used.

Attention: In this kind of problems, we use the $R = 0.082$ L.atm/K.mol.
R: Ideal gas constant

Exercise 2-5

For the following reaction

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$K_p = 1.5\times10^{-5}$ at 500 °C, calculate K_c for the equilibrium reaction at the same temperature.

Answer: 0.06

Exercise 2-6

In the following reaction, $K_c = 1.6$ at 1000 °C.

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$$

When the partial pressure of CO_2 is 0.6 atm at equilibrium, calculate the partial pressure of CO at equilibrium.

Answer: 10 atm

Δn_g symbol is defined with respect to the following relationship:

$$\Delta n_g = \Sigma n_g(\text{Products}) - \Sigma n_g(\text{Reactants})$$

The relationship between K_c and K_p is as below:

1- If Δn_g is equal to 0, $K_c = K_p$

2- If Δn_g is a positive value, $K_p > K_c$

3- If Δn_g is a negative value, $K_p < K_c$

Example 2-8

In an reaction at 227°C, if $\Delta n_g = -1$, $K_c = 4.1$, what is the value of K_p?

Solution:

Firstly, we convert temperature from °C to K unit.

$$T(K) = t(°C) + 273 = 227 + 273 = 500\ K$$

$$K_p = K_c\,(RT)^{\Delta n_g} = 4.1\,(0.082 \times 500)^{-1} = 0.1$$

Example 2-9

The following reaction reaches equilibrium at 300 K.

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

The partial pressures of two gases are 0.3 atm when the equilibrium is set. Calculate K_p and K_c.

Solution:

$$K_p = P_{NH_3} \times P_{H_2S} = (0.3) \times (0.3) = 0.09$$

$$\Delta n_g = \Sigma n_g(\text{Products}) - \Sigma n_g(\text{Reactants}) = 2 - 0 = 2$$

$$K_c = K_p\,(RT)^{-\Delta n_g} = 0.09\,(0.082 \times 300)^{2} = 1.5 \times 10^{-4}$$

2-8 THE SIGNIFICANCE OF THE EQUILIBRIUM CONSTANT

Learning the value of the equilibrium constant is very important. If we know the value of the equilibrium constant, we can estimate the following properties of the reaction:

A- To determine the direction of the reaction

B- To determine the relationship between the equilibrium constant and the method of writing equation.

2-8-1 Finding direction of Reactions by using Equilibrium Constant

If we take the simple example below:

$$A \rightleftharpoons B$$

If K_c = 100, that means:

$$K_c = \frac{[B]}{[A]} \Rightarrow 100 = \frac{[B]}{[A]} \Rightarrow [B] = 100[A]$$

From the last mathematical relationship, we conclude that [B]'s concentration is 100 times bigger than [A]'s concentration. Therefore, the equilibrium shifts to the direction where substance [B] is produced, or to the direction of products. This is especially preferred in industrial production.

But, if K_c = 0.01 for the same reaction:

$$K_c = \frac{[B]}{[A]} \Rightarrow 0.01 = \frac{[B]}{[A]} \Rightarrow [A] = 100[B]$$

Here, at equilibrium, the concentration of substance [A] is 100 times bigger than the concentration of substance [B]. So the equilibrium shifts to the direction of substance [A], or to the reactants. As a general rule:

1- If the value of the equilibrium constant is very big, the concentration of the products are very big. Hence, the reaction direction forward.

2- If the value of the equilibrium constant is very small, the concentration of the products are very small at equilibrium. Hence, the reaction functions backward.

3- If the equilibrium constant is exactly 1 or a value close to 1, the concentrations of the reactants and products are equal or very close to being equal.

If the value of K is much bigger than 1 (K>>1), at equilibrium, the concentration of the products will be much bigger than that of reactants. Thus, the equilibrium shifts towards the products Figure 2-4 .

Figure 2-4

If the value of K is much less than 1 (K<<1), the concentration of the reactants will be much bigger than of products. Thus, the equilibrium shifts towards the reactants Figure 2-5 .

Figure 2-5

Example 2-10

Using the equilibrium constants for the following reactions, estimate the equilibrium state.

$$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)} \qquad K_c = 1 \times 10^{-95}$$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad K_c = 8 \times 10^{25}$$

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad K_c = 1.1$$

Solution:

1- The equilibrium constant for the first reaction is too small. In other words, the amounts of F_2 and H_2 at equilibrium are so little that practically this kind of reaction does not occur.

2- The equilibrium constant for the second reaction is too big. That means the reactants produce nearly 100% SO_3 at equilibrium. The amount of O_2 and SO_2 that enters the reaction but does not interact is too little. Therefore practically this reaction occurs completely.

3- The equilibrium constant for the third reaction is almost 1. Therefore, at equilibrium, the concentrations of the reactants (H_2 and N_2 gases) and products (NH_3) are close to each other.

2-8-2-The Relationship between writing Equations and K_c

Whatever the direction of equilibrium, the relationship in any equilibrium constant depends on the equation for the equilibrium reaction. Here, we will assign 3 rules for writing equations.

Rule: 1

When a reaction's direction is reversed, the new equilibrium constant is the reciprocal of the first equilibrium constant.

For example, in the equilibrium reaction below:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

The equilibrium constant for this reaction is:

$$K_{c1} = \frac{[HCl]^2}{[H_2][Cl_2]}$$

When we reverse this reaction

$$2HCl_{(g)} \rightleftharpoons H_{2(g)} + Cl_{2(g)}$$

The equilibrium constant for this reaction is written as follows:

$$2HCl_{(g)} \rightleftharpoons H_{2(g)} + Cl_{2(g)}$$

When we look at the two reactions above, the relationship between K_{c1} and K_{c2} values is as follows:

$$K_{c2} = \frac{[H_2][Cl_2]}{[HCl]^2} \qquad K_{c2} = \frac{1}{K_{c1}}$$

Rule : 2

When a reaction equation is multiplied with a coefficient (e.g a number), the new equilibrium constant is found as that coefficient is used as the exponent of the first equilibrium constant. Let's explain that rule with the following example. Take the previous equilibrium reaction:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

The equilibrium constant is: $K_{c1} = \frac{[HCl]^2}{[H_2][Cl_2]}$

If this reaction is multiplied with ½ , the equation becomes as follows:

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightleftharpoons HCl_{(g)}$$

The equilibrium constant for the last equation is shown as:

$$K_{c2} = \frac{[HCl]}{[H_2]^{1/2}[Cl_2]^{1/2}}$$

If we examine K_{c1} and K_{c2} values, the new equilibrium constant K_{c2} is equal to the ½ exponent of the first equilibrium constant. Thus,

$$K_{c2} = (K_{c1})^{1/2} = \sqrt{K_{c1}}$$

Rule: 3

If the reaction is a sum of a series of reactions, the total reaction's equilibrium constant is equal to the multiplication of all reactions' equilibrium constants. For example, take the 2 equilibrium reactions below:

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{(g)} \qquad K_{c1} = \frac{[CO]}{[O_2]^{1/2}}$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)} \qquad K_{c2} = \frac{[CO_2]}{[CO][O_2]^{1/2}}$$

Exercise 2-7

The equilibrium constant for the following gaseous reaction is $K_p = 0.39$ at 227 °C.

$$2NO_2 \rightleftharpoons N_2O_4$$

What is the value of K_c in the following reaction at same condition.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Answer: 0.0625

Attention:

carbon is solid material not included in the equilibrium constant.

Exercise 2-8

1 mole of HBr gas was put in a 1 liter closed container. When the gas reaction reached equilibrium at a given temperature, according to the equation below, 0.2 mole of Br_2 gas was produced.

$$2HBr \rightleftharpoons H_2 + Br_2$$

In another 1 liter-container, calculate the mole number of HBr gas at equilibrium state from reaction of 2 moles of Br_2 and 2 mole of H_2 according to the reaction below.

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

Answer: 2.4 moles.

Exercise 2-9

For the following reactions at 2000K, the equilibrium constants in terms of partial pressures are given.

$$\frac{1}{2}Br_{2(g)} + \frac{1}{2}F_{2(g)} \rightleftharpoons BrF_{(g)} \qquad K_p = 150$$

$$\frac{1}{2}Br_{2(g)} + \frac{3}{2}F_{2(g)} \rightleftharpoons BrF_{3(g)} \qquad K_p = 2.5$$

Calculate the equilibrium constant K_c for the reaction below:

$$BrF_{3(g)} \rightleftharpoons BrF_{(g)} + F_{2(g)}$$

Answer: 0.366

If we sum up 2 reactions, we get the following reaction:

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \qquad K_{c3} = \frac{[CO_2]}{[O_2]}$$

Thus, the third reaction's equilibrium constant K_{c3} is equal to the multiplication of equilibrium constants K_{c1} and K_{c2}: $K_{c3} = K_{c1} \times K_{c2}$

Example 2-11

The equilibrium constant for the following reaction is 0.36 at 100 °C,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

At the same temperature, what are the equilibrium constants for the reactions below?

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

$$\frac{1}{2}N_2O_{4(g)} \rightleftharpoons NO_{2(g)}$$

Solution:

The equilibrium constant for the first reaction:

$$K_{c1} = \frac{[NO_2]^2}{[N_2O_4]} = 0.36$$

As the following equation,

$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ is the reverse of the first equation, K_{c2} value is the reciprocal of K_{c1}.

$$K_{c2} = \frac{[N_2O_4]}{[NO]^2} = \frac{1}{0.36} = 2.8$$

The following equation,

$\frac{1}{2}N_2O_{4(g)} \rightleftharpoons NO_{2(g)}$ is as same as the first equation, but it is multiplied by $\frac{1}{2}$. Therefore, the equilibrium constant for this equation is ½ exponent of the first equilibrium constant.

$$K_{c3} = \frac{[NO_2]}{[N_2O_4]^{1/2}} = \sqrt{0.36} = 0.6$$

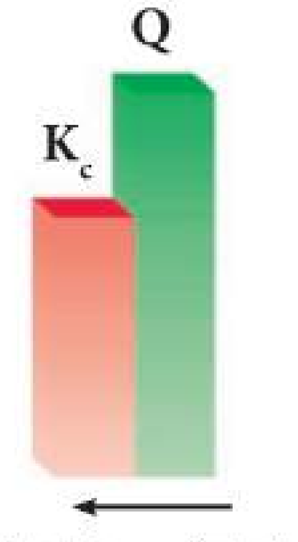
2-9-REACTION QUOTIENTS

If the concentrations of reactants and products are known at any time during a reaction, reaction's direction or equilibrium state for that time can be estimated. For this, a reaction quotient is calculated which is shown with Q_c. This is an imaginary value for the equilibrium constant. It is used to determine if the reaction, at any time, has reached equilibrium or not. The same relationship used to define K_c is also used for Q_c. The most important difference between the two is the concentrations used in Q_c do not necessarily have the values at equilibrium state. By the help of the relationship between K_c and Q_c, the equilibrium state or reaction's direction can be estimated as follows:

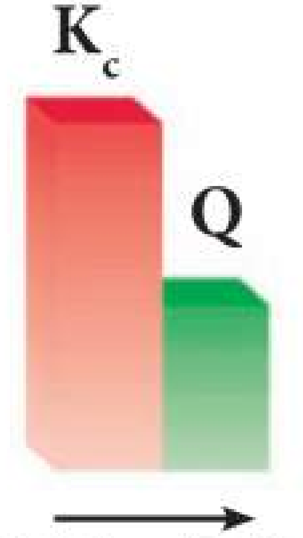
1- **If $K_c = Q_c$**, the system is at equilibrium. The concentrations of the reactants and products are at equilibrium, thus they will remain constant.

2- **If Q_c is bigger than K_c ($Q_c > K_c$)**, the reaction is not at equilibrium. The concentrations of the products are higher than their concentrations at equilibrium. Hence, they need to decrease in order to reach equilibrium. For this, the reaction shifts from right (products) to left (reactants).

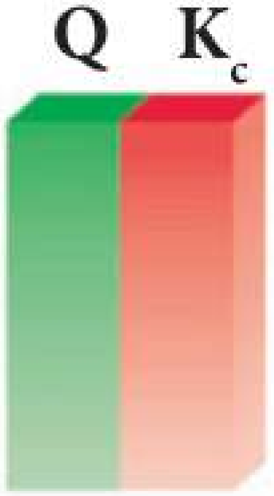
3- **If Q_c is smaller than K_c ($Q_c < K_c$)**, reaction is not at equilibrium. The concentrations of the products are less than their concentrations at equilibrium. Hence, they need to increase in order to reach equilibrium. For this, the reaction shifts from left (reactants) to right (products).



Reactants ← Products



Reactants → Products



Equilibrium: No change in concentrations of reactants or products

Example 2-12

For the following gaseous reactions;

$3H_2 + N_2 \rightleftharpoons 2NH_3$

At 500 °C, the equilibrium constant of the reaction is 0.06. Study the data below and determine the direction of the reaction.

	$[H_2]$	$[N_2]$	$[NH_3]$
(1)	0.002	0.00001	0.001
(2)	0.354	0.000015	0.0002
(3)	0.01	5.00	0.0001

Solution:

In order to determine the direction of the reaction, for each step Q value is found and compared with K_c.

$$(1)\ Q = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.001)^2}{(0.002)^3\,(0.00001)} = 12.5\times10^5$$

As Q is bigger than K_c, the reaction proceeds backward. In other words, the reaction shifts to left (reactants) until the system reaches a new equilibrium.

$$(2)\ Q = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.0002)^2}{(0.354)^3(0.000015)} = 0.06$$

$Q = K_c$, so the reaction is at equilibrium and the concentrations are constant.

$$(3)\ Q = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.0001)^2}{(0.01)^3(5.00)} = 0.002$$

$Q < K_c$, so the reaction is not at equilibrium. It should proceed forward. In other words, it shifts to right (products) until it reaches a new equilibrium.

2-10 THE RELATIONSHIP BETWEEN ΔG, FREE ENERGY AND REACTION QUOTIENT:

In the following reaction,

$$aA + bB \rightleftharpoons gG + hH$$

Non-standard free energy (ΔG) is related to standard free energy ΔG° with respect to the general relation below:

$$(1)\ \Delta G = \Delta G^\circ + RT\ln\frac{[G]^g[H]^h}{[A]^a[B]^b}$$

R is gas constant and R= 8.314 J/K.mole. T is temperature in Kelvin unit. We can rearrange the equation 1 as below:

$$(2)\ \Delta G = \Delta G^\circ + RT\ln Q$$

When the reaction reaches equilibrium, free energy value ΔG becomes equal to 0.

$$\Delta G = 0$$

The value of Q becomes equal to K_{eq}. Thus, the equation 2 can be re-written as follows:

$$\Delta G^\circ = -RT\ln K_{eq}$$

If gases interact in this reaction, as partial pressure terms are used, we use K_p. If the reaction is in solution, as molar concentration terms are used, we use K_c.

This equation is one of the most important equations in thermodynamics. Because it allows us to learn the change in standard free energy $\Delta^\circ G$ as we know equilibrium constant value K_{eq}. Also the opposite of this is valid. This relationship is shown in Table 2-1.

Attention:

symbol (ln) is the natural logarithm under base (e.) In order to find K_{eq}, it can be calculated by taking the reciprocal of (ln) with a calculator.

Table 2-1 K_{eq} and ΔG° relationship according to $\Delta^\circ G = -RT\ln K_{eq}$

K_{eq}	$\ln K_{eq}$	ΔG°	Notes
> 1	Positive	Negative	Reaction occurs spontaneously.
= 1	0	0	Reaction at equilibrium
< 1	Negative	Positive	Reaction does not occur spontaneously. But products transform into reactants spontaneously.

Example 2-13

At 25 °C and under 1 atm pressure, for the following reaction

$\Delta G^\circ = -104$ kJ/mol

$$CCl_{4(l)} + H_{2(g)} \rightleftharpoons HCl_{(g)} + CHCl_{3(l)}$$

Under same conditions calculate K_{eq}?

Solution:

Firstly, we convert temperature from °C to K unit.

$T(K) = t(°C) + 273 = 25 + 273 = 298$ K

$R = 8.314$ J/K.mol

Here, attention is required to use both R and ΔG° in Joule unit. As $\Delta^\circ G$ is kJ, it needs to be converted to J unit.

$$\Delta G^\circ\ (J/mol) = \Delta G^\circ\ (kJ/mol) \times \frac{1000\ J}{1\ kJ}$$

$$\Delta G^\circ\ (J/mol) = -104\ (kJ/mol) \times \frac{1000\ J}{1\ kJ} = -104000\ J/mol$$

$$\Delta G^\circ = -RT\ln K_{eq}$$

$$-104000\ (J/mol) = -8.314\ (J/K.mol)\ 298\ (K)\ \ln K_{eq}$$

$$K_{eq} = 1.7 \times 10^{18}$$

This value is very large, which means that the value of the reactants concentration is very small and the reaction is almost complete.

Exercise 2-10

As standard free energy for the formation of water,

$\Delta G^\circ_f\ (H_2O) = -237$ kJ/mol, for the reaction below at 25 °C and under 1 atm pressure, calculate K_p

$$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

Does this reaction occur spontaneously?

Answer: 8×10^{-84}

$K_{eq} < 1$, it does not occur spontaneously.

As a result of calculation, $K_{eq}=1.7\times10^{18}$. This value is too big. That means the concentrations of the reactants are too small. In other words, the reaction occurred nearly 100% to yield products.

2-11 LE CHATELIER'S PRINCIPLE

The change in equilibrium position is defined as the shift of equilibrium towards reactants or products in an equilibrium reaction. French scientist Le Chatelier's examined the external factors on equilibrium position and defined the following rule: "If a chemical system at equilibrium is disturbed by a change in concentration, temperature, volume or partial pressure, then the equilibrium shifts to minimize the imposed change and a new equilibrium is established." This principle is similar to Newton's Principle in mechanical systems. "Every action has got a reaction in same magnitude but opposite in direction."

External factors disturbing equilibrium position are given below:

2-11-1- The Effect of Changing Concentration

In the following reaction known as The Haber process for ammonia production,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

We can estimate the change occur at equilibrium using Le Chatelier's Principle. If some addition or extraction is made from one of the reactants or products, equilibrium will be disturbed and as a result the equilibrium will shift. For example, if more hydrogen is added to the equilibrium mixture, equilibrium position will try to reduce the added hydrogen and it will shift to the direction of producing ammonia. In other words, the forward reaction's rate will increase. As a result, more ammonia will be produced. This will continue until a new equilibrium is reached. More nitrogen gas addition makes a similar effect. However, if more ammonia is added to equilibrium mixture, direction of the reaction will shift to the way to reduce the added amount that will cause ammonia to decompose to N_2 and H_2.

To summarize, the equilibrium shifts from right to left (from products to reactants) until a new equilibrium is set. Decrease in one of the substances will cause the equilibrium shift to the direction to compensate the loss. According to this, if some ammonia is withdrawn from equilibrium mixture, the reaction will shift from left to right (from reactants to products). But if N_2 or H_2 or both is withdrawn, the reaction will shift from right to left (from products to reactants.)

Increasing or decreasing concentrations in equilibrium reactions are methods applied at industry or laboratories. For this, either the substance in question is reduced or the concentration of reactants is increased some. In the Haber process mentioned above, produced ammonia is constantly withdrawn from mixture in order to promote ammonia production. This process depends on Le Chatelier's Principle. To sum up what is told above for the equilibrium reactions:

1- Upon addition to products, the reaction shifts to left (to reactants).

2- Upon addition to reactants, the reaction shifts to right (to products).

3- Decrease in products causes the reaction shift to right (to products).

4- Decrease in reactants causes the reaction shift to left (to reactants).

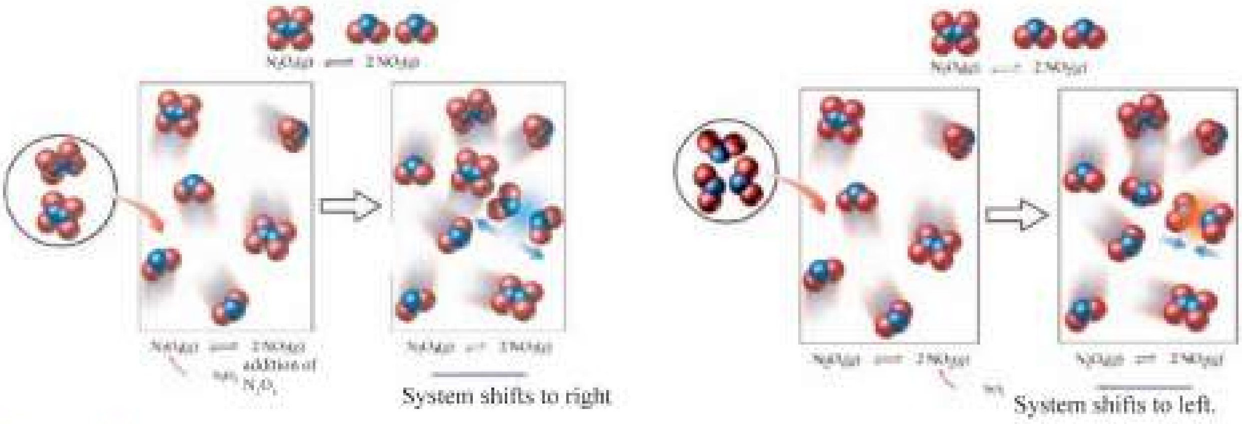


Figure 2-6

The effect of adding one of reactants or products on the equilibrium position with respect to the reaction.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

2-11-2-The Effects of Pressure or Reaction Container's on Equilibrium

In a closed system at constant temperature, for an equilibrium reaction, any change in pressure or in the volume of the reaction container will cause a shift to the direction which compensates the changes. Figure (2 - 7)

This can be explained as:

1- If a decrease in volume occurs in the equilibrium system; in the following gas reaction:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

We observe that Δn_g value is equal to (-1). In other words, the total volume of the reaction has decreased. (The volume of the products is less than the volume of the reactants.) If the pressure of the equilibrium system increases (or if the volume of the container decreases), the equilibrium will shift to the products which are less in volume. It will shift to the direction in which SO_3 is produced. In case of decrease in pressure or increase in the volume of the container, the equilibrium will shift to the reactants which are bigger in volume. That means SO_3 will decompose to produce O_2 and SO_2. In other words, system will shift to the direction with bigger mole numbers.

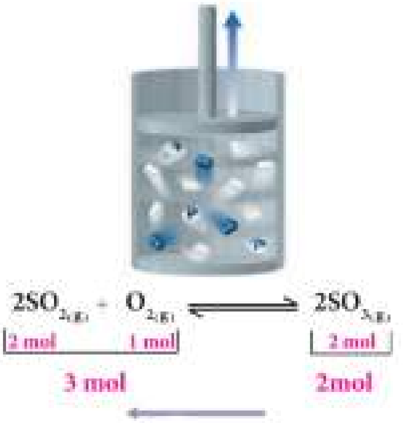


Figure 2-7

As a result of the increase in the volume of the container (the decrease in pressure), the reaction will shift to left.

2- If the volume of the equilibrium reaction increases, Figure (2 - 8)

in the following reaction: $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

The value of Δn_g is equal to (1). The total volume of the reaction has Increased. (This happens when the volume of the products are bigger than the volume of the reactants.) In such an equilibrium reaction, the pressure increases as the volume decreases. In this situation system shifts to the direction where less volume results. Thus, the equilibrium shifts to NO_2 direction with less mole number. If the pressure applied to the system decreases, the reaction will shift to the direction in which substances with bigger volume is produced. In short, the reaction will proceed towards the direction in which NO_2 decomposes to NO and O_2.

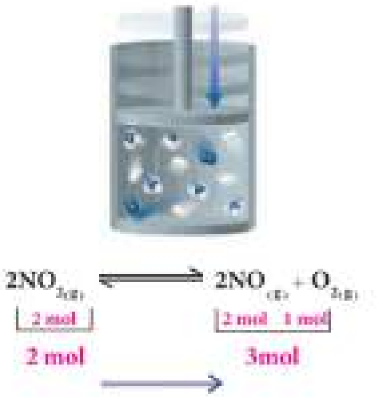


Figure 2-8

As a result of the decrease in the volume of the container (the increase in pressure), the reaction will shift to right

3- If there is no volume change in the system, for the following reaction:

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$$

The value of Δn_g is equal to 0. Therefore, it means there is no volume change in the reaction. In this situation, either pressure change or change in the volume of the container does not affect the amounts of substances in the mixture and equilibrium position remains constant. To sum up what is told above:

Changing	Shift in equilibrium
Increase in pressure	towards gaseous substances with less mole no.
Decrease in pressure	towards gaseous substances with bigger mole no.
Increase in volume	towards gaseous substances with bigger mole no.
Decrease in volume	towards gaseous substances with less mole no.

2-11-3-The Effect of Temperature

According to laws of thermodynamics, chemical reactions are divided into two with respect to their heat absorbing and heat releasing properties:

1- The reactions in which the energies of reactants are less than the energies of products are heat absorbing reactions (endothermic reactions). Their enthalpy change value is positive ($\Delta H = +$)

2- The reactions in which the energies of reactants are higher than the energies of products are heat releasing reactions (exothermic reactions) The value of enthalpy change is negative ($\Delta H = -$)

The temperature change in a reaction at equilibrium can be estimated as follows:

A- Heat Absorbing Reactions (Endothermic Reactions):

In the following reaction;

$$CaCO_{3(s)} + \text{Energy} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

If the energy is written next to the reactants, it means this is an endothermic reaction ($\Delta H > 0$). When the temperature in this kind of reactions is raised, the equilibrium shifts to right. Because, here, the calcium carbonate uses some of this heat to yield products. When it is cooled, the reaction will shift to left (to reactants) to produce $CaCO_3$. The released heat is equal to the heat at the time of temperature raise.

In the endothermic reaction below,

$$\underset{\text{colorless}}{N_2O_{4(g)}} \rightleftharpoons \underset{\text{brown}}{2NO_{2(g)}}$$

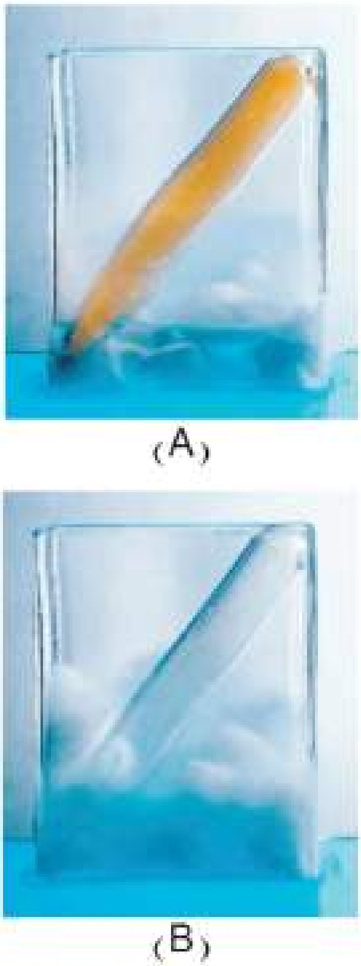


Figure 2-9

The increase in temperature causes the reaction shift to direction where brown NO_2 gas is produced. (Figure 2-9 A)

But cooling the reaction causes the reaction shift to direction where colorless N_2O_4 gas is produced. (Figure 2-9 B)

B- Heat Releasing Reactions (Exothermic Reactions)

In the following reaction,

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} + \text{Energy}$$

If the energy is written next to products, it means that the reaction is an exothermic reaction ($\Delta H < 0$).

In this kind of reactions, an increase in temperature causes the equilibrium shift to left (reactants). As a result, CO_2 will decompose as it uses the given heat. When the reaction is cooled, an equal amount of heat to the heat at the time of the temperature raise will be released. The equilibrium shifts to right (products) to produce CO_2.

The effect of temperature on equilibrium constant K_{eq} can be summarized as below:

Change	Exothermic Reaction	Endothermic Reaction
Increase in Temperature	The equilibrium shifts to reactants.	The equilibrium shifts to products.
	The value of K_{eq} decreases.	The value of K_{eq} increases.
Decrease in Temperature	The equilibrium shifts to products.	The equilibrium shifts to reactants.
	The value of K_{eq} increases.	The value of K_{eq} decreases.

2-11-4-Addition of Catalyst

Addition of catalyst to reversible reactions causes only change in the rate of the reaction. When we add catalyst to an equilibrium reaction, this process does not affect the concentrations of the substances in the system, but it only changes the activation energy. And this only affects the reaction rate. It increases the average of forward (R_f) and backward (R_b) reactions' rates at the same level.

As a result, the equilibrium is reached at a higher rate. Therefore, addition of catalyst does not affect the equilibrium position. The catalyst only accelerates reaching this position.

Do you know this?

A catalyst is a substance that speeds up a chemical reaction without itself being affected.

2-12-FACTORS AFFECTING THE EQUILIBRIUM CONSTANT

Changes in the concentrations, pressure or volume of reactants and products at constant temperature affects the equilibrium position. But the ratio of reactants and products remain constant. Therefore, these changes do not affect the equilibrium constant. The value of the chemical equilibrium constant changes only with temperature change.

Example 2-14

For the following equilibrium reaction;

$$2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$$

At 298 K, the value of ΔH is equal to -181 kJ. K_p is given as 3.2×10^{20}. When the temperature is raised to 500 K, is the value of K_p bigger or smaller than its value at 298 K for the same reaction?

Solution:

The reaction is an exothermic reaction. When the temperature is raised, the reaction shifts to left in order to compensate excessive heat. Therefore, the concentrations of the products decrease at equilibrium. The concentrations of the reactants increase. As a result, at 500 K the value of K_p decreases.

Exercise 2-11

For the following equilibrium reaction;

$$2BrF_{5(g)} \rightleftharpoons Br_{2(g)} + 5F_{2(g)}$$

At 1000 K, the value of ΔH is equal to 858 kJ. K_p is given as 7.4×10^{-16}. When the temperature is raised to 1500 K, is the value of K_p bigger or smaller than its value at 1000 K for the same reaction?

Example 2-15

For the given equilibrium reaction below, what are the effects of following factors on the equilibrium position and equilibrium constant?

$N_2F_{4(g)} \rightleftharpoons 2NF_{2(g)}$ $\Delta H = 38.5$ kJ/mol

1- Heating the equilibrium mixture in a closed container

2- Removing some N_2F_4 from the equilibrium mixture at constant temperature and volume

3- Decreasing pressure on the equilibrium mixture at constant temperature

4- Adding catalyst to the equilibrium mixture

Solution:

1- The value of ΔH shows that the reaction is an endothermic reaction. Therefore, when the reaction is heated, the equilibrium will shift to right (to products) in order to lessen the excessive heat. The equilibrium constant will increase. The reason is that while the concentration of NF_2 is increasing, the concentration of N_2F_4 is decreasing. Because the K_{eq} is directly proportional to the amount of products as it is inversely proportional to the amount of reactants. If the reaction proceeds to the direction of products, some of the reactants will transform to products. In other words, as the concentration of the reactants decreases, the concentration of the products increases. Thus, the equilibrium constant will increase. But here attention is required that, as long as the temperature is constant, the equilibrium constant does not change and remains constant. But with temperature change it also changes. If the reaction shifts to right, the equilibrium constant will increase. If the reaction shifts to left, it will decrease.

2- When some N_2F_4 is removed; its concentration in the equilibrium mixture will decrease. Therefore, the system will try to compensate the loss of N_2F_4. For this, the reaction will shift to left. In other words, some of NF_2 will transform into N_2F_4. Here the equilibrium constant is not affected from this change.

3- After decreasing the pressure on the equilibrium mixture, the system will shift to the direction with higher mole number. In the reaction equation, we see that the value of Δn_g is 1. Therefore, the reaction will shift to right. Here the equilibrium constant will not be affected from pressure change or any change in the volume of the container.

4- Addition of a catalyst only decreases the activation energy. In other words, catalysts increase the reaction rate. Therefore, a catalyst affects neither the equilibrium position nor the value of the equilibrium constant.

Exercise 2-12

As seen in the following reaction,

$C_2H_{4(g)} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}$
$+ 137$ kJ/mol

The mixture of C_2H_4, H_2, C_2H_6 gases reached equilibrium at 25°C. Explain how you can increase the amount of C_2H_6.

note: This equation can be usefull $\ln x = 2.303 \log x$

QUESTIONS OF CHAPTER-2

2-1- Fill in the blanks.

1- In the following equilibrium reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92\ \text{kJ}$$

Decrease in temperature causes increase in the concentrations of ……………………..

2- In the following equilibrium reaction,

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} + 127\ \text{kJ}$$

If hydrogen gas is added to this equilibrium reaction, the reaction heat is ………………

3- In an exothermic equilibrium reaction, if the temperature is ………………………, the equilibrium position shifts to reactants.

4- A change in the ………………………… doesn't affect the equilibrium position of the following reaction.

$$N_{2(g)} + O_{2(g)} + 180\ \text{kJ} \rightleftharpoons 2NO_{(g)}$$

5- In the following equilibrium reaction

$$Cl_{2(g)} + H_{2(g)} \rightleftharpoons 2HCl_{(g)} + \text{Energy}$$

the concentration of HCl can be increased by ………………………….. the reaction temperature.

6 - If K_p is smaller than K_c, the sum of number of moles of reactants is …………………… than the sum of number of moles of products.

7- If the total pressure is increased on a reaction in which the mole numbers of reactant gases are smaller than the mole numbers of product gases, the equilibrium position shifts to …………………………..

8- The relationship between equilibrium constant K_c and the concentrations of products is ……….

9- In an endothermic reaction, if the reaction container is cooled, ……………………………. are produced more.

10- In an endothermic reaction at dynamic equilibrium, the concentrations of products increase at ………. temperatures.

2-2- Circle the correct answer.

1- The equilibrium constant of equilibrium reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 727 °C is 4.17×10^{-2}. After 0.4 M SO_3 , 0.1 M O_2 , 0.02M SO_2 are mixed, the direction of the reaction is:

A- towards reactants.
B- towards products.
C- at a dynamic equilibrium.
D- all answers are wrong.

2- For the equilibrium reaction occurring in a closed container,

$CaCO_{3(s)} \rightleftharpoons CO_{2(g)} + CaO_{(s)}$

when does the amount of $CaCO_3$ increase by applying one of the following?

A- by eliminating some CO_2 gas at equilibrium
B- by increasing total pressure
C- by adding some CaO to the equilibrium mixture
D- all above is incorrect.

3- For the equilibrium reaction $I_{2(g)} + F_{2(g)} \rightleftharpoons 2IF_{(g)}$ the equilibrium constant $K_c = 1 \times 10^6$ at 200 K. If the partial pressures of IF gas is 0.2 atm and F_2 gas is 4×10^{-3} atm at equilibrium, what is the partial pressure of I_2 gas?

A- 5×10^4 atm B- 1×10^{-5} atm C- 1×10^5 atm D- All options are incorrect.

4- As the equilibrium constant K_c is 640.3 at 300 K for the reaction $Li_{(g)} + \frac{1}{2} I_{2(g)} \rightleftharpoons LiI_{(g)}$. What is the equilibrium constant K_c for the reaction $2LiI_{(g)} \rightleftharpoons 2Li_{(g)} + I_{2(g)}$ at the same temperature?

A- 25.3 B- 41×10^4 C- 15.6×10^5 D- All are incorrect.

5- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92$ kJ K_p value of the equilibrium reaction is given as 5.5×10^{-5} at 25 °C. What is the K_c value of the reaction?

A- 22513.3 B- 9×10^{-4} C- 0.03 D- all are incorrect

6- For the equilibrium reaction $Br_{2(g)} \rightleftharpoons 2Br_{(g)}$, K_p value is 2558.4 , k_f value for the reaction in molar consntration is 1.56 at 4000 K. Which of the following is value of k_b?

A-0.2 B-20 C-7.8 D-All are incorrect.

7- For the equilibrium reaction; $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, the equilibrium constant K_p is 2. What should be the concentrations (mol/L) of reactants and products for the equilibrium shift towards products?

A- [HI]= 0.1 mol/L , $[I_2]$= 0.05 mol/L; $[H_2]$= 0.05 mol/L
B- [HI]= 0.4 mol/L , $[I_2]$= 0.1 mol/L; $[H_2]$= 0.2 mol/L
C- [HI]= 0.001 mol/L , $[I_2]$= 0.0002 mol/L; $[H_2]$= 0.0025 mol/L
D- All are incorrect.

2-3- Write down reasons for the following.

1- In equilibrium reactions of gases, Δn_g (Products) < Δn_g (Reactants), increasing the volume of container causes decrease in products.

2- In the imaginary equilibrium reaction, $A_{(g)} \rightleftharpoons B_{(g)}$ + Energy, increase in total pressure doesn't change the temperature of the reaction container.

3- The value of equilibrium constants of irreversible reactions are big.

4- When K_c is 0.3 and $Q = 1$, the temperature of the endothermic reaction increases.

5- When the temperature of reaction increases while value of K_c decreases, the reaction is accepted as an exothermic one.

6- In endothermic reactions, the value of K_c increases with temperature.

7- As a result of pressure increase on the equilibrium mixture in which $\Delta n_g = +1$, the equilibrium shifts to reactants.

8- As some reactions really stop, some reactions seem to be stopped.

9- In the equilibrium reaction, $SO_2Cl_{2(g)} + \text{Energy} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$, if SO_2 is added to the equilibrium mixture, the temperature of the reaction increases.

2-4- Define the following terms.

1- Law of Mass Action 2- Chemical Equilibrium State 3- Le Chatelier's Principle

2-5- In the gas equilibrium reaction, $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$, is exothermic.
After the following changes are applied on the equilibrium reaction, how does the equilibrium position change? Why?

1- Increase in the pressure
2- Increase in the temperate of the container
3- Withdrawal of some N_2O_4 from the equilibrium reaction.

2-6- In the gas equilibrium reaction, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, the value of enthalpy is equal to 92.5 kJ/mol.
What are the effects of the following factors on equilibrium position and the equilibrium constant?

1- Increase in temperature
2- Addition of more Cl_2 to the equilibrium mixture
3- Withdrawal of PCl_3 from the equilibrium mixture
4- Increase in the pressure on the equilibrium mixture
5- Addition of catalyst

2-7- The enthalpy of the reaction, $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ is equal to -198.2 kJ. After applying the following processes, what will be the concentrations of SO_2, O_2 and SO_3.

1- Increase in the reaction temperature
2- Decrease in the pressure on the reaction
3- Increase in the concentration of SO_2 in the equilibrium mixture.
4- Addition of a catalyst.

2-8- Does the increase in temperature of a reaction at equilibrium always cause an increase in concentrations of products? If your answer is no, what are the factors which cause an increase in concentrations of products? Explain with examples.

2-9- The following equilibrium reaction is exothermic.

$$2PbS_{(s)} + 3O_{2(g)} \rightleftharpoons 2PbO_{(s)} + 2SO_{2(g)}$$

Clarify the effect of the following factors on the equilibrium state and the value of equilibrium constant.

1- Decrease in the applied pressure on the container
2- Cooling the container of the reaction.

2-10- An endothermic reaction in a closed container is given. $CaCO_{3(s)} \rightleftharpoons CO_{2(g)} + CaO_{(s)}$
After the following changes are applied, what is the position of equilibrium reaction?

1- Decrease in the volume of the container
2- Addition of more CaO to the equilibrium mixture
3- Withdrawal of some $CaCO_3$ from the equilibrium mixture
4- Addition of more CO_2 to the equilibrium mixture
5- Increase in temperature

2-11- If pure NOCl gas is heated to 240 °C in a closed container; it decomposes according to the following equation. $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$
When the reaction reaches equilibrium, the total pressure of equilibrium mixture is measured as 1 atm and partial pressure of NOCl gas is measured as 0.64 atm. Thus, calculate the following:
1- Partial pressures of Cl_2 and NO gases at equilibrium
2- The equilibrium constant K_c at the same temperature

Answer:
1) 0.12 atm, 0.24 atm
2) 4×10^{-4}

2-12- For the reaction, $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, which occurs without any catalyst, partial pressures were measured as $P_{N_2O_4} = 0.377$ atm and $P_{NO_2} = 1.56$ atm at 100 °C at equilibrium. Calculate the following:

1- K_c and K_p of the reaction.
2- How do the partial pressures of gases in the equilibrium mixture change upon addition of catalyst?

Answer: 6.46; 0.21

2-13- For the gas reaction; $2NO + O_2 \rightleftharpoons 2NO_2$ different amounts of moles of NO and O_2 were put in a 1 liter container at the given temperature. When the reaction reached the equilibrium, it was found that the formed of NO_2 equals to 0.8 mole and the concentration of O_2 and NO equals each other. If K_c is equal to 10, find out mole numbers of O_2 and NO before the reaction started.

Answer: O_2 = 0.8 mol , NO = 1.2 mol

2-14- The gaseous reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, reaches equilibrium at 377 °C. The equilibrium constant is given as $K_c = 1.96$. Calculate the equilibrium constants for the following reactions at the same temperature.

A) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

B) $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

C) $NH_{3(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)}$

Answer: A) 0.51 B) 1.4 C) 0.7

2-15- The equilibrium constant of the following reactions is given.

$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+ + HCO_3^-$ $K_c = 4.2\times10^{-7}$

$CaCO_{3(s)} \rightleftharpoons CO_3^{2-} + Ca^{2+}$ $K_c = 4.7\times10^{-9}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $K_c = 4.7\times10^{-11}$

According to those above, what is K_c for the following equilibrium reaction?

$CO_2 + CaCO_{3(s)} + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$

Answer: 4.1×10^{-5}

2-16- The equilibrium constant of the following reaction is given as $K_c = 19.9$ at 2500 K temperature.

$Cl_{2(g)} + F_{2(g)} \rightleftharpoons 2ClF_{(g)}$

If the concentrations of the substances in the mixture are [ClF]= 1.2 M , $[F_2]$= 1 M , $[Cl_2]$= 0.2 M, how will be the equilibrium position?

2-17- The following reaction;

$NiO_{(s)} + CO_{(g)} \rightleftharpoons Ni_{(s)} + CO_{2(g)}$

is at equilibrium at 727°C. At this temperature the pressure of CO gas is equal to 304 Torr. What is K_c when total pressure is 1 atm?
(Note: 1 atm = 760 Torr)

Answer: 1.5

2-18- In the equilibrium reaction in a closed container, $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$ the partial pressure of PCl_3 is twice the partial pressure of Cl_2. After the reaction reached equilibrium at a certain temperature, the partial pressure of Cl_2 was measured as 1 atm. As $K_p = 1/6$, what are the partial pressures of PCl_3 and Cl_2 gases before the reaction started?

Answer: 2.8 atm; 1.4 atm

2-19- Give four procedures that lead to increase amount of products in the following gas equilibrium reaction which is exothermic.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

2-20- According to the following reaction,

$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

equal number of moles of CO_2 and H_2 were mixed in a 1-litre container. When the reaction reached equilibrium at 2000 K, there were 3 moles of gas in the mixture. As the equilibrium constant K_c is 4, what are the concentrations of substances in the equilibrium mixture?

Answer: $[CO]=[H_2O]$ = 1 mol/L ; $[CO_2]=[H_2]$ = 0.5 mol/L

2-21- For the endothermic reaction, $C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_{2(g)}$ some moles of C_2H_6 were put in a 1L container. When the reaction reached the equilibrium, it was found that quarter of C_2H_6 gas was used. If K_c is 1/2 for the reaction, find out the concentrations of the gases at equilibrium state.

Answer: $[C_2H_6] = 4.5$ mol/L , $[C_2H_4] = [H_2] = 1.5$mol/L

2-22- 4 g of HF gas was placed in a 2 liter closed container at 27 °C and left to decompose until equilibrium was reached according to the following equation.

$$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$$

As K_p is 1.21, calculate the partial pressure of HF gas at equilibrium. (M_{HF} =20 g/mol)

Answer: 0.76 atm

2-23- 20% of 1 mole of N_2O_4 gas decomposed to NO_2 gas in a 1-litre container at 1 atm pressure at 27 °C. Calculate K_p value of the reaction. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Answer: 4.92

2-24- For the following reactions at 1000 K, the equilibrium constants K_p depending on pressure were given.

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{(g)} \qquad K_p = 2.9\times10^{10}$$

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \qquad K_p = 5\times10^{20}$$

Calculate the equilibrium constant K_c of the following reaction.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

Answer: 2.4×10^{22}

2-25- As a result of reaction of CO gas with water vapor in a 1-litre closed container at 700K, CO_2 and H_2 gases were formed. What is the concentration of gas mixture at equilibrium as equilibrium constant K_c is 5.29 and 1 mole of each of reactants and products were placed in the container?

Answer: $[CO] = [H_2O] = 0.606$ mol/L ; $[CO_2] = [H_2] = 1.394$ mol/L

2-26- The equilibrium constant of the following reaction;

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

is $K_c = 6\times10^{-3}$ at 298 K but it is 1.5×10^{-2} at 35 °C. Is the decomposition reaction of dinitrogen tetroxide endothermic or exothermic?

2-27- For the equilibrium reaction,

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

it was observed that the equilibrium mixture at 25 °C contained $[O_2]$= 0.01 mol/L, $[SO_2]$= 0.08 mol/L, $[SO_3]$= 0.002 mol/L. When the temperature was decreased to 10 °C, the equilibrium constant K_c was found as 4. Tell if the reaction is endothermic or exothermic.

2-28- Explain the difference between ΔG and ΔG^0, write down the relationship between them. When does the value of ΔG become equal to ΔG^0? prove this mathematically

2-29- As ionization constant of water is 1×10^{-14} at 25 °C and 1 atm, calculate the ΔG^0 value of the ionization reaction.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Answer: 79881 J/mol

IONIC EQUILIBRIUM

CHAPTER-3

ACHIEVEMENTS

After completing this chapter, the student is expected to :

- Identify electrolytes and non-electrolytes.
- Differ strong electrolytes and weak electrolytes.
- Calculate K_c for weak electrolytes and the relationship obtained by partial ionization of these electrolytes.
- Understand ionization of water and the amphoteric behavior of water.
- Calculate acidity value of solutions.
- Understand solubility and hydrolysis and notice how they change with respect to the type of salt.
- Understand common ion effect and how this effect is used to prepare buffer solutions.
- Differ completely soluble and slightly soluble salts and he/she learns the factors affecting solubility of slightly soluble salts.

Chapter - 3

3-1- INTRODUCTION

Chemical reactions mostly occur in solutions. Therefore solutions are very important in chemistry. In order to prepare solutions, water and organic solvents are used abundantly. But in this chapter, we will focus on water-soluble substances **(aqueous solutions)**. The behavior of a substance solved in water depends on the structure of the substance and the medium it is inside. Therefore, we need to understand the principles controlling the behaviors of substances.

Do you know

Substances like sodium chloride and potassium chromate which behave as electrolytes in water may not show the same behavior when they are solved in solvents like ether or hexane.

3-2- ELECTROLYTES AND NON-ELECTROLYTES

An aqueous solution is a homogeneous mixture which results when a substance **(solute)** dissolves in water **(solvent)**. We can divide the aqueous solutions of substances into two with respect to their conductibility of electric current: The first type is the solutions which have the ability to conduct electricity. These types of solutions are called **electrolytes**. We can give the sodium chloride solution as an example. The second type is the solutions which do not conduct electricity. These are called **non-electrolytes**. Sugar solution is an example. (Figure 3-1) Not only aqueous solutions of salts but also molten salts (liquid salts) show electrolytic properties.

3-2-1-Electrolytes

All ionic and polarized (non-ionic) compounds dissociate into their ions when dissolved in water. Therefore these are accepted as electrolytes. They can be salts, acids or bases. The most important properties of electrolytes are as follows:

1- The capability of conducting electricity in the molten form or in aqueous solutions.

2- The resultant electrical charge of electrolytic solutions is equal to zero. In other words, these solutions are electrically neutral.

3- In aqueous solutions of electrolytes, cations and anions are formed.

4- The electrical conductibility of electrolytic solution depend on the structures and concentrations of ions and temperature of solution.

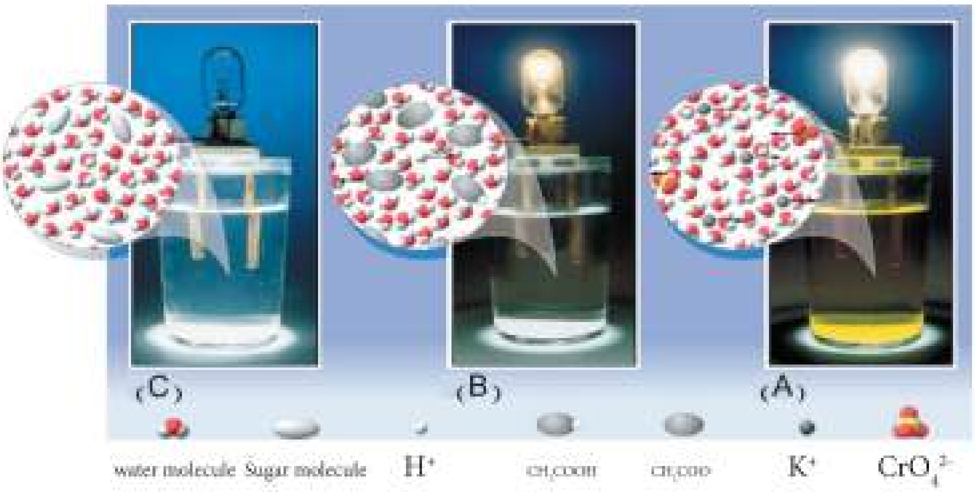


Figure 3-1

Figure 3-1

The experiment that shows the effects of ion presence in a solution. In the beaker, a bulb is connected to two immersed copper electrodes. The substances in the solution are:

a- The aqueous solution of potassium chromate. (The bulb lights strongly as many ions are present in strong electrolyte.)

b- The aqueous solution of acetic acid. (The bulb lights weakly as few ions are present in weak electrolyte.)

c- Sugar solution in pure water. (The bulb does not light as non-electrolytic substance is in the solution.)

A- Strong Electrolytes

Upon dissolution of these electrolytes in water, the resulting solution conducts electricity well. The reason for this is the dissociation of these electrolytes to their ions completely or almost completely in water. The examples for strong electrolytes are hydrochloric acid HCl, sodium chloride NaCl, sodium sulfate Na_2SO_4 , potassium nitrate KNO_3 , sulfuric acid, H_2SO_4 and ammonium chloride, NH_4Cl. We can show the dissolution of these substances (strong electrolytes) in water through the following chemical equations:

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaCl_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

$$Na_2SO_{4(s)} \xrightarrow{H_2O} 2Na^+_{(aq)} + SO^{2-}_{4(aq)}$$

$$KNO_{3(s)} \xrightarrow{H_2O} K^+_{(aq)} + NO^-_{3(aq)}$$

$$H_2SO_{4(l)} \xrightarrow{H_2O} 2H^+_{(aq)} + SO^{2-}_{4(aq)}$$

Generally there are three types of strong electrolytes.

1- Strong acids, 2- Strong bases, 3- Most of the water-soluble salts. This kind of substances dissociate into ions completely or almost completely in dilute aqueous solutions. In Table 3-1, examples for electrolytes and non-electrolytes are given. As shown in the following example, the concentrations of ions in the solutions of strong electrolytes are calculated directly using the concentration of the electrolyte. (Table at the end of the book can be used) for reference.

Exercise 3-1

Calculate the ion concentrations for the following strong electrolytes with given concer trations.

A) HBr = 0.25M

B) KOH = 0.055M

C) $CaCl_2$ = 0.155M

Example 3-1

Calculate the molar concentrations of Ba^{2+} and OH^- ions in 0.03 M barium hydroxide solution.

Solution:

The ionization chemical equation of strong base $Ba(OH)_2$ is written.

$Ba(OH)_{2(aq)}$	$\longrightarrow$	$Ba^{2+}_{(aq)}$	$+ 2OH^-_{(aq)}$	
0.03 M				(Initial Concentrations)
–0.03 M		+ 0.03 M	+ 2 × (0.03 M)	(Change in Concentrations)
0		0.03 M	0.06 M	(Final Concentrations)

It means that the $[Ba^{2+}]$ ion concentration in the solution is equal to 0.03 M. The $[OH^-]$ concentration is equal to 0.06 M.

B- Weak Electrolytes

Upon dissolution of these electrolytes in water, solutions with low conducting properties form. The reason for that is their partial ionization in aqueous solutions. We can give following examples for weak electrolytes. Acetic acid CH_3COOH, ammonia NH_3, carbonic acid H_2CO_3 , and silver chloride AgCl. We can show the dissolution of these substances (weak electrolytes) into their ions in water through the following chemical equations:

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO^{2-}_{3(aq)}$$

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

As seen in the equations above, the dissolution of these substances in water is possible only through reaching **ionic equilibrium**. Each chemical reaction representing the processes are defined as reversible reactions. This is shown with two arrows opposite to each other. $\rightleftharpoons$ .As mentioned in chemical equilibrium chapter, reversible reactions are different from irreversible reactions. Reversible reactions do not reach any end. This reaction system reaches equilibrium when two reactions in opposite directions (forward and backward) occur at the same time and rate.

Attention: When water is used as solvent, K_c of water is not written. Because it's a fixed value and shown in equilibrium constant.

This state is defined as a **dynamic equilibrium**. The average rates of forward and backward reactions are equal. Components of the reactions react constantly and for fixed temperature the concentrations of components remain constant and the system reaches equilibrium. For example, acetic acid CH_3COOH (weak acid) molecules decompose in aqueous solution to hydrogen ($H^+_{(aq)}$) and acetate ($CH_3COO^-_{(aq)}$) ions. Forward reaction occurs. At the same time, hydrogen ions combine with acetate ions and form acetic acid (backward reaction). When this acid solution reaches equilibrium at some temperature, decomposition and formation reaction rates become equal. Therefore, all ion concentrations

($CH_3COO^-_{(aq)}$, $H^+_{(aq)}$, CH_3COOH) remain unchanged.

Ionic equilibrium is shown with equilibrium constant K_c just as in chemical equilibrium. It is the ratio of multiplication of concentrations of products to the multiplication of concentrations of reactants at equilibrium. It should be kept in mind that the mole numbers of components in equilibrium reaction equation are written as exponents. The equation for acetic acid decomposition to ions in aqueous solution is shown as below:

$$K_c = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

At equilibrium, the molar concentrations of components in solution are shown with square brackets "[ ]". The numeric value of K_c is a constant at a given temperature constant .

Example 3-2

Write the mathematical equation to calculate K_c value of aqueous solution of dilute ammonia.

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

Solution:

As shown in the equilibrium equation, water molecules react with ammonia and equilibrium is reached. But, as water is used as solvent, the concentration of water molecules is much bigger than the other components' concentrations. Therefore, in order to reach equilibrium, the concentration of water remains constant. The molar concentration of water can be combined with equilibrium constant. The resulting value is a constant number shown with K_c. The molar concentration of water in dilute solutions can be calculated as pure water's molar concentration. (The density of pure water =1kg/L, 1kg =1000g)

$$M_{(H_2O)} = 2\times 1 + 1\times 16 = 18\ g/mol$$

From definition of molarity, M,

$$M_{\ (mol/L)} = \frac{m_{\ (g)}}{M_{\ (g/mol)} \times V_{\ (L)}}$$

$$= \frac{1000_{\ (g)}}{18\ (g/mol) \times 1_{\ (L)}}$$

$$= 55.55\ mol/L$$

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$$

$$K_c = K_{eq} \times [H_2O] = K_{eq} \times 55.55$$

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

3-3 DECOMPOSITION OF WEAK ELECTROLYTES

According to Bronsted-Lowry acid-base theory, the substance which donates proton in order to form its conjugate base is defined as an acid.

Acid $\rightleftharpoons$ proton + conjugate base

Acids are neutral molecules such as HCl, H_2SO_4, CH_3COOH or a positive ion like NH_4^+ and $C_6H_5NH_3^+$ or a negative ion like HSO_4^- and $H_2PO_4^-$.

A base, according to Bronsted-Lowry acid-base theory, is a substance which accepts a proton in order to form its conjugate acid.

Base + proton $\rightleftharpoons$ Conjugate acid

The following bases can be given as examples of neutral molecule, positive ion or negative ion bases.

OH^-, CH_3COO^-, $Fe(H_2O)_5(OH)_2^+$, $C_6H_5NH_2$, NH_3

Table 3-1

Examples for strong and weak electrolytes and Non-Electrolyte

Strong Electrolytes	
Strong Acids	
HCl	Hydrochloric acid
HNO_3	Nitric acid
$HClO_4$	Perchloric acid
H_2SO_4	Sulfuric acid
Strong Bases	
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
$Ca(OH)_2$	Calcium hydroxide
Soluble Salts	
NaCl	Sodium chloride
KNO_3	Potassium Nitrate
K_2SO_4	Potassium Sulfate
Weak Electrolytes	
Weak Acids	
HF	Hydrofluoric acid
HCN	Hydrocyanic acid
H_2CO_3	Carbonic acid
HCOOH	Formic acid
Weak Bases	
NH_3	Ammonia
CH_3NH_2	Methyl amine
Slightly Soluble Salts	
AgCl	Silver chloride
CaF_2	Calcium fluoride
Non-Electrolytes	
CH_3OH	Methyl alcohol
$C_{12}H_{22}O_{11}$	Sucrose
CH_3COOCH_3	Methyl acetate

According to this theory, the strength of an acid or a base depends on acid's proton donation capability and bases' proton accepting capability.

As it can be understood from the examples above, each acid has got a conjugate base with different strength. This is also valid for bases. According to the theory, if the acid is strong, its conjugate base is weak and vice versa. In aqueous solutions, if the reaction shifts to right and the value of (HCl) is close to zero, the Bronsted acid (e.g HCl) is strong. The same is valid for the Bronsted base.

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Acids can be classified with respect to their reactions with water molecule. All strong acids (or strong bases) decompose to ions in water nearly 100%. But weak acids (or bases) decompose to ions in water only partially. For example, a reaction like acetic acid's decomposition (ionization) shifts to right in an incomplete way.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

3-3-1-Weak Acids

Weak acids are weak electrolytes. Therefore, in their aqueous solutions, ionization equation can be shown as an equilibrium state.

$$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

By applying the special relationship of equilibrium constant;

$$K_{eq} = \frac{[H_3O^+][HCOO^-]}{[H_2O][HCOOH]}$$

$$K_a = K_{eq} \times [H_2O]$$

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

K_a is the equilibrium constant of weak formic acid or the ionization constant of this acid at constant temperature. As mentioned before, the concentration of water can be assumed as constant and a general equation for acidity equilibrium constant can be written for weak acid (HA).

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

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

The most important point here which requires attention is that this relationship can only be written for weak acids. Ionization reactions of strong acids do not occur as equilibrium reactions.

On the other hand, the equilibrium constant values of weak acids are accepted as a measurement of their strength. As the acidity constant of an acid increases (amount of ionization increases), acidity strength increases. In Table 3.1, some weak acids and their acidity constants are given as example. If the concentration of weak acid and acidity constant are known, mathematical relationship for ionization equilibrium state of the acid can be used to calculate the hydrogen ion concentration in water.

Example 3-3

Calculate the hydrogen ion concentration H^+, percent ionization of acetic acid and degree of ionization for 0.1 M aqueous solution of acetic acid. Ionization constant of acetic acid (acidity constant) is $1.8x10^{-5}$

Solution:

Chemical equation for acid's ionization equilibrium is written. Then, the relationship that shows acidity constant of acid is written

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Here, it needs to be kept in mind that in the mathematical equation above, the concentration which are shown with [ ] symbol are only the concentrations of ions at equilibrium. Those, as shown in the equation below, are different from initial concentrations of ions.

$CH_3COOH_{(aq)} \rightleftharpoons$	$H^+_{(aq)}$	$+ CH_3COO^-_{(aq)}$	
$0.1\ M$	0	0	Initial concentration
$(0.1 - x)\ M$	$x\ M$	$x\ M$	Concentration at equilibrium

As seen above, the amount of decomposed weak acid is (x mol/L). According to equilibrium reaction, when x mole acetic acid decomposes, x mole of each of hydrogen and acetate ions are produced. Then, equilibrium concentrations are inserted in the mathematical relationship for acidity constant of weak acid.

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

When we re-arrange the equation above, we get the following relationship:

$$x^2 = (1.8 \times 10^{-6}) - (1.8 \times 10^{-5}\, x)$$

Attention: While solving problems about chemical equilibrium, for changes in concentrations of common substances in equilibrium reactions, reactants are shown with negative signal, products are shown with positive signal.

In this chapter, initial and final concentration values only in equilibrium will be used.

Attention:

If degree of ionization is less than 5%, method of negligence is used while calculating. But if degree of ionization is bigger than 5%, calculations are made through quadratic equation.

In a quadratic equation (ax^2+bx+c), a, b, and c show the exponents of the equation. The roots of quadratic equation is found through the following formula:

$$x = \frac{(-b \pm \sqrt{(b' - 4ac)})}{2a}$$

The relationship above is a second-order equation. We need to use general mathematics rules to solve it. But we will use a different method in this example. Because the K_a value of acid is an extremely small number. The amount of ionized acid is too small when compared to acid's initial concentration. Therefore we can write the relationship below. We conclude the following in acidity constant equation (x is neglected in the solution):

$$(0.1 - x)\ \text{mol/L} \approx 0.1\ \text{mol/L}$$

Using this value in the ionization constant equation,

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

$$x^2 = (0.1) \times (1.8 \times 10^{-5}) = 1.8 \times 10^{-6}$$

$$x = \sqrt{1.8 \times 10^{-6}} = 1.3 \times 10^{-3}$$

$$[H^+] = 1.3 \times 10^{-3}\ \text{mol/L}$$

At equilibrium, when we compare the smaller amount of hydrogen ion (1.3×10^{-3} mol/L) with initial concentration of acid (0.1 mol/L), it proves that this negligence method is correct (x is neglected). Therefore, generally method of negligence can be used if the acidity (or basicity) value of the acid (or the base) is small (i.e. 10^{-7}, 10^{-6}, 10^{-5}). If the value of K_a is big (bigger than 10^{-4}, 10^{-3}, 10^{-2}) this method cannot be used. Because the results will not be correct. Then the equation must be solved through general mathematics rules. Degree of ionization is calculated from the equation below:

$$\text{Degree of ionization} = \frac{\text{Concentration of ionized part of the substance at equilibrium}}{\text{Initial concentration of substance}}$$

Percent ionization is found through the following equation.

$$\text{Percent ionization} = \frac{\text{Concentration of ionized part of the substance at equilibrium}}{\text{Initial concentration of substance}} \times 100\%$$

Percent ionization = Degree of ionization ×100

As in **Example 3-3**

$$\text{Degree of ionization of acid} = \frac{\text{The concentration of hydrogen ions at equilibrium}}{\text{Initial concentration of the acid}} = \frac{1.3 \times 10^{-3}}{0.1} = 0.013$$

$$\text{Decomposition percentage of acid} = \frac{\text{The concentration of hydrogen ion at equilibrium}}{\text{Initial concentration of the acid}} \times 100\%$$

$$\text{Decomposition percentage of acid} = \frac{1.3 \times 10^{-3}}{0.1} \times 100\%$$

Decomposition percentage = 1.3% acid

As the percentage of ionization is under 5%, method of negligence can be used.

Example 3-4

Calculate the percentage of ionization and the degree of ionization of hydrofluoric acid (HF) which has an aqueous solution with concentrations;

A- 0.1 M

B- 0.01 M.

($K_a = 6.8\times10^{-4}$) Explain the relationship between percent ionization and the concentration of solution.

Solution:

A- For the solution with 0.1 M concentration:

$$HF_{(aq)} \rightleftharpoons H^+_{(aq)} + F^-_{(aq)}$$

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

The K_a value of hydrofluoric acid is much bigger than the acetic acid's. Therefore its percent decomposition is expected to be bigger than 5%. Thus, the method of negligence which we used in acetic acid example may not be valid here. So we will solve this question using both methods.

$$\begin{array}{lccl} HF_{(aq)} & \rightleftharpoons H^+_{(aq)} & + \; F^-_{(aq)} & \\ 0.1\ M & 0 & 0 & \text{Initial concentration} \\ (0.1 - x)\ M & x\ M & x\ M & \text{Concentration at equilibrium} \end{array}$$

$$6.8 \times 10^{-4} = \frac{(x)(x)}{(0.1 - x)}$$

Rounding up method:

$$(0.1 - x)\ mol/L \approx 0.1\ mol/L$$

In the equation above, if x is neglected, we get the following one.

$$6.8 \times 10^{-4} = \frac{(x)(x)}{0.1}$$

$$x^2 = (0.1) \times (6.8 \times 10^{-4}) = 6.8 \times 10^{-5}$$

$$x = \sqrt{6.8 \times 10^{-5}} = 8.25 \times 10^{-3}$$

$$[H^+] = 8.25 \times 10^{-3}\ mol/L$$

$$\text{Degree of ionization of acid} = \frac{\text{The concentration of hydrogen ions at equilibrium}}{\text{Initial concentration of the acid}} = \frac{8.25 \times 10^{-3}}{0.1} = 0.0825$$

Exercise 3-2

Calculate the concentration of hydrogen ions in the aqueous solution of 0.2 M of hydrocyanic acid.

$K_a = 4.9\times10^{-10}$

Answer: 1×10^{-5}M

$$\text{Decomposition percentage of acid} = \frac{\text{ion at equilibrium}}{\text{Initial concentration of the acid}} \times 100\%$$

$$\text{Decomposition percentage of acid} = \frac{8.25 \times 10^{-3}}{0.1} \times 100\% = 8.25\%$$

The acid's percent ionization is bigger than 5%. The reason for this is the acidity constant is bigger than 10^{-5}. Therefore this method cannot be used for solution. We will solve it through quadratic equation. (This equation for view only)

$$\mathbf{x^2 = (6.8 \times 10^{-5}) - (6.8 \times 10^{-4}\,x)}$$

$$\mathbf{x^2 + (6.8 \times 10^{-4}\,x) - (6.8 \times 10^{-5}) = 0}$$

$$\mathbf{x = \frac{(-b \pm \sqrt{(b^2 - 4ac)})}{2a}}$$

$$\mathbf{x = \frac{-(6.8 \times 10^{-4}) \pm \sqrt{(6.8 \times 10^{-4})^2 - 4 \times (-6.8 \times 10^{-5})}}{2}}$$

Through solving this equation, there are two roots. One is positive and the other is negative. The negative value is neglected as it is meaningless. (A concentration value can never be negative.)

$$\mathbf{x = 7.91 \times 10^{-3}\ mol/L = [H^+]}$$

The hydrogen ion concentrations in hydrofluoric acid solution at equilibrium are calculated using both methods. It seems that there is a very big difference between results. Since it gives a wrong result, we cannot use method of negligence.

$$\text{Degree of ionization} = \frac{\text{The concentration of hydrogen ion at equilibrium}}{\text{Initial concentration of acid}}$$

$$\text{Degree of ionization of the acid} = \frac{7.91 \times 10^{-3}}{0.1} = 0.079$$

$$\text{Percent ionization} = \frac{\text{ion at equilibrium}}{\text{Initial concentration of the acid}} \times 100\%$$

$$\text{Percent ionization of hydrofluoric acid} = \frac{7.91 \times 10^{-3}}{0.1} \times 100\% = 7.91\%$$

B- For the solution with 0.01 M concentration

The second-order equation for this solution is as follows:

$$6.8 \times 10^{-4} = \frac{(x)(x)}{(0.01 - x)}$$

x value is obtained through solution of the mathematical equation.

$$x = 2.29 \times 10^{-3}\ \mathrm{mol/L}$$

$$\text{Degree of ionization} = \frac{\text{The concentration of hydrogen ion at equilibrium}}{\text{Initial concentration of acid}}$$

$$\frac{2.29 \times 10^{-3}}{0.01} = 0.229$$

$$\text{Percent ionization} = \frac{\text{The concentration of hydrogen ion at equilibrium}}{\text{Initial concentration of acid}} \times 100\%$$

$$\frac{2.29 \times 10^{-3}}{0.01} \times 100\ \% = 22.9\ \%$$

Exercise 3-3

Calculate the concentration of hydrogen ions in the aqueous solution of phenol, C_6H_5OH with concentrations;

A- 0.2 M,

B- the solution diluted by 100 times.

($K_a = 1.3 \times 10^{-10}$)

Answer: A- 0.51×10^{-5} M

B- 0.51×10^{-6} M

The most significant point here which needs attention is that when we dilute acid solution by 100 times, degree of decomposition (or degree of ionization) increases by nearly 3 times (from 0.079 to 0.229). Because diluting the solution is an external factor and the system will determine a new equilibrium state in order to compensate this effect. For this, the substance will dissolve (ionize). As a result of this process, the amount of acid molecules decreases whereas the ions in the solution increase. Thus the solution reaches equilibrium once more.

Attention: Strong acid produces weak conjugate base or vice versa. As weak acid's acidity equilibrium constant increases, acid's strength increases.

Monoprotic and Polyprotic Weak Acids

Monoprotic weak acids have only one hydrogen atom which can ionize (single acid proton). Therefore those has only one acidity constant. But there are many acids which have more than one acid proton. These acids are called as polyprotic weak acids, i.e. oxalic acid ($H_2C_2O_4$). This acid is a substance that has two protons with different acidity equilibrium constants. Therefore the aqueous solution of the acid has 2 ionization reactions and 2 acidity equilibrium constants. These are respectively, K_{a1}, K_{a2}:

$$H_2C_2O_{4\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HC_2O^-_{4(aq)}$$

$$K_{a1} = \frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = 5.37 \times 10^{-2}$$

$$HC_2O^-_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2O^{2-}_{4(aq)}$$

$$K_{a2} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = 5.1 \times 10^{-5}$$

Phosphoric acid (H_3PO_4) has 3 ionization reactions and 3 acidity equilibrium constants. (K_{a1}, K_{a2}, K_{a3})

$$H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO^-_{4(aq)}$$

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$H_2PO^-_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO^{2-}_{4(aq)}$$

$$K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO^{3-}_{4(aq)}$$

$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.80 \times 10^{-13}$$

Do you know that?

If we examine the values of acidity equilibrium constants, the order is as follows.

$K_{a1} > K_{a2} > K_{a3}$

The reason for that is the electrostatic attraction power is strong between different charged ions. So the negative charged substances have a low capability of losing positive proton.

3-2-2-Weak Bases

According to Bronsted acid-base theory, weak base is the substance which has ability to accept proton from solution. It has basicity equilibrium constant K_b. For example, the ionization reaction of ammonia in water is shown as follows:

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Note that the writing method of K_a and K_b are the same. Generally, the ionization reaction of weak base is written as ionic equilibrium as follows:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

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

Example 3-5

Calculate $[OH^-]$ ions concentration, degree of ionization and percent ionization for 0.2 M aqueous ammonia solution. $K_b(NH_3)=1.8 \times 10^{-5}$

Solution:

$$\begin{array}{llll} NH_{3(aq)} + H_2O_{(l)} & \rightleftharpoons & NH^+_{4(aq)} + OH^-_{(aq)} & \\ 0.2\ M & & 0 \qquad\quad 0 & \text{Initial concentration} \\ (0.2 - x)\ M & & x\ M \qquad x\ M & \text{Concentration at equilibrium} \end{array}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.2 - x)}$$

$$x^2 = 0.2 \times 1.8 \times 10^{-5} = 3.6 \times 10^{-6}$$

$$x = [OH^-] = 1.9 \times 10^{-3}\ mol / L$$

The ionization reaction equation is written for ammonia, and molar concentrations of substances are shown in the equation. Then those concentration values are inserted in the basicity equilibrium constant relationship.

Attention: While solving problems about weak bases, whether method of negligence is used or not depends on the rules which are valid for weak acids.

$$\text{Degree of ionization} = \frac{\text{The concentration of hydroxide ion at equilibrium}}{\text{Initial concentration of base}}$$

$$\frac{1.9 \times 10^{-3}}{0.2} = 0.0095$$

$$\text{Percent ionization} = \frac{\text{The concentration of hydroxide ion at equilibrium}}{\text{Initial concentration of base}} \times 100\%$$

$$\text{Percent ionization} = \frac{1.9 \times 10^{-3}}{0.2} \times 100\ \% = \%\ 0.95$$

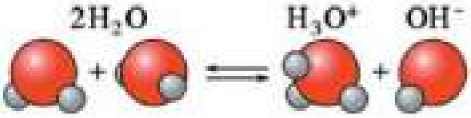
Exercise 3-4

Calculate degree of ionization of 0.1 M aqueous solution of aniline, C_6H_7N. ($K_b = 3.8\times10^{-10}$)

Answer: 6.2×10^{-5}

3-4- SELF-IONIZATION OF WATER (AUTO-IONIZATION OF WATER)

Self-ionization of water or auto-ionization of water is formation of hydronium H_3O^+ and hydroxide ion OH^- in its solution. A proton can be transferred from one water molecule to another in self-ionization of water or in other aqueous solutions of different substances. Self-ionization of water is a process in which a proton is transferred to other molecule by itself. This process gives water amphoteric property.



Scientific experiments have shown that water can conduct electricity. Pure water can ionize very slightly.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

Or in a simpler way,

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Equilibrium state can be defined with a value called as ionization constant and shown with K_w.

$$K_w = [H^+][OH^-] \quad \text{or} \quad K_w = [H_3O^+][OH^-]$$

Hydroxide ion (OH^-) always combines a hydronium ion H_3O^+ (or simply hydrogen ion H^+). Therefore, concentration of hydrogen ion is always equal to concentration of hydroxide ion in pure water. Measurements in pure water at 25 °C have shown that;

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ \mathrm{mol/L}$$

Those experimental values measured at 25 °C can be used to calculate ionization constant of water K_w.

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

K_w value of pure water at 25 °C can also be used successfully for dilute aqueous solutions.

Pure water is a neutral medium. That means it is neither acid nor base. Therefore, in any neutral solution, concentration of hydrogen ion is equal to concentration of hydroxide ion in the same solution ($[OH^-]=1.0\times10^{-7}$ M). But when we add some acid to pure water, according to ionization equilibrium reaction of water, the concentration of hydrogen ion increases and the concentration of hydroxide ion decreases (Le Chatelier's Principle.)

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

In a system at equilibrium, the ionization constant of water, K_w is always a constant value (1.0×10^{-14}). Therefore any increase in the concentration of H^+ causes a decrease in the concentration of OH^- or vice versa. By the same method, if we add some base to water (or to any neutral solution), the concentration of OH^- ions increases and as a result, the concentration of H^+ ions decreases. In the following solutions the concentrations of H^+ and OH^- ions are given:

Solution	General Situation	25 °C
Acidic	$[H^+] > [OH^-]$	$[H^+] > 1.0\times 10^{-7}M$, $[OH^-] < 1.0\times 10^{-7}M$
Neutral	$[H^+] = [OH^-]$	$[H^+] = 1.0\times 10^{-7}$ M, $[OH^-] = 1.0\times 10^{-7}$ M
Basic	$[H^+] < [OH^-]$	$[H^+] < 1.0\times 10^{-7}M$, $[OH^-] > 1.0\times 10^{-7}M$

Example 3-6

Calculate the concentrations of H^+ and OH^- ions in 0.05 M nitric acid, HNO_3 solution.

Solution:

The ionization equation of nitric acid is written. On it, the molar concentrations of H^+ and NO_3^- ions are shown. Then, to find out the concentration of OH^- ions in solution, the following relationship is used.

$$\begin{array}{lcccl} HNO_{3\,(aq)} & \longrightarrow & H^+_{(aq)} & + & NO^-_{3(aq)} & \\ 0.05\text{ M} & & 0 & & 0 & \text{Initial Concentration} \\ 0 & & 0.05\text{ M} & & 0.05\text{ M} & \text{Final Concentration} \end{array}$$

$$[H^+] = [NO_3^-] = 0.05\text{ mol/L}$$

The Value of (OH^-) can be calculated by constant ionization of water with K_w

$$\begin{array}{lcccc} H_2O & \rightleftharpoons & H^+_{(aq)} & + & OH^-_{(aq)} \\ & & 0.05\text{ M} & & \\ & & (0.05 + x)\text{ M} & & x\text{ M} \end{array}$$

$$K_w = 1.0\times 10^{-14} = [H^+][OH^-] = (0.05 + x)(x)$$

Depending on what we have learnt recently, the value of x (the concentration of H^+ formed through ionization of water) is much smaller than concentration of H^+ formed through complete ionization of acid. Therefore, by neglecting x $(x+0.05)$ we can accept its value as 0.05. If we solve the equation;

Exercise 3-5

Calculate the concentrations of hydrogen ions in aqueous solutions which contain;

A- 0.01 M $[OH^-]$

B- 2.0×10^{-9} M $[OH^-]$ ions.

Answer: A- 1×10^{-12} M

B- 5×10^{-6} M

WARNING: [OH^-] and [H^+] concentrations which are released during water ionization always neglect in strong base and strong acid solutions.

$$1.0 \times 10^{-14} = (0.05)(x)$$

$$x = \frac{1.0 \times 10^{-14}}{0.05} = 2.0 \times 10^{-13}\ mol/L = 2.0 \times 10^{-13}\ M$$

When the concentration of OH^- ion in this solution is examined, it is seen that the value of x (the concentration of OH^- ion) is much smaller than 0.05 and this proves the method of negligence.

3-5-THE HYDROGEN ION EXPONENT IN AQUEOUS SOLUTIONS

Making calculations with too small concentrations of H^+ and OH^- ions is difficult and risk of mistake is high. A scientist named Sorensen suggested using pH (acid scale) to express acidity of a solution in 1909. According to this, the concentration is defined with respect to the following relationship.

$$pH = -\log[H^+] = \log\frac{1}{[H^+]}$$

$$[H^+] = 10^{-pH}$$

One of the advantages of this method is that when the molar concentrations of H^+ and OH^- ions are known, the acidity or basicity values of solutions can be expressed with positive numbers between 0-14. Besides, the concentrations of hydroxide ions are found with the same method:

$$pOH = -\log[OH^-] = \log\frac{1}{[OH^-]}$$

$$[OH^-] = 10^{-pOH}$$

Exercise 3-6

Calculate the pH value of the following solutions.

A) Hydrochloric acid 6×10^{-4} M
B) Sulfuric acid 0.03 M
Answer: A) 3.22
B) 1.22

Example 3-7

Calculate pH value of solution which has 0.05 mol/L H^+ ion.

Solution:

In order to find pH value of solution, negative logarithm of H^+ ion concentration needs to be calculated as follows:

$$[H^+] = 0.05\ M$$

$$pH = -\log[H^+] = -\log 0.05 = 1.3$$

Example 3-8

If pH of a solution is 3.301, what is the concentration of H^+ ion in the solution?

Solution:

In $pH=-\log[H^+]$ relationship, pH is inserted in its place and equation is solved.

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

$$3.301=-\log[H^+]$$

By taking the logarithm of both sides of the relationship, we get the following result:

$$[H^+]=10^{-3.301}=5.0\times10^{-4}\ mol/L$$

The relationship between pH and pOH values in a dilute solution at 25 °C is used.

$$\boxed{[H^+][OH^-]=K_w=1.0\times10^{-14}}$$

By taking the logarithm of both sides of the relationship, the equation below is reached.

$$\log[H^+]+\log[OH^-]=\log(1.0\times10^{-14})$$

By multiplying both sides by (-1), we get the following:

$$(-\log[H^+])+(-\log[OH^-])=-\log(1.0\times10^{-14})$$

$$\boxed{pH+pOH=14}$$

This relationship shows that if pH and pOH values in a solution are both lower than 14, they are both positive, but if one of both is bigger than 14, the other one is negative. Generally, pH and pOH values of dilute solutions at 25 °C are as follows:

Substance	General Situation	25 °C
Acidic	$pH<pOH$	$pH<7<pOH$
Neutral	$pH=pOH$	$pH=7=pOH$
Basic	$pH>pOH$	$pH>7>pOH$

Attention:

Nowadays, in order to express concentrations of other ions, "p" term is used. Generally with a "p" before symbol, it means the negative logarithm of the symbol. According to this, pH means negative logarithm of the concentration of H^+ and pOH is negative logarithm of the concentration of OH^-. pK is negative logarithm of ionization constant. In the same manner, the negative logarithm of ionization constant of water is shown as $pK_w=-\log K_w$

pH values of some substances

Substance	pH Value
Content of human stomach	1.6-3.0
Fizzy drinks	2.0-4.0
Lemon	2.2-2.4
Vinegar	2.4-3.4
Tomato	4.0-4.4
Human urine	4.8-8.4
Cow milk	6.3-6.6
Human saliva	6.5-7.5
Human blood plasm	7.3-7.5
White of egg	7.6-8.0
Anti acid	10.5
Dilute ammonia solution	11-12

Exercise 3-7

What is the molarity of the solution if pH of nitric acid solution is 3.32?

Answer: 5×10^{-4} M

Example 3-9

Calculate pOH, [OH⁻], pH and [H⁺] values for 0.015 M hydrochloric acid solution.

Solution:

The ionization equation of HCl is written. We calculate the concentration of hydrogen ions. Then we calculate pH value. According to mathematical relationships mentioned before, pOH and [OH⁻] are found out.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

As HCl is a strong acid, it ionizes completely. That means:

$$[H^+] = 0.015\ mol/L$$

$$pH = -\log[H^+] = -\log(0.015) = -(-1.82) = 1.82$$

As it is known, pH + pOH = 14. Therefore, **pOH = 14.00 – 1.82 = 12.18**

As $[H^+][OH^-] = 1.0 \times 10^{-14}$, [OH⁻] can be easily calculated.

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.015} = 6.7 \times 10^{-13}\ mol/L$$

The pH value of fizzy drinks is calculated by a pH meter. Many fizzy drinks show acidic property due to dissolved CO_2 and some other ingredients they contain.

Exercise 3-8

Calculate the values of [H⁺],[OH⁻], pH and pOH of 0.015 M of $Ca(OH)_2$ aqueous solution. Is solution acidic or basic? Why?

Answer:

$[H^+] = 3.3\times10^{-13}$

$[OH^-] = 0.03$ M

pOH= 1.52

pH= 12.48

3-6 SOLVOLYSIS

The term "solvolysis" means a substance dissociates homogeneously by interacting with a suitable solvent. The important solvolysis reactions in our scope are the aqueous ones (water is used as solvent.) The interaction of a substance with water is called as hydrolysis. Hydrolysis reactions include interactions with H⁺ and OH⁻ ions. For example, the interaction of the negative conjugate of a weak acid with water in order to yield non-ionized weak acid is a kind of hydrolysis. As a result, H⁺ and OH⁻ ions in water produce base solution and weak HA acid. The reaction is shown as follows:

$$\underset{\text{Conjugate of weak acid}}{A^-_{(aq)}} + \underset{\text{water}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{weak acid}}{HA_{(aq)}} + \underset{\text{As OH}^-\text{ ion concentration increases, solution becomes basic.}}{OH^-_{(aq)}}$$

The reaction of acetate ion CH_3COO^- with water can be given as an example.

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

In a similar way, the interaction of the positive cation of weak base (conjugate acid) with water is an example. Here the resulting solution is acidic.

$NH_{4\ (aq)}^{+} + H_2O \rightleftharpoons NH_{3(aq)} + H_3O^{+}_{(aq)}$

According to Bronsted acid-base theory, the conjugate base of strong acid shows a very weak base property. Similarly, the conjugate base of a weak acid shows a strong base property. All those properties are also valid for bases.

With respect to interactions of salts in aqueous solutions, we can divide them into for parts:

1- Salts of strong base-strong acid

2- Salts of strong base-weak acid

3- Salts of weak base-strong acid

4- Salts of weak base- weak acid

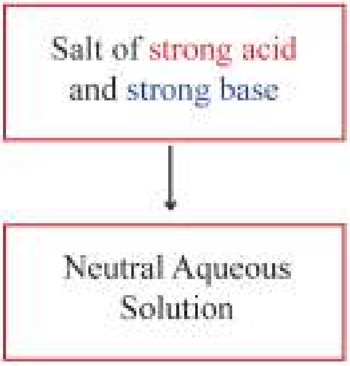
Now we will study each of those separately.

3-6-1-Salts of Strong Base-Strong Acid

These salts are formed from positive ion of strong base and negative ion of strong acid. The solution of this kind of salts is neutral. Because neither positive ions nor negative ions interact with water molecules significantly. For example, in dilute solution of NaCl (the salt formed from NaOH base and HCl acid) salt decomposes (dissolves) to its ions. Besides, water molecules also ionize.

$$NaCl_{(s)} \xrightarrow{H_2O} Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$H_2O_{(l)} \rightleftharpoons H^{+}_{(aq)} + OH^{-}_{(aq)}$$

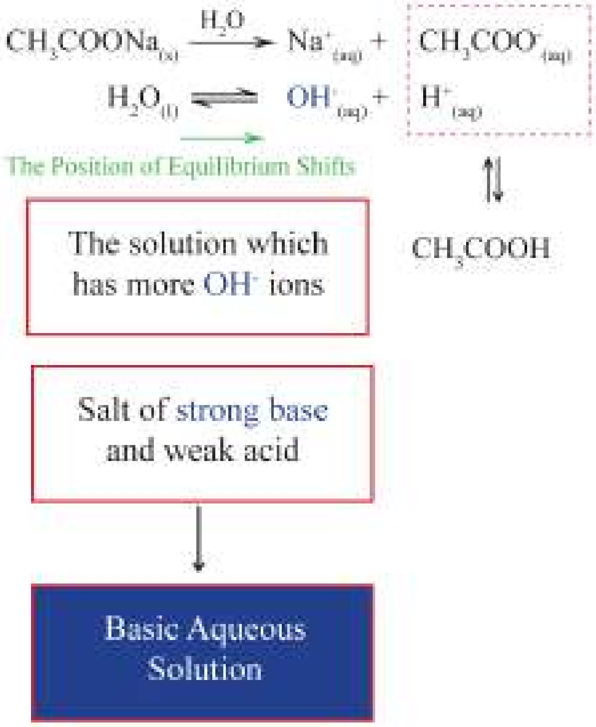


The aqueous solution of this salt includes 4 types of ions. These are OH^-, H^+, Cl^- and Na^+. Na^+ is a conjugated weak acid and it does not react with water at a significant level. Also the negative ion of salt Cl^- is a conjugated weak base and it does not react with water at a significant level. As a result, it can be said that the aqueous solutions of salts formed from strong bases and strong acids are neutral.

Because neither ions (positive or negative) have the capability to react with water and disrupt the equilibrium between H^+ and OH^- ions.

3-6-2-Salts of Strong Base - Weak Acid

When a salt formed from a strong base and a weak acid dissolves in water, the resulting solution is always basic. The reason is that the negative ion (which belongs to weak acid) interacts with water in order to form OH^- ion. For example, sodium acetate salt, CH_3COONa (the salt formed from NaOH strong base and CH_3COOH weak acid) ionized completely when dissolved in water as below:



The acetate ion represents the conjugate base of weak acid CH_3COOH. Therefore, these acetate ions interact with H^+ ions in order to form CH_3COOH. As a result, the amount of H^+ ions in the solution decreases. H_2O molecules ionize to compensate the decrease. Thus the amount of OH^- ions increases and the solution becomes basic. In order to define the hydrolysis of acetate ions, the total of equations above can be expressed with a single equation as follows:

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant of this reaction is called as **hydrolysis constant.** It is shown with K_h.

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Generally, the value of hydrolysis constant of a salt formed from strong base and weak acid can be expressed as follows:

In the equation, [HA] represents the concentration of weak acid, $[OH^-]$ the concentration of hydroxide ion and $[A^-]$ the concentration of negative ion of the salt (initial concentration of salt).

The value of K_h hydrolysis constant can be calculated through relationships known beforehand. For this, numerator and denominator are multiplied with $[H^+]$:

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

$$K_h = \frac{[HA][OH^-]}{[A^-]} \times \frac{[H^+]}{[H^+]}$$

$$K_h = \frac{[HA]}{[A^-][H^+]} \times \frac{[OH^-][H^+]}{1}$$

$$\boxed{K_h = \frac{1}{K_a(HA)} \times \frac{K_w}{1} = \frac{K_w}{K_a(HA)}}$$

The value of hydrolysis constant for any derived salt from astrong base and a weak acid

$$K_h = \frac{K_w}{K_a(HA)}$$

Example 3-10

What is the value of hydrolysis constant (K_h) of sodium acetate salt? The acidity constant of acetic acid $K_a(CH_3COOH)= 1.8\times10^{-5}$, the ionization constant of water, $K_w=1.0\times10^{-14}$

Note: As K_w is not given in such questions, students need to know it by heart.

Solution:

Sodium acetate salt is formed from strong base NaOH and weak acid CH_3COOH. Therefore, if the acidity constant K_a of weak acid and ionization constant of water K_w is known, the hydrolysis constant of salt is calculated as follows:

$$K_h = \frac{K_w}{K_a(CH_3COOH)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

In short, the hydrolysis constant of any salt formed from strong base and weak acid is calculated through the following relationship:

$$\boxed{K_h = \frac{K_w}{K_a} \quad \text{or} \quad pK_h = pK_w - pK_a}$$

K_a is the acidity constant of weak acid that forms salt, pK_h , pK_w, pK_a, are the negative logarithms of K_b, K_w, K_a, values respectively. The concentrations of H^+ ion can be calculated easily for this kind of solutions. Because the amounts of HA and OH^- ions formed as a result of hydrolysis are equal can consider $[A^-]$ is equal $[HA]=[OH^-]$.The molar concentration of salt in the solution is [M].

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]} = \frac{[OH^-]^2}{c} = \frac{K_w}{K_a}$$

$$[OH^-] = \sqrt{c \times \frac{K_w}{K_a}} \text{ or}$$

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

$$[H^+] = \sqrt{\frac{K_w \times K_a}{c}}$$

or

$$pH = \frac{1}{2}\,[pK_w + pK_a + \log c]$$

Attention: If pH and $[H^+]$ is asked to be calculated, students can choose which equation to be used. Any of the two relationships can be used in calculation.

Example 3-11

Calculate pH value of 0.01 M sodium acetate salt at 25 °C.

$K_a(CH_3COOH) = 1.8\times10^{-5}$

Solution:

We use the following relationship to calculate pH of this salt solution.

$$pH = \frac{1}{2}[pK_w + pK_a + \log c]$$

$$pH = \frac{1}{2}[-\log K_w - \log K_a + \log c]$$

$$pH = \frac{1}{2}[-\log(1.0\times10^{-14}) - \log(1.8\times10^{-5}) + \log 0.01]$$

$$pH = \frac{1}{2}(14 + 4.74 - 2) = 8.37$$

Exercise 3-9

Calculate the concentration of hydroxide ions in 0.1 mol/L potassium cyanide, KCN, salt aqueous solution.

$K_a(HCN) = 4.9\times10^{-10}$, is the solution acidic or basic.

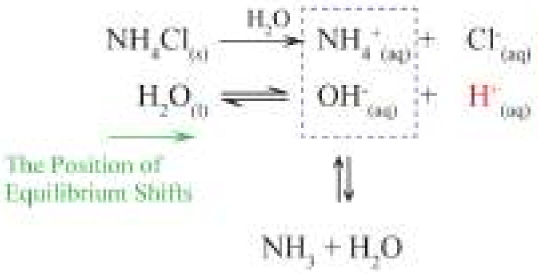
Answer: 1.43×10^{-3} M
The salt is basic

3-6-3-Salts of Weak Base-Strong Acid

In the second type of hydrolysis reactions, positive ions of salt (which belong to weak base) react with OH^- ions in water to form non–disintegrating weak base particlesin addition to H^+ ions. This reaction disrupts the equilibrium between H^+ and OH^- ions.

As a result, $[H^+]$ ion increases and the solution becomes acidic.

Therefore, ammonium chloride salt NH_4Cl (salt formed from weak base NH_3 and strong acid HCl) decomposes completely when dissolved in water as follows;



The solution which has more H^+ ions

Ammonium ion (the conjugate acid of weak base NH_3) reacts with OH^- to produce non-ionized NH_3 and H_2O molecules. This reaction consumes OH^- ions in the medium. Therefore, to compensate this decrease and establish a new equilibrium, H_2O molecules ionize. As a result, the amount of H^+ increases and the solution becomes acidic.

In order to define the hydrolysis of ammonium ion NH_4^+, a final equation representing all of the reactions above can be written.

Salt of strong acid and weak base

↓

Acidic Aqueous Solution

$$NH_4^+{}_{(aq)} + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b}$$

$K_a = \frac{K_w}{K_b}$ Relationship can be proved. K_b is the ionization constant of weak base. Besides a general equation expressing hydrolysis of this kind of salts can be written as follows:

$$M^{+} + H_2O \rightleftharpoons MOH + H^{+}$$

$$K_h = \frac{[MOH][H^{+}]}{[M^{+}]} = \frac{K_w}{K_b}$$

[MOH] represents the concentration of weak base, $[H^{+}]$ concentration of acid ion that formed from reaction $[M^{+}]$ for unhydrolysed salt.

As [MOH] and $[H^{+}]$ are formed through hydrolysis of salt molecules, their concentrations in the salt solution are equal.

For the solution with [c] molar concentration:

$$K_h = \frac{[H^{+}]^2}{[M^{+}]} = \frac{[H^{+}]^2}{c} = \frac{K_w}{K_b}$$

We get the following relationship from above equation:

$$[H^{+}] = \sqrt{c \times \frac{K_w}{K_b}}$$

By taking negative logarithm of both sides:

$$pH = \frac{1}{2}[pK_w - pK_b - \log c]$$

K_b represents the basicity constant of the weak base which the salt is formed from.

Exercise 3-10

Calculate pOH value of 0.5 M ammonium nitrate (NH_4NO_3) solution. Is the solution acidic or basic?

(pK_b (NH_3) = 4.74)

Answer: 9.22, The solution is acidic.

Example 3-12

What is the pH of 0.2 mol/L ammonium chloride solution?

$K_b(NH_3) = 1.8\times10^{-5}$

Solution:

We need to know the basicity constant of weak base and the ionization constant of water to find pH of solution. Then the following relationship is used to calculate pH:

$$pH = \frac{1}{2}[pK_w - pK_b - \log c]$$

$$pH = \frac{1}{2}[-\log K_w + \log K_b - \log c]$$

$$pH = \frac{1}{2}[-\log(1.0 \times 10^{-14}) + \log(1.8 \times 10^{-5}) - \log 0.2]$$

$$pH = \frac{1}{2}(14 - 4.74 - (-0.7)) = 4.98$$

3-7 COMMON ION EFFECT

We have studied the aqueous solutions of weak electrolytes and their behaviors. In this chapter, we will study the behaviors of aqueous solutions with two electrolytes (one is weak). The similarity of these two electrolytes is that they have a common ion. The concentration of an ion in any solution can increase as a result of decomposition of added compound into its ions. The ion which is present in the solution and added compound is called as **common ion**.

At this level, we will focus on the situation which the electrolyte in solution is weak and added compound is strong. As a result of addition, a significant amount of increase occurs in the concentration of common ion. This increase can be understood when the concentration of weak electrolyte is compared to the concentration after addition. Disequilibrium results from this process. Therefore, the solution forms a new equilibrium.

When some amount of ion is added to weak electrolyte solution, the ionization of weak electrolyte decreases. This phenomena result from the establishment of ionic equilibrium again in electrolyte solution. This is called as **common ion effect**. This situation is a result of Le Chatelier's Principle.

Example 3-13

How does the concentration of H^+ ion change when 8.2 grams (0.1 mol) sodium acetate salt, CH_3COONa, is added to 1 liter 0.1 mol/L acetic acid solution at 25 °C? $K_a(CH_3COOH) = 1.8\times10^{-5}$

Solution:

The ionization equations of weak electrolyte and added salt are written. On them, the molar concentrations at equilibrium are shown.

	$CH_3COOH_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	+	$CH_3COO^-_{(aq)}$
Initial concentration	0.1 M		0		0
Concentration at equilibrium	(0.1- x) M		x M		x M
	$CH_3COONa_{(s)}$	$\longrightarrow$	$Na^+_{(aq)}$	+	$CH_3COO^-_{(aq)}$
Initial concentration	0.1 M		0		0
Final concentration	0		0.1 M		0.1 M
					Common ion

Ionization equations show that common ion in that solution is acetate ion. Because it has two sources: One is acetic acid (weak electrolyte), the other is sodium acetate (strong electrolyte). The concentration of common ion is found by addition of concentrations result from ionization of both compounds.

In order to calculate the effect of common ion, the concentration of H^+ ion in 0.1 M acetic acid solution is calculated as below before the addition of sodium acetate:

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]} = \frac{(x)\,(x)}{(0.1 - x)}$$

We get the following and apply the method of negligence

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

$$x^2 = (0.1) \times (1.8 \times 10^{-5}) = 1.8 \times 10^{-6}$$

$$x^2 = \sqrt{1.8 \text{ x } 10^{-6}} = 1.3 \times 10^{-3}$$

$[H^+] = \mathbf{1.3 \times 10^{-3}}$ **mol/L**

Then, after adding sodium acetate (common ion effect), the concentration of H^+ ion in acid solution is calculated as follows:

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{(x')\,(0.1 + x')}{(0.1 - x')} = \frac{(x')\,(0.1)}{(0.1)}$$

$x' = \mathbf{1.8 \times 10^{-5}}$ **mol/L** $= [H^+]$

When we compare the concentrations of H^+ ion before and after (common ion effect) addition of salt, we see that the concentration decreases to 1.8×10^{-5} mol/L from 1.3×10^{-3} mol/L. The reason for that due to a common ion (acetate) presence between two compounds, the ionization of acetic acid decreases by addition of sodium acetate salt.

Exercise 3-11

How does the ionization degree of base change when 26.75 grams (0.5 mol) ammonium chloride salt is added to 0.1 M 1 liter ammonia solution? $K_b(NH_3)=1.8\times10^{-5}$

Answer:

Ionization degree of the base is greater than 360 times.

3-8 BUFFER SOLUTIONS

pH values of strong acid and base solutions can be calculated easily through their molar concentrations. According to this, the pH value of 10^{-4} M hydrochloric acid is equal to 4. But this value changes considerably even a small amount of basic substance is added to acid solution. The same is also valid for base solutions. For example,

pH value of 1M ammonium acetate salt (salt of weak acid and weak base) and sodium chloride salt solution is approximately equal to 7 (Why?). But when a small amount of strong acid or base is added to this solution, its behavior changes. Because when 1.0 M 1 mL HCl solution is added to 1 liter salt solution, the pH of NaCl solution becomes 3.0, but the pH of CH_3COONH_4 changes very slightly.

In many solutions, common ion effect is observed. But there are two very common situations:

1- A solution formed from a weak acid and the salt of this acid (e.g. CH_3COONa and CH_3COOH)

2- A solution formed from a weak base and the salt of this base (e.g. NH_3 and NH_4Cl)

There are some reactions occurring in scientific laboratories or in industrial processes or in bodies of living beings which need the pH value to remain constant upon addition of small amounts of acid or base. For example, most of the metabolic activities occurring inside human body are sensitive to pH values of body liquids. Transportation of oxygen and activities of enzymes in cells can be given as examples. Therefore, our bodies use a compound mixture called buffer solution (the system preserves from pH change) that preserves pH value between certain limits. When a small amount of strong acid or a base is added to a solution, the resistance of H^+ ion to change is called as buffer effect or buffer action, and solutions which have this property is called as **buffer solutions**.

In buffer solutions, generally two interactions occur. First one neutralizes added base by interacting with it. The other one neutralizes the added acid. This way the buffer effect of solution occurs. This kind of solutions are generally formed by mixing a weak acid and its derived salt or a weak base and its derived salt. The buffer solution formed from mixing acetic acid (weak acid) and sodium acetate (salt derived from acetic acid) is an example. In order to observe how such a solution resists to pH change, we will examine the effects of addition of some strong HCl into buffer solution and into pure water.

As a result of addition of some strong acid into water, a big increase occurs in the concentration of H^+ ion and a big decrease in the pH value of solution. But an addition of same amount of acid into acetic acid-sodium acetate mixture does not result in a significant amount of increase in H^+ ion concentration. Because this ion does not remain free in the solution but interacts with CH_3COO^- ion from sodium acetate in order to form acetic acid. Thus the pH value of solution does not decrease but remain almost constant.

When some amount of strong base as NaOH is added to water, as a result of complete decomposition of base, the concentration of OH^- ions will increase. Therefore, the pH value of solution will increase. If the same amount of base is added to buffer solution (CH_3COONa and CH_3COOH), the OH^- ions cannot remain in the solution but react instantly with H^+ ions from decomposition of acetic acid and form water.

As a result, the pH value of this mixture does not change significantly. With respect to what is mentioned above, buffer solution neutralizes as it reacts with components of added strong acid or base.

Thus the pH value of the solution remains constant. But in fact, when HCl is added, the concentration of acetic acid increases a bit. This is a weak acid. The increase in the concentration of solution causes a slight decrease in pH of solution. On the other hand, the addition of NaOH to buffer solution causes formation of sodium acetate. The increase in the amount of this salt results in a slight increase in pH of solution. (Why?)

We will examine the equilibrium position of weak acid HA (or weak base) solution and the reactions of weak acid's salt.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$$MA_{(s)} \longrightarrow M^+_{(aq)} + A^-_{(aq)}$$

Here the equilibrium position is as follows:

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

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

If we assume the $[H^+]$ in solution as very small (as a result of common ion effect which works to decrease weak acid's decomposition), we can simplify this relationship (after applying method of negligence). In equilibrium, the concentration of unionized acid will be equal to initial acid concentration. The concentration of $[A^-]$ in equilibrium will be only equal to salt's concentration. Therefore we can rewrite previous relationship as follows:

$$\boxed{[H^+] = K_a \times \frac{[acid]}{[salt]}}$$

[acid] represents the concentration of acid, whereas [salt] is the concentration of salt. We can re-arrange the equation by taking the logarithm of both sides:

$$\boxed{pH = pK_a - \log \frac{[acid]}{[salt]} = pK_a + \log \frac{[salt]}{[acid]}}$$

$$\boxed{pOH = pK_b - \log \frac{[base]}{[salt]} = pK_b + \log \frac{[salt]}{[base]}}$$

By the same method, it is possible to derive a relationship that defines the equilibrium position of a mixture formed from weak base and its salt.

$$\boxed{[OH^-] = K_b \times \frac{[base]}{[salt]}}$$

In the equation, [base] is the concentration of base and [salt] is the concentration of salt.

A- When respiration stops, the amount of CO_2 in blood increases.

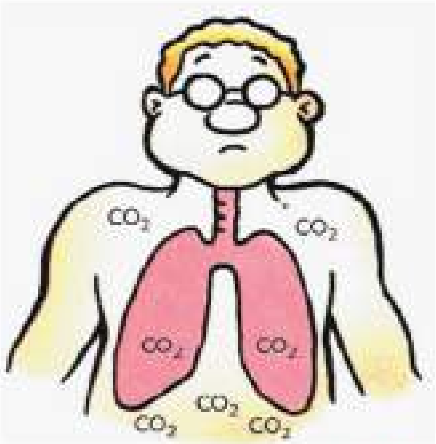
As a result, the amount of carbonic acid increases and the pH value of blood decreases.

B- During breathing heavily, the amount of CO_2 in veins decreases.

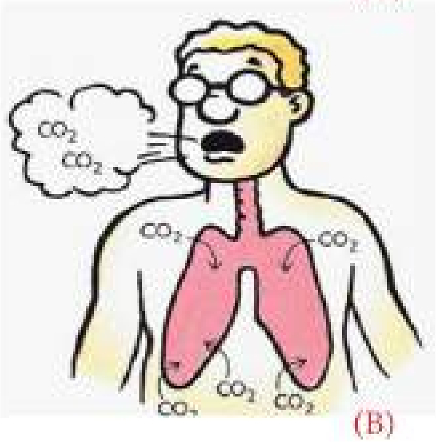
As a result, the amount of carbonic acid in blood decreases and the pH value of blood increases.

Do you know

(A) When breathing stops, it increases the amount of CO_2 in the blood, which leads to an increase in the amount of carbonic acid and a decrease in the blood pH value, (B) When breathing quickly, the level of CO_2 decreases in the bloodstream, as this leads to a decrease in the amount of carbonic acid and an increase in the blood pH value.



(A)



(B)

Example 3-14

Calculate the concentration of H^+ ions and pH value of the solution of 0.1 M acetic acid and 0.2 M sodium acetate. $K_a(CH_3COOH)=1.8\times10^{-5}$

Solution:

We can use the mathematical relationship above to calculate the concentration of H_3^+ ions and pH value of the mixture of weak acid and its salt. The mixture has got buffer solution property. Therefore:

$$[H^+] = K_a \times \frac{[acid]}{[salt]}$$

[acid]= 0.1M , $K_a(CH_3COOH) = 1.8\times10^{-5}$ and [salt]=0.2M

We get the result below:

$$[H^+]=1.8 \times 10^{-5} \times \frac{0.1}{0.2} = 9.0 \times 10^{-6}$$

We can calculate the pH of solution using the following relationship:

$$pH = -\log [H^+] = -\log 9.0 \times 10^{-6} = 5.04$$

or using the following equation directly:

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

As $pK_a = -\log K_a$

$$pH = -\log 1.8 \times 10^{-5} + \log \frac{0.2}{0.1}$$

$$pH = 4.74 + \log 2 = 4.74 + 0.30 = 5.04$$

Here we can compare the concentration of H^+ ions and pH value of the solution (buffer solution) with the calculated values of 0.1 M acetic acid. This comparison is ($[H^+] = 1.35\times10^{-3}$ M) and (pH = 2.87) respectively.

Example 3-15

what should be the concentration of ammonium chloride in asolution containing ammonia at aconcentration 0.1 M, so that the pH value of the solution is equal to 9.0 ? $pK_b = 4.74$

Solution:

$$pH + pOH = 14$$

$$pOH = 14 - pH = 14 - 9 = 5$$

Exercise 3-12

0.3 M sodium acetate salt forms a buffer solution with acetic acid. What should be the concentration of acetic acid for the solution to have a pH value of 4.31? $K_a = 1.8 \times 10^{-5}$

Answer: 0.81 M

The pOH value of the solution with a pH value of 9.0 is equal to 5.0. The solution of ammonia and ammonium chloride is a buffer solution. Therefore we can calculate using the previous mathematical relationships. We can use the following relationship for the solution of weak base and its salt.

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

$$5.00 = -\log 1.8 \times 10^{-5} + \log \frac{[salt]}{0.1}$$

$$\log \frac{[salt]}{0.1} = 5 - 4.74 = 0.26$$

$$\frac{[salt]}{0.1} = 10^{0.26} = 1.82$$

$$[salt] = 0.1 \times 1.82 = 0.182 \text{ mol/L}$$

Example 3-16

Calculate the pH value of new solution formed after addition of 1 mL of 10M hydrochloric acid solution into 1 liter 0.1 M acetic acid and 0.1 M sodium acetate buffer solution. $pK_a = 4.74$

(Note: While solving the question, ignore the volume change in solution occurs after addition of strong acid or base.)

Solution:

The buffer solution formed by acetic acid and sodium acetate can be expressed by following equations:

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$CH_3COONa_{(s)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

1- The amounts (mole numbers) of sodium acetate and acetic acid in solution before addition of strong acid is calculated as follows:

Mole number of acetic acid in 1 liter solution = $M_{CH_3COOH} \times V(L)$

0.1 mol/L × 1 L = 0.1 mol

Mole Number of salt in 1liter solution = $M_{CH_3COONa} \times V(L)$

0.1 mol/L × 1 L = 0.1 mol

2- HCl acid decomposes completely as in the following equation

$$HCl_{(aq)} \longrightarrow Cl^-_{(aq)} + H^+_{(aq)}$$

In order to produce H^+ ions equal to the added amount of acid:

$M_{HCl} \times V(L)$ (Mol number of H^+ ions equals to the added amount of acid:

$$= 10\ mol/L \times 1\ mL \times \frac{1\ L}{1000\ mL} = 0.01\ mol$$

H^+ ions produced from decomposition of HCl combine with the same amount of acetate ions to produce the same amount of acetic acid.

3- The amounts and concentrations of acetate ions and acetic acid are calculated as follows after addition:

The amount of produced H^+ ions + the amount of acetic acid before addition = The amount of acetic acid after addition

$$= 0.1\ mol + 0.01\ mol$$

$$= 0.11\ mol$$

$$[CH_3COOH] = \frac{n\ (mol)}{V\ (L)} = \frac{0.11\ (mol)}{1\ (L)} = 0.11\ mol/L$$

The amount of produced H^+ ions - the amount of sodium acetate before addition = The amount of sodium acetate after addition

$$= 0.1\ mol - 0.01\ mol$$

$$= 0.09\ mol$$

$$[CH_3COO^-] = \frac{n\ (mol)}{V\ (L)} = \frac{0.09\ (mol)}{1\ (L)} = 0.09\ mol/L$$

4- The special equation to calculate pH value in buffer solution is applied as follows:

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$pH = 4.74 + \log \frac{0.09}{0.11}$$

$$pH = 4.74 + (-0.087) = 4.66$$

3-9-SOLUBILITY AND SOLUBILITY PRODUCT CONSTANT

Dissolution of solids in water is accepted as one of the important procedures in chemistry. Because solubility of any ionic substance depends on the difference between the amounts of energy necessary to break the bonds between ions constituting the matter and energy released during ionization and hydration. Therefore solubility of substances in water differ.

In this chapter, we have studied the behaviors of substances dissolved in water. But there are many substances which are slightly soluble in water. The solubility of these substances depends on an equilibrium state between the solid

Exercise 3-13

Calculate values of pH of the following;

A- 1 liter buffer solution is formed from 0.1M ammonia, NH_3, and 0.1M ammonium chloride NH_4Cl.

B- Calculate the change in value of pH of the same solution after adding 10M of 1mL sulfuric acid, H_2SO_4. Discuss the results.
$pK_b = 4.74$

Answer:
A) 9.26
B) 9.06
$\Delta pH = -0.2$

Do you know?

When ammonium sulfide solution is mixed with cadmium nitrate solution, a sediment called cadmium sulfide forms.

$$\begin{array}{c}(NH_4)_2S_{(aq)} + Cd(NO_3)_{2(aq)} \\ \downarrow \\ CdS_{(s)} + 2NH_4NO_{3(aq)}\end{array}$$

Cadmium sulfide, which is a slightly soluble salt, is used in production of yellow dye used in paintings.

part of the substance and produced ions (between the decomposed and non-decomposed). This solution is called as **saturated solution**. The dissolution of a slightly water soluble substance can be defined as follows:

$$AB_{(s)} + H_2O_{(l)} \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

The equilibrium constant (K_{eq}) of this equilibrium reaction is shown with the following relationship.

$$K_{eq} = \frac{[A^+][B^-]}{[AB][H_2O]}$$

We assume that the concentration of [AB] remains constant as the compound dissolves slightly in water and only a very small part of it decomposes. Besides, as the solvent is water, the concentration of [H_2O] is assumed as constant. Therefore, the previous relationship can be re-arranged as follows:

$$K_{sp} = [A^+][B^-]$$

Because:

$$K_{sp} = K_{eq}[AB][H_2O]$$

The value of K_{sp} is called as solubility product constant. This value remains constant at a certain temperature. Solubility product constant is used to express (or measure) the solubility of slightly soluble salts in water. The solubility of a compound is directly proportional to its solubility product. Generally, the solubility product of a slightly soluble ionic compound is calculated through the molar concentrations of ions making up of the compound at equilibrium (in saturated solutions molar solubility is shown with -s-). When writing solubility product constant in equilibrium chemical equation, the concentrations of ions formed from decomposition of compounds are multiplied. Mole numbers are written as exponents. The molar solubility of slightly soluble salts -s- is defined as the molar concentration of ions formed from decomposition of salt in solution at equilibrium.

The solubility product constant of salts like AgCl, $BaSO_4$ and $PbSO_4$ which have two moles of ions in their solutions is expressed as follows:

$$K_{sp} = s \times s = s^2$$

The solubility product constant of salts like Ag_2SO_4 or CaF_2 which have three moles of ions in their solutions is expressed as follows:

$$K_{sp} = s \times (2s)^2 = 4s^3$$

The solubility product constant of a salt like $Ca_3(PO_4)_2$ which have 5 moles of ions in its solution is expressed as follows:

$$K_{sp} = (3s)^3 \times (2s)^2 = 108\,s^5$$

These rules are applied only when a saturated solution of a slightly soluble salt is at equilibrium.

Example 3-17

As the solubility product constant of lead sulfate salt $PbSO_4$ is $K_{sp} = 1.6\times10^{-8}$, what is the molar solubility of $PbSO_4$?

Solution:

First, the chemical equilibrium equation for dissolution of $PbSO_4$ is written.

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

Let's assume that the molar solubility of $PbSO_4$ salt is s mol/L. As seen in the equation, when 1 mole of $PbSO_4$ is dissolved, 1 mole of Pb^{+2} and 1 mole of SO_4 ions are formed in the solution. Depending on this, solubility constant K_{sp} is written mathematically as follows:

$$\begin{array}{lcccc} PbSO_{4(s)} & \rightleftharpoons & Pb^{2+}_{(aq)} & + & SO^{2-}_{4(aq)} \\ & & s\,(mol/L) & & s\,(mol/L) \end{array}$$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

$$K_{sp} = s \times s = s^2 = 1.6 \times 10^{-8}$$

$$s = \sqrt{1.6 \times 10^{-8}} = 1.26 \times 10^{-4}\ mol/L$$

Exercise 3-14

Calculate the solubility product constant of Ag_2CrO_4 salt, as the saturated solution of 1 liter silver chromate, contains 0.0215 g salt. (M=332 g/mol)

Answer: 1.09×10^{-12}

Example 3-18

Calculate the solubility product constant K_{sp} of $BaSO_4$ salt as 1 liter saturated solution of $BaSO_4$ contains 0.0025 g/L $BaSO_4$ (M = 233 g/mol).

Solution:

First, chemical equilibrium equation for dissolution of $BaSO_4$ salt is written. Then, the mathematical expression for solubility product constant K_{sp} is written. From the solubility value of salt (0.0025 g/L), the molar solubility (mol/L) and the concentrations of ions in solution can be calculated. An equilibrium is established between the decomposed and non-decomposed parts of this salt in its saturated solution as follows.

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$(M = 233\ g/mole)\ BaSO_4$$

-s- molar solubility (M = 233 g/mol) of $BaSO_4$ is calculated depending on its solubility.:

$$\textbf{Molar solubility of } BaSO_4 = \textbf{solubility of } BaSO_4\ \textbf{(g/L)} \times \frac{1\,(mol)\ BaSO_4}{233\,(g)\ BaSO_4}$$

$$s\ BaSO_4\ (mol/L) = 0.0025\ (g/L) \times \frac{1\ (mol)\ BaSO_4}{233\ (g)\ BaSO_4}$$

$$s\ BaSO_4 = 1.1 \times 10^{-5}\ mol/L$$

Ba^{2+} and SO_4^{2-} ions are formed from dissolution of $BaSO_4$ as shown in the equilibrium equation. Therefore,

$$\begin{array}{llll} BaSO_{4(s)} & \rightleftharpoons\ Ba^{2+}_{(aq)} & + & SO^{2-}_{4(aq)} \\ 1.1 \times 10^{-5}\ M & 1.1 \times 10^{-5}\ M & & 1.1 \times 10^{-5}\ M \end{array}$$

That means, in the saturated solution of this salt, $[Ba^{2+}] = [SO_4^{2-}] = 1.1\times10^{-5}M$. These values are inserted in the mathematical relationship for solubility product constant K_{sp}.

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (1.1\times10^{-5})(1.1\times10^{-5}) = 1.2\times10^{-10}$$

Solubility product constant K_{sp} is accepted as a measurement of solubility of compounds which are slightly water soluble. Knowing the solubility value enables us to make sure if precipitation of the substance is completed or not in a precipitation process. If the product (multiplication) of concentrations of ions of a precipitate in a solution is greater than the solubility product constant of the precipitate, precipitation starts. In this process, the ions of the precipitate accumulate and form unionized molecules. But if the product of concentrations of ions of precipitate is less than the solubility product constant of the precipitate, the molecules of precipitate start dissolving. When the solubility product constant is equal to the product of ions, the solution becomes saturated. Therefore, an equilibrium is established between the dissolution and precipitation of the precipitate.

Exercise 3-15

What is the lowest (pH) of asolution contains Iron ion (III) in equal concentration 2×10^{-10} M which, if adeposit Iron hydroxide (III) $Fe(OH)_3$ begins to appear in the solution.

$K_{sp}(Fe(OH)_3) = 5\times10^{-38}$

Answer: 4.8

Example 3-19

As the fluoride ion F^- concentration in a solution is 2×10^{-2} M, what should be the minimum calcium ion concentration in the solution for CaF_2 salt to precipitate? ($K_{sp} = 4.9\times10^{-11}$)

Solution:

First, the precipitation equation for the calcium fluoride salt is written. Then, the mathematical relationship for the solubility constant is written.

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

As known, the precipitation starts when the product of concentrations of ions of precipitate is equal to/greater than solubility constant. As the concentration of fluoride ion in solution is 2×10^{-2} M, the concentration of calcium ion can be calculated through inserting this value in the following equation.

$K_{sp} = (xM) \times (2 \times 10^{-2}\,M)^2$

$4.9 \times 10^{-11} = (x) \times (2 \times 10^{-2}\,M)^2$

$x = 1.23 \times 10^{-7}\,M = [Ca^{2+}]$

3-9-1- Factors Affecting Solubility

There are many factors causing solubility of precipitates to increase or decrease. The most important of those are temperature, common ion effect and pH effect.

1- The effect of temperature

In order to dissolve a substance in a solution, the solute needs to gain the energy to break the bonds between the molecules. The substance obtains this energy through hydration. In the end, the difference between absorbed and released energy (Study the Thermodynamics chapter) defines the temperature of solution. Practically, the solubility of slightly soluble substances increases with temperature. But this increase changes from substance to substance.

2- Common Ion Effect

As we have studied before, according to Le Chatelier's Principle, the solubility of any weak electrolyte (e.g. slightly soluble salt) decreases when a substance with a common ion is added to solution. Practically this phenomenon is used to control the dissolution of precipitates.

Example 3-20

Calculate the molar concentration of barium iodate salt $Ba(IO_3)_2$,

A- In pure water,

B- In 0.02 mol/L potassium iodate, KIO_3, solution. Then, make a comparison between results. $K_{sp} = 1.57\times10^{-9}$

Solution:

First, the dissolution equilibrium equation for $Ba(IO_3)_2$ is written. Then, the mathematical relationship for solubility product constant is written. The problem is solved following the steps we have seen in the previous examples.

A-If we assume the molar concentration of $Ba(IO_3)_2$ as s,

$$\begin{array}{lcll} Ba(IO_3)_{2\,(s)} & \rightleftharpoons & Ba^{2+}_{(aq)} \;+ & 2IO^{-}_{3\,(aq)} \\ s\,M & & s\,M & 2s\,M \end{array}$$

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = (s)(2s)^2 = 1.57 \times 10^{-9}$$

By solving the equation, s value is obtained.

$s = 7.3\times10^{-4}$ mol/L

The molar solubility of in $Ba(IO_3)_2$ pure water is to equal 7.3×10^{-4} mol/L.

B- KIO_3 is accepted as a strong salt which dissolves completely. Therefore, the concentration of $(IO_3)^-$ ion is calculated as follows:

Exercise 3-16

A 1L solution contains 0.001 mole of both of Fe^{3+} and Al^{3+} ions. Certain amount of NaOH solution is added to it. Show mathematically, which one of $Al(OH)_3$ and $Fe(OH)_3$ precipitates first and why?

$K_{sp}(Al(OH)_3) = 3.5\times10^{-34}$

$K_{sp}(Fe(OH)_3) = 5\times10^{-38}$

Answer: $Fe(OH)_3$ precipitates first because it needs less amount of OH^- ions to precipitate.

$$\begin{array}{ccccc} KIO_3 & \rightarrow & K^+ & + & IO_3^- \\ 0.02M & & 0.02M & & 0.02M \end{array}$$

We take the molar concentration of $Ba(IO_3)_2$ in 0.02 M KIO_3 solution as y.

$$\begin{array}{ccccc} Ba(IO_3)_{2\,(s)} & \rightleftharpoons & Ba^{2+}_{(aq)} & + & 2IO^-_{3\,(aq)} \\ y\,M & & y\,M & & 2y\,M \end{array}$$

As IO_3^- is the common ion, the concentration of $[IO_3^-]$ is equal to the sum of concentrations of IO_3^- ions from the ionization of $Ba(IO_3)_2$ and KIO_3 salts. That is (0.02 + 2y) mol/L. Therefore,

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = (y)(0.02 + 2y)^2 = 1.57 \times 10^{-9}$$

We can assume the concentration of IO_3^- ion obtained from $Ba(IO_3)_2$ is too small in comparison with IO_3^- ion obtained from KIO_3. That is $2y < 0.02$. Therefore;

$(0.02 + 2y) \approx 0.02$ mol/L

$K_{sp} = [Ba^{2+}][IO_3^-]^2 = (y) \times (0.02)^2 = 1.57 \times 10^{-9}$

$y = 3.9 \times 10^{-6}$ mol/L

The molar solubility of $Ba(IO_3)_2$ salt in 0.02 mol/L potassium iodate KIO_3 solution is equal to 7.3×10^{-4} M. When we compare the results, it is seen that the solubility of $Ba(IO_3)_2$ salt in pure water is much greater than its solubility in KIO_3 solution (common ion effect). The percentage of solubility of this salt in two different medium can be calculated as follows:

$$\frac{\text{Molar solubility in pure water}}{\text{Molar solubility in } KIO_3 \text{ solution}} = \frac{7.3\times10^{-4}\ \text{mol/L}}{3.9\times10^{-6}\ \text{mol/L}} \simeq \frac{187}{1}$$

In other words, the molar solubility of $Ba(IO_3)_2$ salt in 0.02 mol/L KIO_3 solution is 187 times less than its solubility in pure water.

3- The pH Effect

The concentrations of many substances depend on the concentration of H^+ ion in solution. The substances which contain hydrogen or hydroxide ions in their components can be given as examples. e.g $Mg(OH)_2$.

The solubility of these substances change with the changing of pH value of the solution and through the effect of common ion.

$$Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$$

When an acid is added to the saturated solution of this compound, hydrogen and hydroxide ions react to yield water molecules and this causes the disruption of equilibrium shown in the equation. The compound ionizes more (in other words its solubility increases) in order to compensate the decrease in OH^- ion concentration. When a base is added to the solution in equilibrium of this compound, its solubility decreases as a result of common ion effect.

Exercise 3-17

A solution of 0.01M, 20 mL silver nitrate ($AgNO_3$) is added to a solution of 0.05M, 80 mL potassium chromate (K_2CrO_4). Will silver chromate precipitate?

$K_{sp}(Ag_2CrO_4) = 1.1\times10^{-12}$

Answer: Yes, it will precipitate.

Exercise 3-18

The solubility product constant of magnesium fluoride, MgF_2, salt is equal to $K_{sp} = 6.5\times10^{-9}$.

A- Calculate the molar solubility of this salt in pure water.

B- Calculate its molar solubility in 0.1 mol/L sodium fluoride, NaF, (strong electrolyte) and compare both results.

Answer: A- 1.18×10^{-3} M

B- 6.5×10^{-7} M

Solubility decreases.

Example 3-21

Calculate the molar solubility of magnesium hydroxide solution with a pH= 10.5. (K_{sp} =1.8×10^{-11})

Solution:

First, the concentration of H^+ ion in solution with pH = 10.5 is calculated. Then the hydroxide ion concentration in solution is found.

$$pH = -\log[H^+] = 10.5$$

$$[H^+] = 10^{-10.5} = 3.2 \times 10^{-11}\ mol/L$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{3.2 \times 10^{-11}} = 3.1 \times 10^{-4}\ mol/L$$

That means the concentration of hydroxide ion in solution is equal to 3.1×10^{-4} mol/L. After writing chemical equation showing dissolution of $Mg(OH)_2$, we find the value of s by using molar solubility of $Mg(OH)_2$ in the solution with pH 10.5.

$$\begin{array}{cccc} Mg(OH)_{2(s)} \rightleftharpoons & Mg^{2+}_{(aq)} & + & 2OH^-_{(aq)} \\ s\ M & s\ M & & 3.1 \times 10^{-4}\ M \end{array}$$

Then we insert the values above in the mathematical equation showing solubility constant as follows:

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$1.8 \times 10^{-11} = (s)(3.1 \times 10^{-4})^2$$

$$s = \frac{1.8 \times 10^{-11}}{(3.1 \times 10^{-4})^2} = 1.9 \times 10^{-4}\ mol/L$$

The molar solubility of $Mg(OH)_2$ in solution with pH = 10.5 is equal to 1.9×10^{-4} M.

Exercise 3-19

Calculate the solubility of zinc hydroxide in solutions;

A- pH=6,

B- pH=9.0, then discuss the results.

$K_{sp}(Zn(OH)_2) = 1.2\times10^{-17}$

Answer: A- 0.12 M,

B- 1.2×10^{-7} M

Solubility decreases.

QUESTIONS OF CHATER-3

3-1- In the following equation, equilibrium state is shown between molecules and ions of water:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

A- Does the equilibrium changes with temperature change?

B- What is the value of solubility constant of water at 25°C? What are the concentrations of hydrogen and hydroxide ions in pure water?

Answer: B- $K_w = 1 \times 10^{-14}$, $[H^+] = [OH^-] = 1\times 10^{-7}M$

3-2- Find the change in pH value of water after the addition of the following solutions to 1 liter of water.

1. 10 M HCl with 1 mL volume
2. 10 M NaOH with 1 mL volume

Answer: 1. ΔpH= -5 , 2. ΔpH= 5

3-3- Say if the following substances are acidic, basic, neutral and why?

A) NH_4Cl B) Na_2SO_4 C) CH_3COOK D) CaF_2 E) $MgSO_4$ F) KCl

3-4- How many grams of CH_3COOH (M=60g/mol) should be added to 250 mL of water in order to make value of pH of the solution 2.7? $K_a = 1.8 \times 10^{-5}$

Answer: 3 g

3-5- Circle the correct answer:

1- Find number of mg of barium Iodate,$BaIO_3$,dissolved in 150 mL of distilled water. ($K_{sp}=1.57\times10^{-9}$ and M=487g/mol)

A- 34.4 mg B- 44.4 mg C- 53.4 mg

2- What are the molar concentrations of Na^+ and SO_4^{2-} ions in aqueous solution of 0.4 M sodium sulfate?

A) $[Na^+]= 0.4M$, $[SO_4^{2-}]= 0.4M$

B) $[Na^+]= 0.2M$, $[SO_4^{2-}]= 0.4M$

C) $[Na^+]=0.8M$, $[SO_4^{2-}]= 0.4M$

3- Find the pH and pOH values of 0.05 M sodium hydroxide solution:

A) pH= 1.3, pOH= 12.7

B) pH= 7.0, pOH= 7.0

C) pH= 12.7, pOH= 1.3

4- Find the pOH value of 0.5 M aqueous solution of ammonium nitrate, NH_4NO_3: (pK_b= 4.74)

A- 7.00

B- 9.22

C- 4.78

3-6 - As K_a value of propanoic acid (C_2H_5COOH) is 1.3×10^{-5}, what is the percentage of decomposition of acid in 0.65 M aqueous solution?

Answer: 0.45%

3-7 - What is the concentration of ammonia [NH_3] in a solution in which [NH_4^+]=0.01 M and [OH^-]=1.2×10^{-5} M at equilibrium? $K_b = 1.8\times10^{-5}$

Answer: 6.67×10^{-3} M

3-8 -Calculate the mass of sodium acetate salt (M=82 g/mol) needed to be added into 1 liter 0.125 M acetic acid solution to obtain a buffer solution with a pH value of 4.74. pK_a= 4.74

Answer: 10.25 g

3-9 - Answer the following question.

A- What is the pH value of a buffer solution which is made up of 0.15 M sodium nitrite, $NaNO_2$, and 0.12 M nitrous acid, HNO_2? $K_a(HNO_2) = 4.5\times10^{-4}$.

B- Calculate the pH value of solution after 1.0 g of sodium hydroxide (M= 40 g/mol) added to 1 liter same buffer solution above.

Answer: A- 3.45, B- 3.62

3-10- What should be the $\frac{[NH_4^+]}{[NH_3]}$ ratio in order to prepare a buffer solution with pH= 9.0 by mixing NH_3 and NH_4Cl? pK_b=4.74

Answer: 1.82

3-11- What is the molar solubility of $BaSO_4$ in its aqueous saturated solution? What is its molar solubility after adding 1mL 10M H_2SO_4 to 1L of the same saturated solution? $K_{sp}(BaSO_4) = 1.6\times10^{-10}$, $\sqrt{1.6} = 1.26$

Answer: 1.6×10^{-8} mol/L, 1.26×10^{-5} mol/L

3-12- Calculate pH and [OH^-] values of the following salt solutions: $K_a(HCN) = 4.9\times10^{-10}$ and $K_b(NH_3) = 1.8\times10^{-5}$.

1- 0.1 M sodium cyanide NaCN

2- 0.25 M ammonium nitrate NH_4NO_3

3- 0.5 M sodium nitrate $NaNO_3$

3-13- If 0.01 M acetic acid ionizes in aqueous solution to 4.2%, calculate the acidity constant of it.

Answer: 1.76×10^{-5}

3-14- In order to make the pH value is 9.0 for 500 mL of 0.15 M of ammonia solution what should be the mass of ammonium chloride (M=53.5 g/mol)? $K_b(NH_3) = 1.8\times10^{-5}$

Answer: 7.22 g

3-15- Calculate the molar solubility (mol/L) and solubility (g/L) of silver sulfate, Ag_2SO_4, salt in the following solutions.

A- Distilled water,

B- 0.15 M potassium sulfate, K_2SO_4 (pK_{sp} =4.92 and M= 314 g/mol)

Answer: A) 0.014 M ; 4.396 g/L B) 4.4×10^{-3} M; 1.38 g/L

3-16- As $K_{sp} = 1.1\times10^{-12}$, what is the number of grams of silver chromate, Ag_2CrO_4 (M=332 g/mol) dissolved in 100 mL distilled water?

Answer: 2.161×10^{-3} g

3-17- What is the molar solubility of barium chromate, $BaCrO_4$ in 0.1M barium chloride, $BaCl_2$ (strong electrolyte) solution? $K_{sp}(BaCrO_4)=1.2\times10^{-10}$

Answer: 1.2×10^{-9} M

3-18- What should be the mass of potassium hydroxide (M=56 g/mol) needed to be added into 200 mL of water to get a solution with a pH value of 11?

Answer: 0.0112 g

3-19- As percent ionization of 0.1 M hydrocyanic acid, HCN is 0.01%, what is the ionization constant of this acid?

Answer: 1×10^{-9}

3-20- As $K_{sp}(Zn(OH)_2) = 1.2\times10^{-17}$, calculate the solubility of zinc hydroxide (M = 99.4 g/mol) in g/L unit and molar solubility mol/L (molar concentrations of ions from decomposition of salt).

Answer: 1.43×10^{-6} M, 1.42×10^{-4} g/L

3-21- Calculate the pH value of solution obtained from diluting 1 mL 13.6 M hydrochloric acid in 1 liter of water.

Answer: 1.866

3-22- The concentration of calcium (M=40 g/mol) ion in blood plasma is 0.1 g/L. If the concentration of oxalate ion in blood plasma is 1×10^{-7} M, do you expect calcium oxalate CaC_2O_4 to precipitate?

$pK_{sp} = 8.64$

Answer: No precipitation occurs.

REDOX REACTIONS and ELECTROCHEMISTRY

CHAPTER-4

ACHIEVEMENTS

After completing this chapter, the student is expected to :

*Define oxidation number and learn to calculate oxidation number in compounds and chemical radicals.

*Know the meaning of reduction and oxidation, reducing agent and oxidizing agent; know how to balance chemical equations including these concepts.

*Know the meaning of the following terms:
pole, anode, cathode, electric current, Nerst equation, galvanic cell, electrolytic cell.

*Learn the standard cell structure of hydrogen; understand hydrogen standard cell voltage as a criterion to measure other standard cell voltages.

*Understand dissociation and electrolysis processes.

*Describe the structure of cells; write the equations for reactions occurring at poles of cells when they produce electric current.

* Find out the weight of elements freed by electrolysis at poles and the relationship between the amount of electric current passing the electrolytic cell.

*Describe the relationship between standard cell current and non-standard cell current, and the relationship between standard free energy change and equilibrium constant.

Chapter - 4

4-1 PREFACE

Electrochemistry is one of the branches of chemistry. It deals with the changes between chemical energy and electrical energy. During the pass of electric current, some chemical changes occur and also some chemical reactions cause production of electric current. Electrochemical processes are reduction and oxidation reactions. During spontaneous reactions (reactions occur by itself, without an external force) energy is released. Then this energy is converted to electrical energy or non-spontaneous reactions can be realized using electrical energy.

Besides designing different types of cells, dyeing and electrolysis processes have been derived from electrochemistry. Electrochemical principles are present in every part of daily life. Cars, radios, music players, watches, electrical appliances use chemical reactions in order to supply their energy. The dyeing of utensils, electrical hardware and appliances; production of electric circuits, purification of metals and production of some elements are other examples for reactions that use electrical energy.

4-2 OXIDATION NUMBER

Reduction and oxidation numbers are used to define redox reactions. These numbers are written over the symbols of the elements which take place in reactions. These are called oxidation numbers or oxidation steps. The oxidation number of each atom in a compound represents the electrical charge (number of electrons) that this atom gains or loses. The rules for calculation of oxidation numbers are given below:

1- The oxidation number of free elements is equal to zero.

$Na, Be, K, Pb, H_2, O_2, P_4 = 0$

2- The oxidation number of a monoatomic ion is equal to the charge on this ion.

$Li^+, Li = +1, Fe^{3+}, Fe = +3, O^{2-}, O = -2$

3- The oxidation number of hydrogen is equal to (+1), except the oxidation number of hydrides is (-1).

The oxidation number of hydrogen in H_2O is (+1).

The oxidation number of hydrogen in sodium hydride NaH is (-1).

4- The oxidation number of oxygen is (-2). except the oxidation number of oxygen in peroxides is (-1).

The oxidation number of oxygen in H_2O is (-2). The oxidation number of oxygen in hydrogen peroxide H_2O_2 is (-1).

5- A-The oxidation number of Group IA element in a compound is +1.

Li, Na, K, Rb = +1

B- The oxidation number of Group IIA element in a compound is +2.

Be, Mg, Ca, Sr = +2

C- The oxidation number of Group IIIA element in a compound is +3.

B, Al, Ga, In = +3

6- The oxidation number of halogens Group VIIA element in a compound is -1.

F, Cl, Br, I = -1

For the atoms which are not mentioned above, the following rules can be used:

Rule 1: The sum of the oxidation numbers of all of the atoms in a neutral compound is 0.

Na = +1 and Cl = -1 in NaCl

According to this rule, (+1) + (-1) = 0

Rule 2: The sum of the oxidation numbers in a polyatomic ion is equal to the charge of the ion.

In $H_2PO_4^-$ compound O = -2 and P = P and H= +1

According to the rule; $\{2\times(+1)\}+(P)+\{4\times(-2)\}= -1$

Here we find that the oxidation number of phosphorus is P=+5. Atoms which have more than one oxidation numbers show different colors for different oxidation numbers (Figure 4-1). Table 4-1 shows the oxidation numbers of elements.

Figure 4-1
The color of solutions which have different chromium salts are different depending on the oxidation number of the chromium.

Example 4-1

Find out the oxidation numbers of atoms in the following compounds, ions and elements.

SO_2, KCl , Mg^{2+} , PO_4^{3-} , BaO , F_2

Solution:

F_2 : F=0 (According to Rule 1)

BaO: We can find out the oxidation number. of Ba according to Rule 1. O = -2, thus (Ba) + (-2) = 0 so Ba = +2

PO_4^{3-} :We can find out the oxidation number of (P) according to Rule 2. O = -2
(P) + $\{4\times(-2)\}$ = -3 thus P = +5.

Mg^{2+} : Mg = +2 (According to Rule 2)

KCl : Cl = - 1 and K = +1 (According to Rule 2)

SO_2 : We can find out the oxidation number of S according to Rule1.
O = -2, (S) + $\{2\times(-2)\}$ = 0 thus S = +4.

Exercise 4-1

Find the oxidation number which are in red following ion and compounds.

MnO_4^-, $K_2Cr_2O_7$, $NaIO_3$,H_2SO_4, H_2CO_3, HPO_4^{2-}

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** +1 −1																	2 **He**
3 **Li** +1	4 **Be** +2											5 **B** +3	6 **C** +4 +2 −4	7 **N** +5 +4 +3 +2 +1 −3	8 **O** +2 −1/2 −1 −2	9 **F** −1	10 **Ne**
11 **Na** +1	12 **Mg** +2											13 **Al** +3	14 **Si** +4 −4	15 **P** +5 +3 −3	16 **S** +6 +4 +2 −2	17 **Cl** +7 +6 +5 +4 +3 +1 −1	18 **Ar**
19 **K** +1	20 **Ca** +2	21 **Sc** +3	22 **Ti** +4 +3 +2	23 **V** +5 +4 +3 +2	24 **Cr** +6 +5 +4 +3 +2	25 **Mn** +7 +6 +4 +3 +2	26 **Fe** +3 +2	27 **Co** +3 +2	28 **Ni** +2	29 **Cu** +2 +1	30 **Zn** +2	31 **Ga** +3	32 **Ge** +4 −4	33 **As** +5 +3 −3	34 **Se** +6 +4 −2	35 **Br** +5 +3 +1 −1	36 **Kr** +4 +2
37 **Rb** +1	38 **Sr** +2	39 **Y** +3	40 **Zr** +4	41 **Nb** +5 +4	42 **Mo** +6 +4 +3	43 **Tc** +7 +6 +4	44 **Ru** +8 +6 +4 +3	45 **Rh** +4 +3 +2	46 **Pd** +4 +2	47 **Ag** +1	48 **Cd** +2	49 **In** +3	50 **Sn** +4 +2	51 **Sb** +5 +3 −3	52 **Te** +6 +4 −2	53 **I** +7 +5 +1 −1	54 **Xe** +6 +4 +2
55 **Cs** +1	56 **Ba** +2	57 **La** +3	72 **Hf** +4	73 **Ta** +5	74 **W** +6 +4	75 **Re** +7 +6 +4	76 **Os** +8 +4	77 **Ir** +4 +3	78 **Pt** +4 +2	79 **Au** +3 +1	80 **Hg** +2 +1	81 **Tl** +3 +1	82 **Pb** +4 +2	83 **Bi** +5 +3	84 **Po** +2	85 **At** −1	86 **Rn**

Table 4-1 The oxidation numbers of elements in periodic table.

4-3 REDUCTION AND OXIDATION (REDOX) REACTIONS

Reduction and oxidation reactions are one of the most important types of reactions. The energy released from combustibles, electric current from batteries and oxidation of iron are examples for these reactions (Figure 4-2).

Redox reactions occur via transfer of electrons. The first definition of redox reactions was made as "loss or gain of oxygen". This definition is correct but incomplete as it is true for only a number of compounds. Today redox reactions are defined as follows:

Oxidation:

It is the chemical change following loss of electrons of an atom. As a result of this, an increase occurs in oxidation numbers. Below, the exothermic reaction of Na and Cl ions in which crystal latticed solid forms is given.

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

The formation of sodium ions is a result of oxidation process. Because each sodium atom loses an electron in order to become sodium ion. Oxidation state is shown by writing oxidation number on the atom or ion.

$$Na^0 \rightarrow Na^+ + e^-$$

By this equation, we see that the oxidation number of sodium in free state has changed from 0 to (+1). In other words, sodium atom was oxidized to sodium ion and its oxidation number has increased by (+1).

Reduction:

It's a chemical change. An atom or group of atoms gain/s electrons. At the end of reaction, the oxidation number of the element decreases. According to this, in the reaction above, during interaction of sodium and chloride each chlorine atom gains an electron and the oxidation number decreases to (-1). The process is accepted as a reduction reaction.

$$Cl_2^0 + 2e^- \rightarrow 2Cl^-$$

Reduction occurs in the reaction in which oxidation number is reduced. Chlorine atom whose oxidation number decreases from 0 to -1 is reduced to chloride ion. In a reaction, reduction does not realize without oxidation. Because along with a reduced atom there must be an oxidized one. The number of electrons which are gained during reduction is equal to the number of electrons lost during oxidation. As shown in the equation below, the general equation of redox reaction is obtained from sum of reduction and oxidation reaction equations. As the number of lost and gained electrons must be equal, electrons are not shown in the total equation. This reaction is called as oxidation-reduction (redox) reaction. During this reaction electrons are transferred from one atom to another. According to this, the atom that loses electron is a reducing agent, the atom that gains electron is an oxidizing agent. Therefore, in this reaction, sodium atom is the reducing agent, whereas chlorine atom is the oxidizing agent.

$$2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^-$$

If we sum up what is told above, knowing oxidation numbers allows us to know if a reaction is a redox reaction. Let us take a look at the reaction between phosphorus pentachloride and water:

$$P^{5+}Cl_5^- + 4H_2^+O^{2-} \rightarrow H_3^+P^{5+}O_4^{2-} + 5H^+Cl^-$$

As there is no change occurs in the oxidation numbers of elements, this reaction cannot be called as a redox reaction. But in the following reaction of copper and nitric acid, we can make some comments:

$$Cu^0 + 4H^+N^{5+}O_3^{2-} \rightarrow Cu^{2+}(N^{5+}O_3^{2-})_2 + 2N^{4+}O_2^{2-} + 2H_2^+O^{2-}$$

From the change in oxidation numbers of copper and nitrogen, we can easily say that this is a redox reaction. The oxidation number of copper atom has changed from 0 to +2. Therefore it has been oxidized by losing 2 electrons. Meanwhile, the oxidation number of nitrogen atom has been changed from (+5) to (+4). That means it has been reduced by gaining 1 electron. Carbon and sulfur react in order to yield carbon sulfide. In this reaction, as seen at the side, carbon is oxidized and sulfur is reduced.

In redox equations, we can explain the loss or gain of electrons by dividing it in

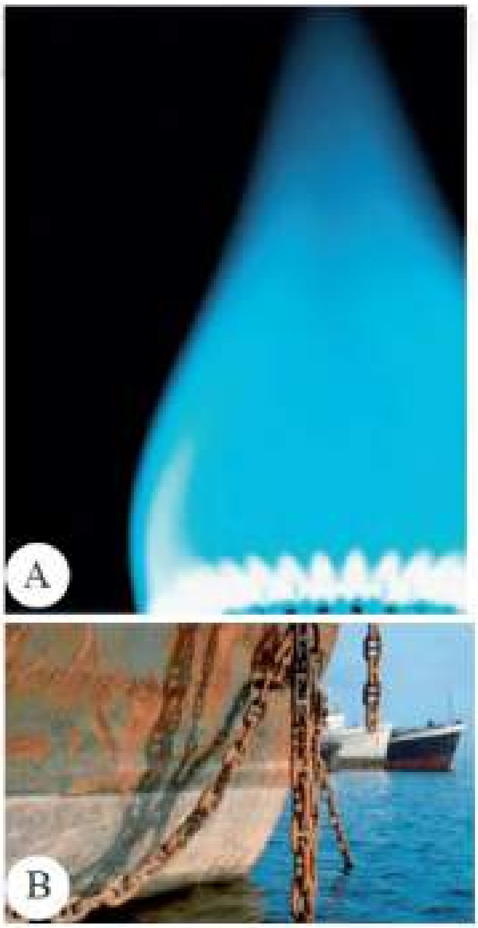


Figure 4-2

A) Combustion reaction of methane gas is a redox – reduction reaction

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} + \text{Energy}$$

B) Oxidation reaction of iron (rusting of iron) is an oxidation-reduction reaction.

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + \text{Energy}$$

two parts: The half of the reaction is oxidation and the other half is reduction. Therefore, we can divide the reaction of sodium and chlorine into two:

$$2Na^0 + Cl_2^0 \rightarrow 2Na^+ + 2Cl^-$$

$Na^0 \rightarrow Na^+ + e^-$ (oxidation) half reaction.

$Cl_2^0 + 2e^- \rightarrow 2Cl^-$ (reduction) half reaction.

When two halves of the reaction is added up, firstly the number of electrons lost need to be equal to the number of electrons gained. According to this, in order to obtain the following equations, the half oxidation reaction is multiplied by 2:

$2Na^0 \rightarrow 2Na^+ + 2e^-$

$Cl_2^0 + 2e^- \rightarrow 2Cl^-$

After eliminating equal numbers of electrons on both sides, by adding two equations, we get the general reaction below:

$$2Na^0 + Cl_2^0 \rightarrow 2Na^+ + 2Cl^-$$

The oxidation number of sodium has increased from 0 to +1. Therefore, the process is called as oxidation. The oxidation number of chlorine has decreased from 0 to (-1). So the reaction is called as reduction. Thus, the total reaction is called as an oxidation-reduction reaction, shortly a redox reaction.

Example 4-2

In the following reactions, specify the reduced and oxidized atoms. Also write down the reduction and oxidation half reactions.

1) $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

2) $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$

Solution:

1) $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

$2I^- \rightarrow I_2^0 + 2e^-$ (oxidation) half reaction.

$Cl_2^0 + 2e^- \rightarrow 2Cl^-$ (reduction) half reaction.

When both sides of the reaction are added up, the number of lost and gained electrons must be equal. We can only write down the general reaction (total reaction) when number of electrons are equal.

$$Cl_2^0 + 2I^- \rightarrow 2Cl^- + I_2^0$$

The oxidation number of iodine has increased from (-1) to 0. Therefore this is called oxidation. The oxidation number of chlorine has decreased from 0 to (-1). This is called reduction. Thus, this reaction is a redox reaction.

2) $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$

$Mg^0 \rightarrow Mg^{2+} + 2e^-$ (oxidation) half reaction.

$Fe^{2+} + 2e^- \rightarrow Fe^0$ (reduction) half reaction.

Firstly we need to make sure the number of electrons lost and gained must be equal when they are summed up, we get the general reaction:

$Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$

The oxidation number of magnesium has increased from 0 to (+2). This process is called oxidation. As the oxidation number of iron has decreased from (+2) to 0, this is a reduction. Therefore this reaction is a reduction reaction.

Exercise 4-2

In the following reactions, specify the reduced and oxidized atoms. Also write down the reduction and oxidation half reactions.

1) $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

2) $Mg + 2HCl \rightarrow MgCl_2 + H_2$

4-4 REDUCING AND OXIDIZING AGENTS

4-4-1 Reducing Agent

A reducing agent is a substance which can reduce another substance. It loses electron/s and its oxidation number increases. Therefore the reducing agent is oxidized. For example, in the reaction of copper element with concentrated nitric acid:

$$Cu^0 + 4HN^{5+}O_3 \rightarrow Cu^{2+}(NO_3)_2 + 2N^{4+}O_2 + 2H_2O$$

Copper is the reducing agent as it has been oxidized by losing 2 electrons. The oxidation number increases by from 0 to +2.

4-2-2 Oxidizing Agent

An oxidizing agent is a substance which can oxidize another substance. An oxidizing agent gains electron/s. During redox reactions, their oxidation numbers decrease. Therefore the oxidizing agent is reduced. In the example above, nitric acid is the oxidizing agent. Because the oxidation number of nitrogen in the acid is reduced to 4 from 5 in nitrogen dioxide by gaining an electron. In the same manner, the substance in a reduction reaction is the oxidizing agent.

The Oxidizing Agent	The Reducing Agent
A substance which takes place in reduction reaction and causes another substance to oxidize.	A substance which takes place in oxidation reaction but causes another substance to reduce.

Example 4-3

Specify the oxidizing and reducing agents in the following reactions:

1) $Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$

2) $Cu_{(s)} + 2AgNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2Ag_{(s)}$

Exercise 4-3

Specify the oxidizing and reducing agents in the following reactions:

1) $2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$
2) $Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$
3) $Mg_{(s)} + Fe^{2+}{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + Fe_{(s)}$

Solution:

1) $Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$
$Zn \rightarrow Zn^{2+} + 2e^-$ Zn: It has undergone oxidation so it's reducing agent.
$Cu^{2+} + 2e^- \rightarrow Cu$ Cu: It has undergone reduction so it's oxidizing agent.
2) $Cu_{(s)} + 2AgNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2Ag_{(s)}$
$Cu \rightarrow Cu^{2+} + 2e^-$ Cu^{2+}: It has undergone oxidation so it's reducing agent.
$Ag^+ + e^- \rightarrow Ag$ Ag^+: It has undergone reduction so it's oxidizing agent.

4-5 ELECTROCHEMICAL CELLS

When we study redox reactions, we see that some of those occur spontaneously. For example, in the reaction of a piece of solid magnesium and dilute hydrochloric acid, a salt forms and hydrogen gas evolves.

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

However, some redox reactions do not occur spontaneously. For example, water dissociates to its components, hydrogen and oxygen, only when energy given from outside. Therefore, what is the relationship between electrical energy and reactions that occur spontaneously or non-spontaneously? And what is the relationship between these reactions and electrochemical cells? Electrochemical cells are made up of two poles: One is positive pole or anode. This pole is the source of electrons that undergo oxidation. The second pole is the negative one which is called cathode. This pole is the place that reduction occurs and electrons are transferred from positive pole via outer circuit. Both poles are inside electrical solution. The components of solution take place in the reduction and oxidation reactions occur at the surfaces of poles.

Electrochemical cells are divided into two: Galvanic or voltic cells and electrolytic cells such as electrolysis cells (Electroplating cell).

4-6 GALVANIC CELLS

These are cells where chemical energy is transformed into electrical energy during spontaneous chemical reaction. This kind of cells is called galvanic or voltaic cells. These names are taken from two Italian scientists. One is (Luigi Galvani) and the other is (Alessandro Volta).These two scientists were the first people who designed these cells. Batteries are one of the types of galvanic cells. Let's study the following example before we go into what is going on inside galvanic cells. When a zinc rod is dipped into copper sulfate solution, it starts to corrode and disappear. The concentration of zinc ions increases. That means a spontaneous reaction occurs. At the same time, brownish copper element starts plating zinc rod as a spongy layer. Some of the copper settles at the bottom. The blue color of the solution starts to disappear due to the decrease in the concentration of copper ions and finally it becomes colorless (Fig. 4-3)as in the following reaction.

$$Zn_{(s)} + Cu^{2+}SO_4^{2-}{}_{(aq)} \rightarrow Zn^{2+}SO_4^{2-}{}_{(aq)} + Cu_{(s)}$$

As it seems SO_4^{-2} ions hasn't changed at all during oxidation (in other words they haven't joined the reaction) Therefore we can simply rewrite the reaction above as follows: $Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$

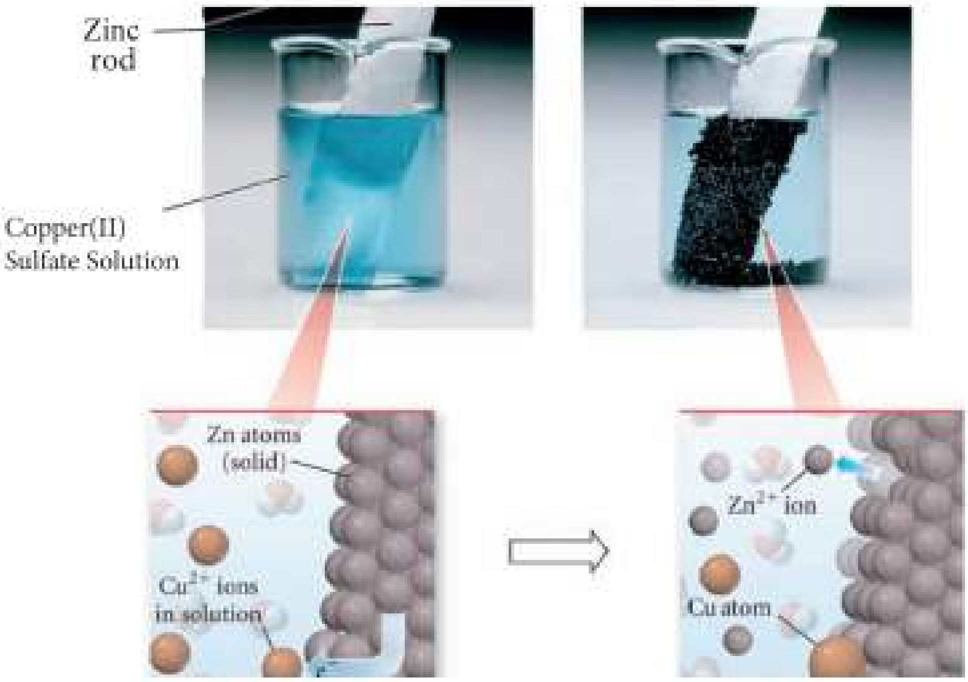


Figure 4-3
The reaction that occurs when zinc dipped into copper sulfate solution.

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

The most famous and simplest Galvanic cells are Daniell cells (Figure 4-4). A zinc rod is immersed into zinc sulfate $ZnSO_4$ solution. The cell depends on Zn, Zn^{+2} oxidation and Cu^{+2} - Cu reduction. This event occurs in two different containers. Electrons are displaced between two poles through an external wire. Zinc and copper rods are called electrodes. The poles of cell are the immersed or the contacting pole with ions in its solution. The battery cell formed with copper and zinc rods dipped into $ZnSO_4$ and $CuSO_4$ solutions is called the (Daniell) cell. According to the definition above, positive pole (zinc rod) is called as anode. This pole is the place where oxidation occurs.(the source of electrons) Negative pole is called as cathode.

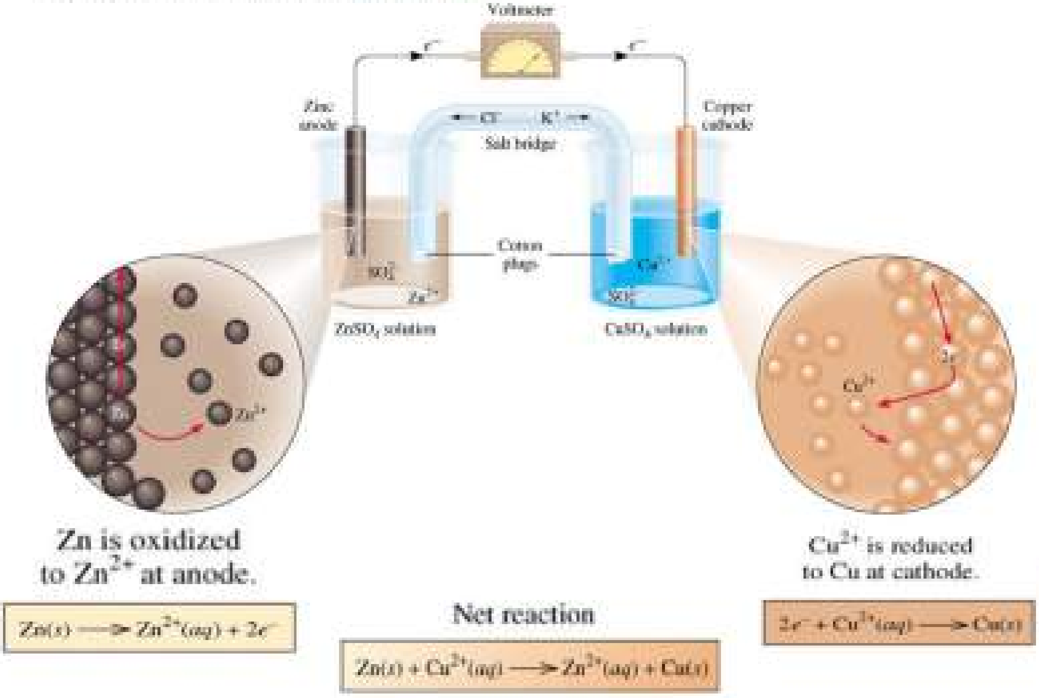


Figure 4-4
Daniell Galvanic Cell

At this pole reduction occurs. During this process, electrons are observed to be transferred through external wire from anode to cathode (copper rod). These electrons cause copper atoms accumulate over negative pole's surface by reacting with copper ions Cu^{+2} in solution. The reduction and oxidation reactions occurring in the Daniell cell are called half cell reactions at poles. These are:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ Half cell reaction / Zn pole (anode) oxidation

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ Half cell reaction / Cu pole (cathode) reduction

We see that each zinc atoms have lost 2 electrons (undergone oxidation) to yield Zn^{+2} ion whereas each Cu^{+2} ions have gained 2 electrons (undergone reduction) to yield Cu atom. The general reaction of the cell is obtained by adding both half reactions after making equal the number of gained and lost electrons. (Here we see that the numbers of gained and lost electrons are equal.)

General reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

The most important point here that needs attention is if copper sulfate and zinc sulfate solutions were not in different containers, Cu^{2+} ions would react with zinc rod directly, as mentioned above. In this case, there would be no electricity produced. In order to complete the electric circuit, a conducting medium that allows negative and positive ions to be transferred from one pole to the other is required. This conducting medium is called as salt bridge. The bridge is formed from a turned down U-shaped glass tube. Inside the tube there is an inert solution which does not change chemically during the process. The solution contains ager substance. (Ager is a natural, sticky substance. It has different uses. When heated it liquefies, it solidifies at room temperature.) The compounds which are used while filling the salt bridge are K_2SO_4, KNO_3, KCl. A cell reaction starts spontaneously and continues until zinc rod or the concentration of copper ions is used up completely. As a result of zinc atoms change into Zn^{2+} ions, electrons are transferred from positive zinc pole (zinc atoms) to copper pole through external wire. Here ions undergo reduction. The SO_4^{2-} sulfate ions remaining in the solution pass to the zinc sulfate solution through salt bridge (because of increase in the number of positive charges in solution) Potassium K^+ ions pass to copper sulfate through salt bridge (in simple terms, negative ions pass to positive pole anode. Positive ions pass to negative pole cathode.) Conduct of electricity occurs by transfer of electrons at external circuit (wire). It occurs at inner circuit (salt bridge) through transfer of ions.

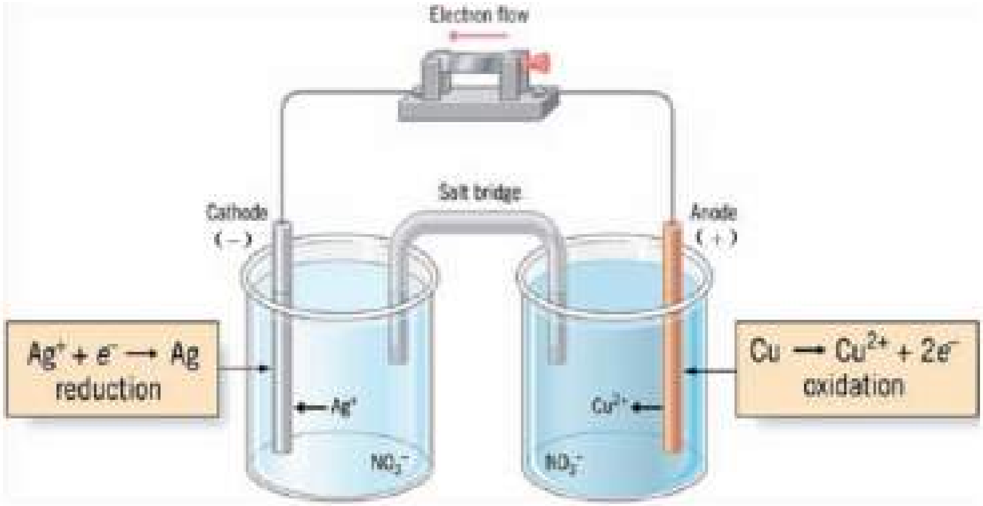
Example 4-4

As the following reaction occurs spontaneously at the given galvanic cell,

$$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

A- Write down both half cell reactions.

B- Explain the direction of electrons flow along outer wire and direction of ion movement through salt bridge which is full of KNO_3 solution.



Solution:

A)

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ Half cell reaction / Cu pole (anode) oxidation

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$ Half cell reaction / Ag pole (cathode) reduction

B) Electrons flow from anode (copper rod) towards cathode (silver rod) via outer wire. Positive ions K^+ move towards negative pole "cathode" while negative ions NO_3^- move towards positive pole "anode" through salt bridge.

4-7 POTENTIAL OF GALVANIC CELL

Electric current flows from anode to cathode due to the potential difference between poles. This flow of electric current is similar to fall of water at a waterfall because of its potential or similar to flow of gas from high-pressure region to low-pressure region. This potential occurs between electrodes and the ions of solution. It is divided into two:

1-Oxidation Potential: The tendency of matter losing its electrons

2-Reduction Potential: The tendency of matter gaining electrons

The potential between two poles of galvanic cell is called as cell potential and shown with E. Cell potential is also called as electromotive force and shown with emf. Contrary to the meaning of the term, here potential is named instead of force. The cell potential is measured by a voltmeter (Fig. 4-5). As we will study later, cell potential depends not only on the properties of electrodes or ions but also on concentrations of ions and temperature at which cell works.

Figure 4-5
A voltmeter is used measure cell potential or electromotive force.

Cell potential is defined as the electrical potential difference between electrodes in a galvanic cell. Cell potential is shown with E_{cell} symbol. Therefore, cell potential is a measurement of motive force of the reaction which occurs in a cell. Cell potential depends on the potential of poles at which oxidation (anode) and reduction (cathode) occurs. If we show oxidation potential with E_{ox} and reduction potential with E_{red}, cell potential is the sum of oxidation and reduction potentials of the cell.

1) $\mathbf{E_{cell} = E_{ox} + E_{red}}$

As oxidation occurs at anode, we can use E_{anode} symbol instead of E_{ox}. Similarly, reduction occurs at cathode, so for reduction potential we can use $E_{cathode}$ instead of E_{red}. Therefore, we can rewrite equation 1 above as follows:

2) $\mathbf{E_{cell} = E_{anode} + E_{cathode}}$

Under standard conditions, 25°C and 1 atm pressure, when cell potential is measured for the concentrations of solution at two poles are the same (1 M or 1 mol/L), this measured value is called as standard cell potential. It is shown with E°_{cell}. Under same conditions, the potentials measured at electrodes are called standard electrode potential and shown with $E^{\circ}_{cathode}$ and E°_{anode} symbols. Thus, equation 2 can be rewritten under standard conditions.

3) $\mathbf{E^{\circ}_{cell} = E^{\circ}_{anode} + E^{\circ}_{cathode}}$

Electrical potential unit is volt and its symbol is (V).

4-7-1 Measurement of Cell Potential

As we studied above, in order to measure standard cell potential (E°_{cell}), anode and cathode potentials need to be measured under standard conditions.

The question is how the potential of a single electrode can be measured as a cell cannot be set up with a single electrode and its potential cannot be measured. Therefore, a reference electrode is necessary. A (reference electrode) is used to measure other electrode potentials. There are different types of electrodes used as reference. The most important of those is standard hydrogen electrode.

4-7-2 Standard Hydrogen Electrodes

Standard hydrogen electrode is chosen as a reference electrode (with a known standard potential). Hydrogen electrode is chosen from other elements with respect to its chemical medium activity. Therefore, it can be used as anode or catho pole. Standard hydrogen electrode is made up of a glass tube. Into 1M solution (as HCl) containing H^+ ions, hydrogen gas is pumped under 1 atm pressure and 25°C. At the bottom of the glass tube, a piece of platinum is placed. That piece of platinum is attached to a platinum wire. The reason why platinum is used with this kind of electrodes is that it never oxidizes or reduces under any conditions. But platinum performs two duties:

A- It supplies a surface on which hydrogen molecules can dissociate.

B- It supplies a method to conduct electricity through outer circuit.

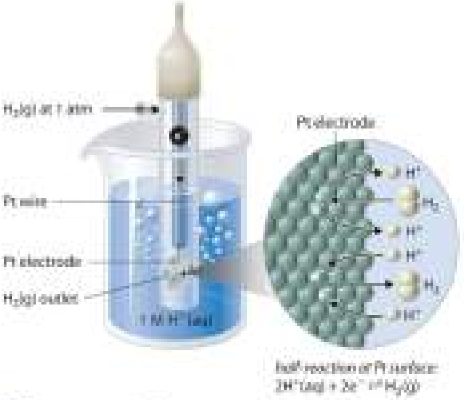


Figure 4-6
Standard hydrogen electrode

Figure 4-6 shows a standard hydrogen electrode. It is shown with (SHE) symbol. According to IUPAC, the potential of standard hydrogen electrode is accepted as ($E^{\circ}_{H_2} = 0.0$ V). If standard hydrogen electrode is used as anode (oxidation), the reaction which occurs on it is as follows:

$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$ $\qquad E^{\circ}_{anode} = 0.0$ V

But if it is used as cathode, the reaction is as follows:

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ $\qquad E^{\circ}_{cathode} = 0.0$ V

4-7-3 The Potentials of Standard Electrodes

We can use standard hydrogen electrode to measure standard potentials of other electrodes. When this electrode is connected with any other electrode to set up a cell, the standard cell potential is equal to the sum of element's standard electrode potential and standard hydrogen electrode potential. As (SHE) potential is equal to zero that means element's standard electrode potential is equal to cell potential. Over this fundamental, standard oxidation potentials of elements were measured. These potentials were put in a chart named as Standard Reduction Potentials Chart. Table 4-2 shows reduction half reactions and standard reduction potentials of different electrodes.

$$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$$

It is observed that E°_{cell} value of this cell is +0.763 V. As (SHE) potential is equal to zero, then:

$$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$$

$$0.763\ V = E^\circ_{anode} + 0.0\ V$$

$$E^\circ_{anode} = +\ 0.763\ V$$

That means standard oxidation potential of zinc is equal to +0.763 V. Therefore, standard reduction potential of this electrode is equal to -0.763 V. In other words, standard cell potential is equal to standard potential of zinc electrode. Because the other electrode is (SHE).
Standard Oxidation Potentials Table of elements is used to compare potentials when elements are used as oxidizing and reducing agents. Because reduction potential values are accepted practically as a measurement of reduction and oxidation capabilities. We need to learn following important points about the table to use it in calculations.

1- Standard Potential Values of electrodes in table 4-2 show their standard reduction potentials.

2- Standard reduction potentials reduce as we scroll down the table. This means their oxidation properties increase. In other words, their strength as reducing agents increase. At the top, fluorine element is placed with the highest reduction potential that is +2.87 V

$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$ $E^\circ_{cathode} = +2.87\ V$

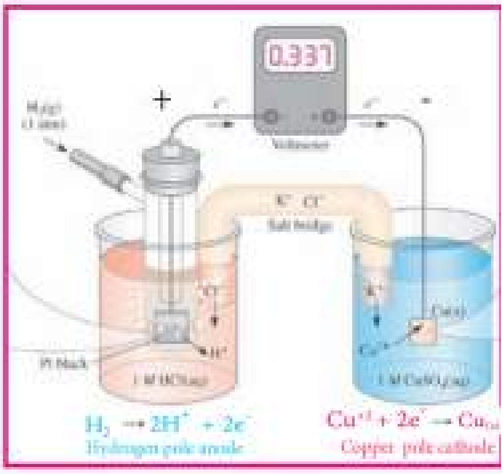
For Lithium element -3.04 \ Reduction potential decreases downwards the table

$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$ $E^\circ_{cathode} = -3.04\ V$

Therefore, as lithium is the hardest reduced substance, Li^+ is accepted as the weakest oxidizing agent.
Contrary to this, as fluorine is the least oxidized substance, it is the weakest reducing agent.

Exercise 4-4

The cell consists of anode which is hydrogen pole and cathode which is copper pole. Calculate the standard reduction potential of copper pole.
Standard cell potential= +0.337 V



Answer: +0.337V

Table 4-2 Standard Reduction Potentials of elements in (V) volt unit measured at 1M concentration at 25 °C

Potentials increase in oxidizing agents

Potential of reducing agents increase

$F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}$	+2.87
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \longrightarrow 2H_2O$	+1.77
$Au^{3+}_{(aq)} + 3e^- \longrightarrow Au_{(s)}$	+1.50
$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$	+ 1.36
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O$	+ 1.23
$Br_{2(l)} + 2e^- \longrightarrow 2Br^-_{(aq)}$	+ 1.07
$2Hg^{2+}_{(aq)} + 2e^- \longrightarrow Hg^{2+}_{2(aq)}$	+ 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
$I_{2(s)} + 2e^- \longrightarrow 2I^-_{(aq)}$	+0.53
$O_{2(g)} + 2H_2O + 4e^- \longrightarrow 4OH^-_{(aq)}$	+ 0.40
$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$	+ 0.34
$Sn^{4+}_{(aq)} + 2e^- \longrightarrow Sn^{2+}_{(aq)}$	+ 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
$Cd^{2+}_{(aq)} + 2e^- \longrightarrow Cd_{(s)}$	- 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
$Ba^{2+}_{(aq)} + 2e^- \longrightarrow Ba_{(s)}$	- 2.90
$K^+_{(aq)} + e^- \longrightarrow K_{(s)}$	- 2.93
$Li^+_{(aq)} + e^- \longrightarrow Li_{(s)}$	- 3.05

3-The standard cell potential of any cell of which one of its poles is standard hydrogen electrode, equals to element's standard electrode potential as in the example above.

4-The potential of an oxidation reduction (loss of electron) is the oppiste of the potential for a reduction potential (gain of electron). For example, the potential of reduction half reaction of lithium electrode is -3.04 V. Therefore, potential of oxidation half reaction of this electrode is +3.04V.

$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$ $\qquad E^\circ_{cathode} = -3.04\ V$

$Li_{(s)} \rightarrow Li^+_{(aq)} + e^-$ $\qquad E^\circ_{anode} = +3.04\ V$

4-7-4 Measurment of Standard Cell Potential

The following points must be considered while calculating standard cell potential:

Attention:

The means standard cell potential describes the differ between reduction potentials of both electrodes

1- The element which has the lowest standard reduction potential is chosen as anode pole. Similarly, the element with the highest reduction potential is chosen as cathode pole.

2- The number of electrons lost at anode (oxidation) must be equal to the number of electrons gained at cathode (reduction). When they are not equal, they need to be made equal by taking least common multiple of number of electrons. Then by eliminating electrons from both sides of half reactions, general cell reaction is written.

Attention:
Characteristic property does not depend on amount of substance.

3- If the number of electrons lost in reduction is not equal to the number of electrons gained in oxidation; both sides of equations are multiplied with a certain number. But standard electrode potentials remain unchanged. Because potential is a characteristic property which does not depend on the amount of substance. Potential depends only on the concentrations of ions in electrode solutions. For example:

$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$ $\qquad E^\circ_{I_2/I^-} = 0.53\ V$

$2I_{2(s)} + 4e^- \rightarrow 4I^-_{(aq)}$ $\qquad E^\circ_{I_2/I^-} = 0.53\ V$

4- Both half cell reactions are reversible reactions. Each electrode can be used as anode or cathode depending on the conditions they are used.

5- In order to find out standard cell potential value E°_{cell}, both half-cell reactions at electrodes are written. At the end of the reactions, standard cell potential values are written. Then while calculating E°_{cell}, the following relationship is used.

$$\mathbf{E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}}$$

If standard reduction potentials are given directly taken from the table, they must be used as is;

$$\mathbf{E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}}$$

That means standard cell potential describes oxidation potentials of both electrodes.

6- If the value of standard cell potential is positive ($E°_{cell} = +$), the reactions at poles occur spontaneously. But if the value of $E°_{cell}$ is negative ($E°_{cell} = -$), the reactions at poles do not occur spontaneously and energy must be given externally.

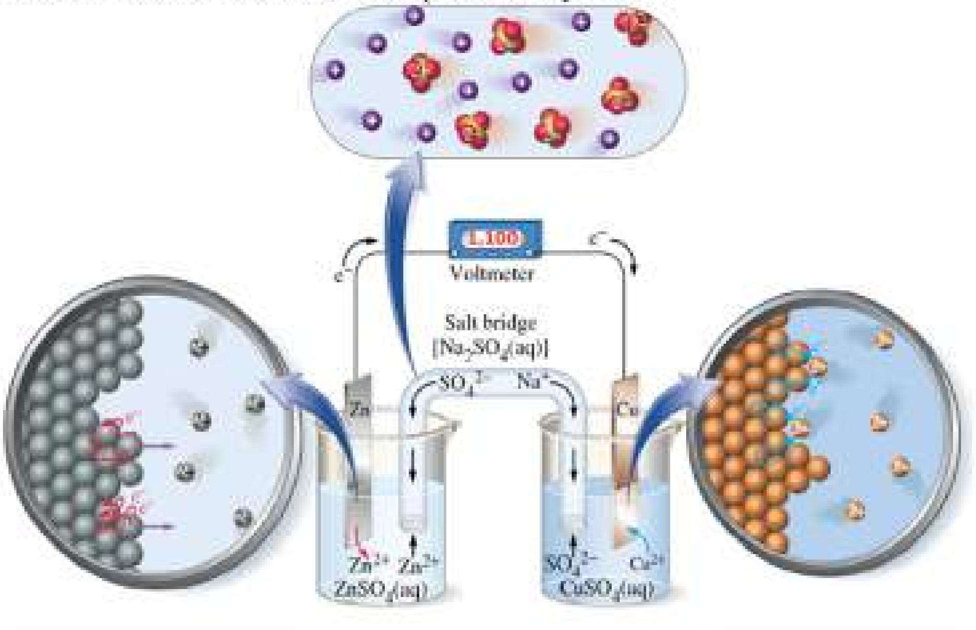
Example 4-5

Write down both Daniell cell half reactions and calculate standard cell potential. As standard reduction potentials $E°_{Cu^{2+}/Cu} = +0.34V$ and $E°_{Zn^{2+}/Zn} = -0.76$

Note: To show standard potential is a reduction potential $E°_{Cu^{2+}/Cu}$ symbol is used.

Solution

When we examine standard reduction potential values, we see that we need to choose copper pole as cathode because this pole has the highest standard reduction potential. We need to use zinc pole as anode because this electrode has the lowest standard reduction potential. (point 1)



$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $\qquad E°_{anode} = +0.76V$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $\qquad E°_{cathode} = +0.34V$

Here what needs attention is that when we use zinc as anode, we have to reverse the sign of standard reduction potential. (point 4) If the number of lost electrons is equal to the number of gained electrons, from the sum of two half cell reactions, we get the general cell reaction as follows:

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

$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$E^\circ_{cell} = (+0.76\ V) + (+0.34\ V) = 1.10\ V$

Note: To calculate standard Daniell cell potential, we can use the following relationship:

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

If we take the standard reduction potentials from the chart directly, If we take the standard reduction potentials from the chart directly,

$$E^\circ_{cell} = (+0.34\ V) - (-0.76\ V) = 1.10\ V$$

4-7-5 Types of Electrodes

Here we will mention types of electrodes widely used in setting up galvanic cells.

1- Metal Electrodes / Metal Ion

This kind of electrodes are obtained by dipping a metal rod into the solution containing the metal's ions. For example, zinc electrode which is dipped into zinc sulfate solution. The interaction of (Zn/Zn^{+2}) electrode as anode or cathode is as follows:

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ Reduction (cathode)

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ Oxidation (anode)

2- Gas Electrodes

They are set up by pumping gas into a glass tube filled with solution containing the ions of the gas under a certain pressure. As gas does not conduct electricity, this electrode will supply a conducting medium for electricity. Generally, platinum strip which does not have tendency to react is used inside the glass tube. For example, into the solution like HCl which has H^+ ions, hydrogen gas is pumped under 1 atm pressure. The anode reaction of hydrogen electrode over the piece of platinum is as follows:

$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$ Oxidation (anode)

In a different way, chlorine gas is pumped into a solution of NaCl or HCl which has chloride ions. The reaction of chlorine cathode reaction over the piece of platinum is as follows:

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

Exercise 4-5

Calculate the standard cell potential which consists of Cd pole dipped in 1M solution of Cadmium nitrate and Cr pole is dipped in 1M solution of chromium nitrate. If you know standard reduction potential;

$E^\circ_{Cd^{2+}/Cd} = -0.40\ V$

$E^\circ_{Cr^{3+}/Cr} = -0.74\ V$

Answer: +0.34 V

Exercise 4-6

Do the oxidation and reduction reactions expressed with equations below occur spontaneously?

Standard reduction potentials:

$E^\circ_{Co^{2+}/Co} = -0.28\ V$

$E^\circ_{Ni^{2+}/Ni} = -0.25\ V$

$E^\circ_{Fe^{2+}/Fe} = -0.44\ V$

$E^\circ_{Au^{3+}/Au} = +1.50\ V$

1) $Ni_{(s)} + Co^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Co_{(s)}$

2) $3Fe_{(s)} + 2Au^{3+}_{(aq)} \rightarrow 3Fe^{2+}_{(aq)} + 2Au_{(s)}$

Answer:

1- Ni-Co reaction does not occur spontaneously.

2- Fe-Au reaction occurs spontaneously.

3- Reduction and Oxidation Electrodes

They are set up by dipping a graphite rod or platinum strip into a solution containing ions of an element which has double oxidation state. For example, it is set up by dipping platinum strip into the solution containing Fe^{2+} and Fe^{3+} (or Sn^{4+} and Sn^{2+}) ions. When this electrode is used as anode, oxidation reactions can be written as follows:

$$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$$

4-7-6 The expression of the Galvanic cell in writing

Generally, in order to express a galvanic cell, notation method is used. Therefore, we need to symbolize the poles. Later, they will be used to express the cell. The electrode is written as element electrode/element ion. For example, let's consider zinc electrode which is dipped into zinc sulfate solution where reduction reaction occurs. It is expressed as follows:

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad \text{Reduction (Cathode)}$$

It is expressed as seen in half cell equation. Firstly, the symbol of metal ion is written. Next to it, in parentheses, its molar concentration is written then a vertical line is drawn and symbol of metal is written. It is as follows:

$$Zn^{2+}\,(1M)\,|\,Zn$$

or for oxidation reaction:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

For this situation, firstly the symbol of the metal is written. Then a vertical line is drawn and the symbol metal ion is written. Next to it, its molar concentration is written in parentheses. All these are as seen in half cell reaction.

$$Zn\,|\,Zn^{2+}\,(1M)$$

Vertical line shows the phase boundary. If attention is given, zinc is in solid phase and zinc ions in aqueous solution are in liquid phase. Therefore, in order to divide two phases, a vertical line is drawn. The concentration of the solution is written after the sign of the ion. Because 1M shows the standard concentration.

As an example for expressing gas electrodes by writing, we can give the notation of hydrogen electrode.

In the following oxidation reaction:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \qquad \text{Oxidation (anode)}$$

In order to express the electrode, as in the order in the equation, half cell components are placed. Firstly hydrogen gas and next to it the value of gas pressure is written (this is for gases only). Then the symbol of gas ion and next to it, its molar concentration is written.

$$Pt\,|\,H_2\,(1atm)\,|\,H^+\,(1M)$$

As gas cannot conduct electricity, to conduct it, platinum strip is used. If it is used as anode, it is written in the beginning of the notation, if it is used as cathode, it is written in the end. In the electrodes used in reduction and oxidation reactions, for the oxidation reaction, the notation of the electrode containing Fe^{+2}, Fe^{+3} ions will be as follows:

$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ Oxidation reaction (anode)

$Pt \mid Fe^{2+}\ (1M)\ ;\ Fe^{3+}\ (1M)$

In this kind of reactions, as they do not conduct electricity just like gases, platinum strip needs to be immerse into the solution. While the electrode is expressed by writing, the symbol of platinum, Pt is written just as the gas electrode is expressed. As both ions are found in the same solution, a semicolon (;) is put between symbols of two ions.

As we have learnt expressing electrodes by notation, we can easily express a cell. For this, we join anode (oxidation) and cathode (reduction) poles. To express by notation, on the left hand side, the reaction in anode is written. The reaction in cathode is written on the right hand side. Between those two parallel vertical lines are drawn to express salt bridge in the cell.

As an example, we express the Daniell cell with general reaction given:

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

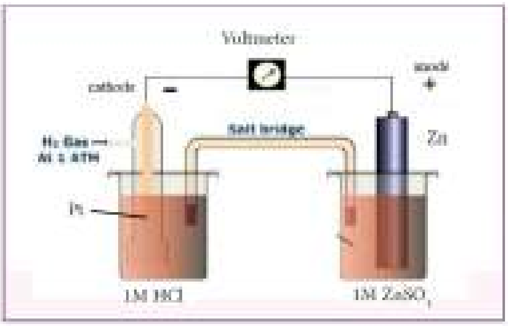
We can express the cell as follows:

$Zn \mid Zn^{2+}\ (1M) \parallel Cu^{2+}\ (1M) \mid Cu$

Oxidation reaction in anode || Reduction reaction in cathode
(Two vertical lines between expresses the salt bridge.)

Example 4-6

Express the cell in the figure by notation. Then write down both half cell reactions.



Solution

The sum of two half cell reactions gives general reaction and it is as follows:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ Oxidation reaction (anode)

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ Reduction reaction (cathode)

The sum of two half cell reactions gives general reaction and it is as follows:

$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$

The notation of this cell is below:

$Zn \mid Zn^{2+}\ (1M) \parallel H^+\ (1M) \mid H_2\ (1atm) \mid Pt$

4-7-7 The Cell Potential E, Gibbs Free Energy (ΔG°) and Equilibrium Constant Keq

As we know, galvanic cells transform chemical energy into electrical energy. The electrical energy (joule unit) the cell produces is equal to the multiplication of cell potential E°_{cell} (volt unit) with total charge that passes through cell (C) (coulomb unit).

Attention:

Unit of coulomb (C) multiple unit of Volt (V) equals to Unit of Joule (J)

Exercise 4-7

The general reaction of a galvanic cell is as follows:

$Cl_{2(g)} + 2Ag_{(s)} \rightarrow 2Cl^-_{(aq)} + 2Ag^+_{(aq)}$

Express the cell by notation under standard conditions. Later, write down the oxidation and reduction reactions.

Exercise 4-8

Standard reduction potential of silver is $E°_{Ag^+/Ag} = +0.80$ V. Can HCl solution dissolve silver metal found in the following cell containing a solution with 1 M Ag^+ ion? (Note: Dissolution of metal in solution means that reaction occurs spontaneously.)

$Ag \mid Ag^+(1M) \mid H^+(1M) \mid H_2(1atm) \mid Pt$

Answer: HCl does not dissolve the metal.

Electrical Energy (J) = Cell potential(V) × Total Charge(C)

Therefore, joule unit is equal to the multiplication of Volt unit (V) with electrical charge unit (C).

1J = 1V × 1C

The total charge passing through the cell is equal to the multiplication of mole number of electrons (n) and charge of 1 mole of electron which called Faraday (and shown with F). In other words, the total charge passing through the cell is equal to (n×F). As known, 1 mole contains as many charges as Avogadro number (N_A). Therefore, Faraday (F) is equal to the multiplication of electron charge and Avogadro number.

F = electron charge (e^-) × Avogadro number (N_A)

$F = N_A (mol^{-1}) \times e^- (C)$

Value of Avagodros' number $(N_A) = 6.023\times10^{23}$

If we insert $e^- = 1.6\times10^{-19}$ (C) in the equation, we get the following:

$F = 6.023\times10^{23} (mol^{-1}) \times 1.6\times10^{-19}(C) = 96478$ C/mol.e^-

In chemical calculations, this value is taken as 96500 C/mol.e^-. Therefore, electrical energy is equal to:

Electric charge(J) = Total charge (nF) × Cell potential ($E°_{cell}$) = $nFE°_{cell}$

Electrical energy produced in Galvanic cells ($nFE°_{cell}$) is equal to reverse sign of free Gibbs energy ΔG°.

Therefore:

1) $\Delta G° = -nFE°_{cell}$

As known, when the free energy is negative, reaction occurs spontaneously. In the relationship (1) above, to have a negative free energy ΔG°, the sign of $E°_{cell}$ needs to be positive. According to this, as long as the sign of $E°_{cell}$ is positive, the reactions occurring at poles have a higher possibility of being spontaneous. Besides, if we examine relationship (1), we see that it does not include concentration and pressure units. Also the temperature values are also missing. Therefore, standard cell potential $E°_{cell}$ and standard Gibbs free energy ΔG° can be shown as follows:

2) $\Delta G° = -nFE°_{cell}$

Previously, in Chemical Equilibrium chapter, we have written the relationship between standard free energy ΔG° and equilibrium constant K_{eq}.

3) $\Delta G° = -RT\ln K_{eq}$

If we exchange the ΔG° in (3) with the one in (2):we get

4) $-RT\ln K_{eq} = -nFE°_{cell}$

If we re-arrange (4):

5) $$E°_{cell} = \frac{RT}{nF} \ln K_{eq}$$

At 25 °C (298K), If we insert temperature C, F and R values in Equation (5), we get the following equation:

F = 96500 C/mol.e$^-$, R = 8.314(J/K.mol)

$$E^\circ_{cell} = \frac{8.314\ (J/K.mol) \times 298\ (K)}{n \times 96500\ (C/mol.e^-)}\ \text{In}K_{eq}$$

$$\mathbf{E^\circ_{cell} = \frac{0.026\ (V)}{n}\ InK_{eq}}$$

(n) is the mole number of electron taken or given (in oxidation and reduction reactions) when we add both half cell reactions to get the general reaction. This equation is only used for a certain temperature (25 °C).

Table 4-3 explains the relationship among ΔG° standard free energy, E°_{cell} standard cell potential and equilibrium constant.

Example 4-7

The reaction equation of a galvanic cell is as follows:

$$2Ag^+_{(aq)} + Pb_{(s)} \rightarrow 2Ag_{(s)} + Pb^{2+}_{(aq)}$$

Calculate ΔG° and equilibrium constant (K_{eq}) values at 25°C.

Standard reduction potential : $E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Pb^{2+}/Pb} = -0.13$ V

Solution:

We write down anode (oxidation) and cathode (reduction) half cell reactions.

$Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2e^-$ $\qquad E^\circ_{Pb^{2+}/Pb} = +0.13$ V

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$ $\qquad E^\circ_{Ag^+/Ag} = +0.80$

When we add both half cell reactions, we get a general reaction equation as below:

$$2Ag^+_{(aq)} + Pb_{(s)} \rightarrow 2Ag_{(s)} + Pb^{2+}_{(aq)}$$

We can calculate standard cell potential E°_{cell}.

$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$E^\circ_{cell} = (+0.13\ V) + (+0.80\ V) = 0.93$ V

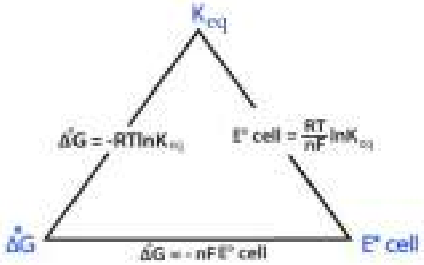
We can calculate ΔG° standard Gibb's free energy using the relationship between ΔG° and standard cell potential E°_{cell}.

$\Delta G^\circ = -nFE^\circ_{cell} \Rightarrow \Delta G^\circ = -2 \times 96500\ (C/mol.e^-) \times 0.93\ V$

$\Delta G^\circ = -179490$ J/mol

We use the formula below to calculate equilibrium constant K_{eq}:

$$E^\circ_{cell} = \frac{RT}{nF}\ InK_{eq}$$



Reaction under standard conditions	E°_{cell}	K_{eq}	ΔG°
Products are preferred	positive	$K_{eq}>1$	negative
Reactants and products equally preferred	null (zero)	$K_{eq}=1$	zero
Reactants are preferred	negative	$K_{eq}<1$	Pozitive

Table 4-3
the relationship among ΔG° standard free energy, E°_{cell} standard cell potential and equilibrium constant. K_{eq}

Attention:

This reaction occurs only at 25 °C (298 K) temperature.

Exercise 4-9

Calculate ΔG° standard Gibb's free energy in Standard Cell reaction at 25 °C.

$$3Hg_2^{2+}{}_{(aq)} + 2Cr_{(s)} \rightarrow 6Hg_{(l)} + 2Cr^{3+}{}_{(aq)}$$

Standard reduction potential of

$E^0_{Hg_2^{2+}/Hg} = +0.85$ V

$E^0_{Cr^{3+}/Cr} = -0.74$ V

Answer: -920610 J/mol

Exercise 4-10

The reaction equation of a standard cell at 25°C is as follows:

$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$

Standard reduction potential:

$E^{\circ}_{I_2/I^-} = +0.53$ V
$E^{\circ}_{Fe^{3+}/Fe^{2+}} = +0.77$ V

Calculate the followings;
A) Standard cell potential
B) Standard Gibb's free energy
C) Equilibrium Constant (K_{eq})

Answer:
A) +0.24 V
B) -46320 J/mol
C) 1×10^{8}

The number of electrons lost or gained in two half cells is n= 2 and reaction occurs at 25 °C therefore:

$$0.93\ V = \frac{0.026\ (V)}{2} \ln K_{eq}$$

When we insert the values in the equation, K_{eq} is as follows:
$K_{eq} = 2.5 \times 10^{31}$

4-7-8 The Effect of Concentration on Cell Potential (The Nernst Equation)

So far, we have examined reactants and products in reduction and oxidation reactions only under standard conditions that is their concentrations are equal to 1M. But sometimes we need different concentrations. Therefore, we need to know the relationship between non-standard cell potential and concentrations of cell components.
In Thermodynamics, we have learnt the relationship between standard free Gibbs energy ΔG° and non-standard Gibbs energy ΔG.

$aA + bB \rightarrow gG + hH$

The relationship between Gibbs energy ΔG and standard free Gibbs energy ΔG° is shown in the formula below:

$$1)\ \Delta G = \Delta G^{\circ} + RT\ln \frac{[G]^g[H]^h}{[A]^a[B]^b}$$

ΔG° standard free Gibbs energy, R is gas constant (8.314 J/K.mol). T is temperature in Kelvin unit and ΔG non-standard free Gibbs energy.
The result of quotient is shown with Q.

$$\frac{[G]^g[H]^h}{[A]^a[B]^b}$$

We can rewrite Equation (1) as follows:

2) $\Delta G = \Delta G^{\circ} + RT\ln Q$

From the relationship between standard and non-standard free energy and cell potential, we get the following equations:

3) $\Delta G = -nFE_{cell}$

4) $\Delta G^{\circ} = -nFE^{\circ}_{cell}$

We get Equation (5) when we insert ΔG and Δ°G value from (3) and (4) in (2).

5) $-nFE_{cell} = -nFE^{\circ}_{cell} + RT\ln Q$

When we divide equation (5) with -nF, we get equation 6:

$$6)\ E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$

Equation 6 is called as the Nernst Equation. It relates division of cell potential and standard cell potential with Q. If the substances in mixture are under standard conditions that is 1M, Q is equal to 1, so lnQ is equal to zero. The second part of Equation (6) is equal to zero therefore, we get $E_{cell} = E^o_{cell}$.

We can simplify Equation (6) by inserting 25°C (298K), mole number and $F = 96500 C/mol.e^-$ in their places:

7) $$E_{cell} = E^o_{cell} - \frac{0.026\ (V)}{n} \ln Q$$

This equation can be used only at 25°C (298K).

The nernest equation enables us to calculate E_{cell} as a function of the concentration of the reactants and products in a cell reaction. for example the general reaction Daniel cell:

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

At 25°C, for the cell with standard potential 1.10 V, we can write Nernst equation as follows:

$$E_{cell} = E^o_{cell} - \frac{0.026\ V}{n} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Here attention is needed as the concentration values of solid substances [Zn]=1, [Cu] =1, they are not written in the quotient.

Example 4-8

Calculate cell potential E_{cell} of the following equation at 25°C.

$$2Ag^+_{(aq)} + Cu_{(s)} \rightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$$

The concentrations of ions: $[Ag^+]= 0.01$ M, $[Cu^{2+}]= 0.01$M and

Standard reduction potential: $E^o_{Ag^+/Ag} = +0.80$ V, $E^o_{Cu^{2+}/Cu} = +0.34$ V

Solution:

We write reaction equations at anode or cathode.

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ $\qquad E^o_{anode} = -0.34$ V

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$ $\qquad E^o_{cathode} = +0.80$ V

$$2Ag^+_{(aq)} + Cu_{(s)} \rightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$$

Standard cell potential:

$$E^o_{cell} = E^o_{anode} + E^o_{cathode}$$

$$E^o_{cell} = (-0.34\ V) + (+0.80\ V) = 0.46\ V$$

Exercise 4-11

Calculate the E_{cell} , E°_{cell} and ΔG values for the following cell.

$Mg \mid Mg^{2+}(0.05M) \parallel Sn^{2+}(0.04M) \mid Sn$

Standard reduction potential:

$E^{\circ}_{Sn^{2+}/Sn} = -0.14\ V$

$E^{\circ}_{Mg^{2+}/Mg} = -2.37\ V$

Answer:

$E_{cell} = 2.227\ V$

$E^{\circ}_{cell} = 2.23V$

$\Delta G = -429811\ J/mol$

We calculate E_{cell} from Nernst Equation:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.026\ V}{n} \ln \frac{[Cu^{2+}]}{[Ag^{+}]^2}$$

$$E_{cell} = 0.46\ V - \frac{0.026\ V}{2} \ln \frac{0.01}{(0.01)^2}$$

$$E_{cell} = 0.40\ V$$

4-8 ELECTROLYTIC CELLS

These cells consume electrical energy. They convert electrical energy into chemical energy. Reactions do not occur spontaneously. Electrical energy is given in order to start reactions. That means free energy has got a positive sign ($\Delta G = +$). Electrolytic cells have many applications in industry. For example, in purification of metals and in electroplating , this method is used. In this part, we will explain some electrolytic cells.

4-8-1-Electrolytic cell of fused sodium chloride :

The reactions in electrolytic cells occur using electrical energy **to make non-spontaneous electrolytic cell reaction happen. in fused**

Sodium chloride contains sodium and chloride ions in free state. In Fig. 4-7, the electrolytic cell of fused sodium chloride is shown. Carbon and platinum electrodes are dipped into fused sodium chloride in the cell. In electrolysis reaction, reduction occurs at cathode. Sodium ions are reduced to sodium metal. The reaction at cathode is as follows:

$Na^{+} + e^{-} \rightarrow Na$

Oxidation occurs at anode. Chloride ions oxidize to chlorine atom. Later atoms combine and form chlorine gas.

Reaction at anode:

$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$

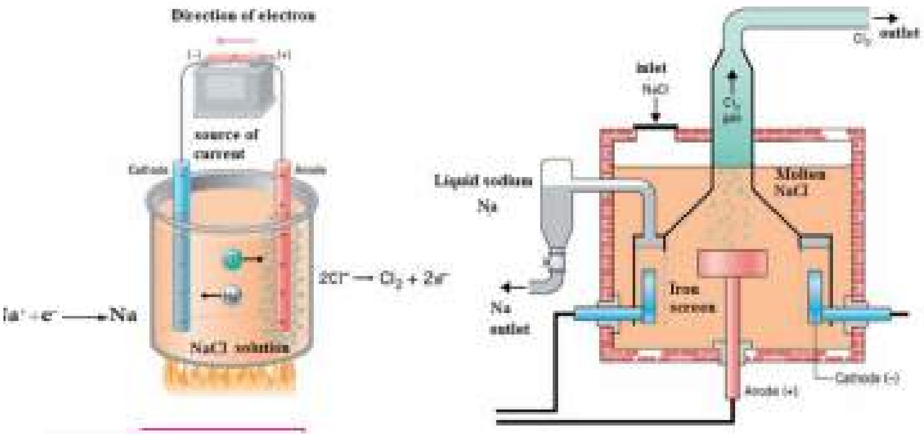


Figure 4-7

Electrolytic cell of fused sodium chloride .

To make number of electrons equal, reduction half reaction is multiplied by 2 and electrons are omitted from both cell equations. Then both half cell equations are added.

$2Na^{+} + 2e^{-} \rightarrow 2Na$ Reduction half reaction (cathode)

$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$ Oxidation half reaction (anode)

$2Na^{+} + 2Cl^{-} \rightarrow 2Na + Cl_2$ general reaction cell

Sodium and chlorine need to be collected at different containers to avoid them reacting again and forming sodium chloride.

4-8-2-Electroplating Cell

Electroplating is plating of a metal with another metal as a thin layer by electrolysis. This process is very important as it is used to protect metals from corrosion.

Electroplating cell consists of anode and cathode poles. Anode includes metals like gold or silver which we choose as plating material. Cathode is formed from spoon or alike which we want to plate.

Salt solutions of plating metal as $AgNO_3$ silver nitrate or gold nitrate $Au(NO_3)_3$ is filled into the cell. Fig 4-8 shows a plating cell which uses silver to plate a fork.

The quality of plating depends on the voltage of electric current and the concentration of the plating metal.

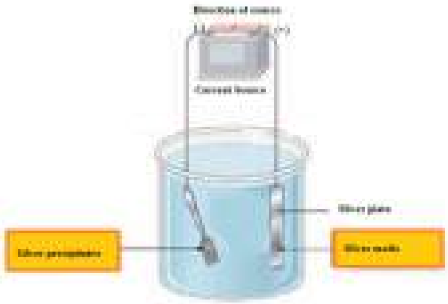


Figure 4-8
Electroplating Cell

4-9 FARADAY'S LAW

In the early 19th century, English scientist Faraday formulated electrolysis laws known with his name through experiments.

These laws:

First Law:

The mass of substance is precipitates on the cathode or melts at the anode or is released as gases at these electrodes are directly proportional to the amount of electric current passing through the electrolysis circuit.

Second Law:

When equal amount of electric current passes, the mass of each substance at electrodes is directly proportional to their equivalent masses.

To understand those laws, we need to learn reactions occurring at electrodes well.

Reactions at Cathode:

A- At cathode, ions reduce to their atoms and deposits.

B- At cathode, positive gas ions evolve as a gas as H_2.

Reactions at Anode:

A- At anode, metals dissolve in electrolyte solution.

B- At anode, negative gas ions evolve gases like Cl_2 and O_2.

Before we apply Faraday's Laws, let's learn terms and units in this law:

1- Electric current is represented with (I). Its unit is ampere and shown with (A).

2-The symbol of electrical charge is (Q) and its unit is coulomb and shown with (C). $F = 96500\ C/mol.e^-$, F is Faraday constant. Q, electrical charge is obtained from multiplication of current (ampere) and time (second).

$(mol.e^-)$= mole number of electrons

$$Q\,(C) = I\,(A) \times t\,(s)$$

In order to convert electrical charge into mole number of electrons, Q is divided by Faraday constant.

$$Q_{(mol.e^-)} = \frac{I(A) \times t\,(s)}{96500\ (C/mol.e^-)}$$

Let's explain calculation of Faraday's Law here. The mass of substances that gathered at cathode or dissolved at anode or evolved as gas is directly proportional to their equivalent masses. The pass of 1 mole of electron 96500 C or 1 Faraday current from circuit means evolution of 1 equaivalent-gram substance or dissolution at anode or evolution of gas at electrode. If we do not want to use equivalent-gram unit, we can convert mole number of electrons to mole number of according to number of electrons gained or lost electrons in reduction

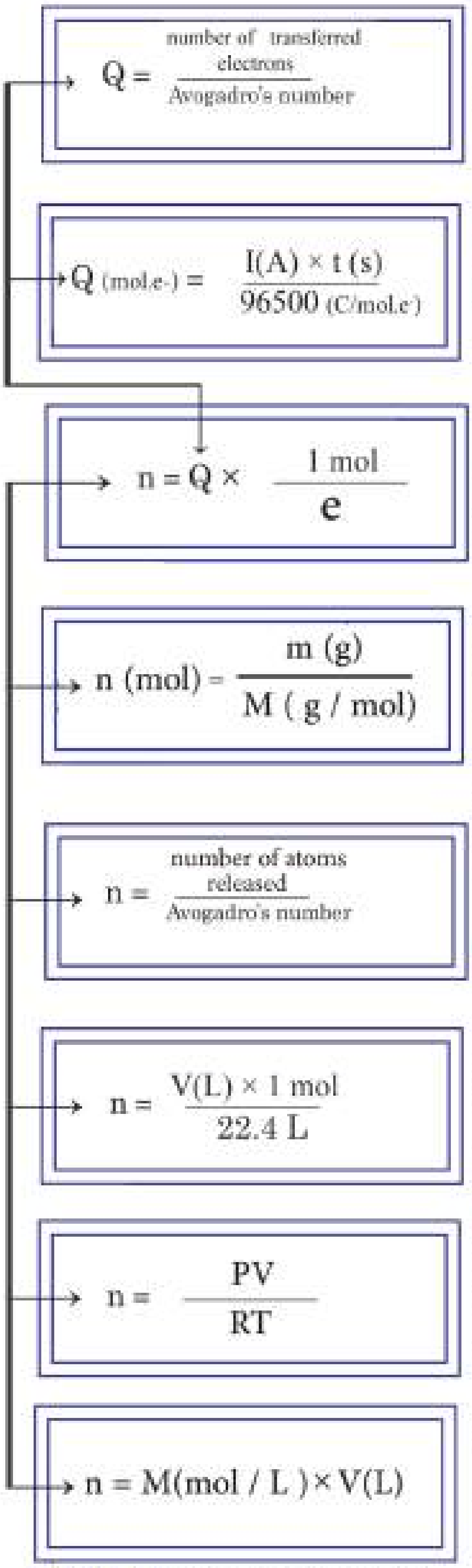


Table 4-1 Table showing steps to be followed while solving problems about Faraday's law

or oxidation. We follow the steps in Table 4-1 while solving problems about Faraday.

1- We can convert electrical charge to mole electron ($Q_{(mol.e^-)}$) by using following equation.

$$Q_{(mol.e^-)} = \frac{I(A) \times t\ (s)}{96500\ (C/mol.e^-)}$$

2- We get the mole number by using number of gained or lost electrons in two half cell reactions.

3- Using the formula below, mole number of evolved or deposited substance is found after passing electric current through cells.

$$\underset{\substack{\text{deposit or}\\ \text{evolved}}}{n} = \underset{\text{cell}}{Q} \times \frac{1\ mol}{\underset{\text{half - cell reaction}}{e}}$$

4- Using the formula below, by multiplying number of mole (n (mole)) with molar mass M (g/mol), we convert to mass of substance deposited at cathode or dissolved at anode.

$$m\ (g) = n\ (mol) \times M\ (g/mol)$$

Or using the following formula, we convert number of mole to volume of released gas.

$$PV = nRT$$

While solving some mathematical questions, the atom numbers of elements in electrolysis or molecule numbers or number of electrons gained or lost in the cell might be needed. We can solve these questions by assuming that atom, electron or molecule number of any substance in cell is equal to Avogadro's number.

Example 4-9

The half cell reaction is as follows:

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

How many grams of magnesium are obtained in an electrolysis cell in which 25 A current passes in an hour?

Atomic mass of magnesium is 24. Calculate the number of magnesium atoms accumulating at the cathode under same conditions.

Solution:

In the Faraday's Law, the time unit is second. Therefore, we convert hour to second:

$$t\ (s) = t\ (hr) \times \frac{3600\ (s)}{1\ (hr)} \Rightarrow t\ (s) = 1\ (hr) \times \frac{3600\ (s)}{1\ (hr)} = 3600\ s$$

With respect to number of moles of electrons, we calculate the amount of electricity passing through the cell:

$$Q_{(mol.e^-)} = \frac{I(A) \times t\ (s)}{96500\ (C/mol.e^-)}$$

$$Q_{(mol.e^-)} = \frac{25(A) \times 3600\ (s)}{96500\ (C/mol.e^-)} = 0.9\ mol.e^-$$

According to the magnesium's reduction equation, we can say that when 1 mole of magnesium deposits, 2 mole of electrons pass through the cell. Therefore, the mole number of magnesium is as follows:

$$n = Q \times \frac{1\ \text{mol}}{e}$$

$$n_{Mg}(\text{mol}) = 0.9\ \cancel{\text{mol.e}^-} \times \frac{1\ (\text{mol})}{2\ (\cancel{\text{mol.e}^-})} = 0.45\ \text{mol}$$

From the following equation, we can get the mass in gram unit:

$$n\ (\text{mol}) = \frac{m\ (g)}{M\ (g/\text{mol})}$$

In order to find the number of Mg atoms depositing at the cathode, we need to know that 1 mole consists of as many atoms as Avogadro's number.

$$m\ (g) = n\ (\text{mol}) \times M\ (g/\text{mol})$$

$$m\ (g) = 0.45\ (\text{mol}) \times 24\ (g/\text{mol}) = 10.8\ g$$

Number of atoms = number of moles x Avogadro's number

$$N = N_A\ (\text{atoms}/\text{mol}) \times n\ (\text{mol})$$

$$N = 6.02\times10^{23}\ (\text{atoms}/\text{mol}) \times 0.45\ (\text{mol})$$

$$N = 2.7\times10^{23}\ \text{atoms}$$

4-10- BATTERIES AND FUEL CELLS

Generally galvanic cells are called as batteries and divided into two: Rechargeable and non-rechargeable batteries.
A battery generally consists of a few galvanic cells that are connected one after another. The total charge is equal to the sum of the charges of these cells. Let's talk about these batteries we often use in our daily lives.

4-10-1 Lead Storage Batteries (Accumulator)

This type of battery is used in industry and to supply energy for many appliances and vehicles. It consists of lead galvanic cells that have potentials alittle more than 2V. Every cell has got two poles one of which is made up of lead Pb and works as anode and the other is made up of lead oxide PbO_2 and works as cathode. These two poles are immerse in sulfuric acid solution which is an electrolysis solution and has a density between 1.2 g/mL and 1.3 g/mL. This battery consists of 3 or more cells and works as a galvanic cell with a potential of 6 V or 12 V. Fig 4-9

As long as the battery works, lead sulfate $PbSO_4$ deposits as a solid on both poles. While sulfuric acid is consumed as ions, the amount of water increases and therefore, the density of acid solution decreases. When the car starts moving, with voltage effect battery half reactions are reversed.

Exercise 4-12

Calculate the electric current we need to supply in 200 seconds in order to deposit 3 grams of gold at the cathode in gold chloride, $AuCl_3$, solution.
(Au = 197 g/mol)

Answer: 21.7 A

Exercise 4-13

96.5 A of electric current was given to the copper sulfate, $CuSO_4$, solution with 0.2 M concentration and 600 mL volume. Calculate the length of time needed to remain 0.03 mole of copper ion, Cu^{2+}, in the solution.

Answer: 180 s

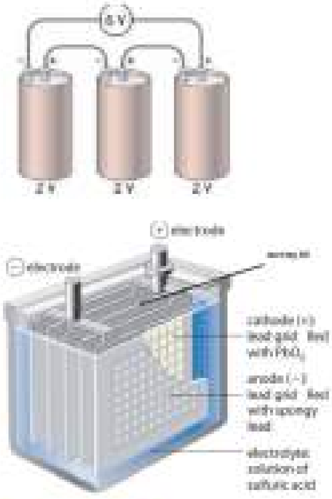


Figure 4-9
Lead Storage Batteries
(Accumulator)

Pb, PbO_2 and H_2SO_4 are formed again. By supplying an electric current opposite to the reaction in the battery, it can be recharged again. In this case, it becomes a battery that consists of a group of electrolysis cells. $PbSO_4$ solution decomposes at two poles and the density of acid returns to the original state.

4-10-2 Dry Cell Batteries:

This type of battery is made up of a zinc box which works as anode filled with MnO_2, carbon (graphite) and ammonium chloride (NH_4Cl) wet paste. Fig. 4-10

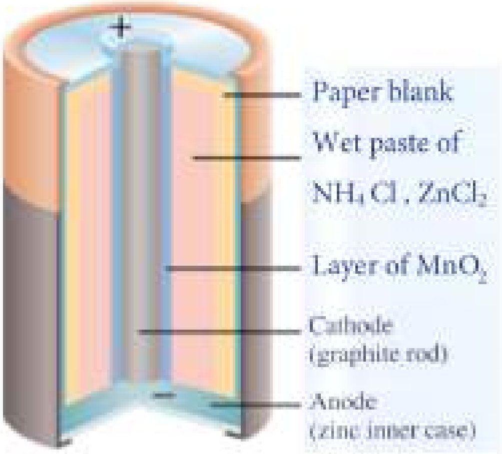


Figure 4-10
Dry cell (Zn-c)

Properties: They have a potential of 1.48V and they are used in many appliances like radios, calculators, toys, etc., and they are not rechargeable.

note: This equation can be usefull $\ln x = 2.303 \log x$

QUESTIONS OF CHAPTER-4

4-1- Explain the following terms:
Anode, electromotive force, standard reduction potential, salt bridge

4-2-Calculate Faraday's constant and tell their units.

4-3- Under standard conditions, which of the following pairs are preferred as oxidizing agents?
Standard reduction potentials $E^0_{Ag^+/Ag} = +0.80$ V, $E^0_{Au^{3+}/Au} = +1.50$ V, $E^0_{Br_2/Br^-} = +1.07$ V,
$E^0_{Cr^{3+}/Cr} = -0.74$ V, $E^0_{Cd^{2+}/Cd} = -0.40$ V
a) Au^{3+} or Br_2 b) H_2 or Ag^+ c) Cd^{2+}or Cr^{3+}

4-4- Write down the equation depending on the relationship between ΔG^0, K_{eq} and E^0_{cell} and all their symbols.

4-5- In an aqueous solution containing Fe^{2+}, Fe^{3+}, Ce^{3+} and Ce^{4+} ions under standard conditions 25^0C and 1 atm pressure, the reaction occurs spontaneously. Calculate the ΔG^0 and K_{eq} values of this reaction. ($In^{-1}(32.3)=1.1\times10^{14}$)
Standard reaction potentials: $E^0_{Fe^{3+}/Fe^{2+}} = +0.77$ V and $E^0_{Ce^{4+}/Ce^{3+}} = +1.61$ V
Answer: -81060 J/mol, 1.1×10^{14}

4-6- Write down the Nernst Equation with all its symbols.

4-7- Calculate the ΔG, E^0_{cell} and E_{cell} for the following cell reaction. ($In1.25= 0.2$, $In10^{-5}= -11.5$)
a) $Mg_{(s)} + Sn^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} \rightarrow Sn_{(s)}$ $[Mg^{2+}] = 0.05M$, $[Sn^{2+}] = 0.04M$
b) $3Zn_{(s)} + 2Cr^{3+}_{(aq)} \rightarrow 3Zn^{2+}_{(aq)} + 2Cr_{(s)}$ $[Cr^{3+}] = 0.01M$, $[Zn^{2+}] = 0.001M$
Standard reduction potentials:
$E^0_{Mg^{2+}/Mg} = -2.37$ V, $E^0_{Sn^{2+}/Sn} = -0.14$ V, $E^0_{Zn^{2+}/Zn} = -0.76$ V and $E^0_{Cr^{3+}/Cr} = -0.74$ V
Answer: a) +2.23 V; +2.227 V ; -429811 J/mol b) +0.02 V; +0.07 V; -40530 J/mol

4-8- Calculate the potential of E_{cell} and E^0_{cell} of the cell formed from SHE and Zn/Zn^{2+} half cell.
$[H^+] = 1.8M$, $P_{H_2}= 1$ atm, $[Zn^{2+}] = 0.45M$, $E^0_{Zn^{2+}/Zn} = -0.76$ V, $In0.14 = -2$
Answer: +0.79V; +0.76V

4-9- Tell the differences between a galvanic cell and an electrolytic cell.

4-10- In the electrolytic cell, one of the half cell reaction is as follow.
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
At 25^0C an 755 mmHg pressure, 0.08L of O_2 gas was accumulated at the electrode. Calculate the number of mole electron to pass the circuit during electrolysis. (1 atm = 760 mmHg)
Answer : 0.012 mol.e^-

4-11- Which of the two different solution containing aluminum and gold ions produce hydrogen gas?
Standard reduction potential of gold $E^0_{Au^{3+}/Au} = +1.50$ V, standard reduction potential of aluminum $E^0_{Al^{3+}/Al} = -1.66$V
Answer: Hydrogen gas is released from aluminum.

4-12- In the following cell, Does the cell reaction take place spontaneously or not?
Standard cell potential $E^0_{Br_2/Br^-} = +1.07$ V, $E^0_{Fe^{3+}/Fe^{2+}} = +0.77$ V,

$$Pt \mid Fe^{2+} (1M) ; Fe^{3+} (1M) \parallel Br^- (1M) \mid Br_2 (1atm) \mid Pt$$

Answer: Iron ion can oxidize.

4-13- Calculate potential of the hydrogen gas (H_2) pole in an electrolytic solution which is pH = 1 at 1 atm and 25°C?

Answer: -0.0592 V

4-14- Specify the reducing and oxidizing agents in the following equation.

$$AgNO_2 + Cl_2 + 2KOH \rightarrow AgNO_3 + 2KCl + H_2O$$

4-15- Can we keep the solution of the table salt in copper cup.
Standard reduction potential. $E^0_{Cu^{2+}/Cu} = +0.34$ V, $E^0_{Na^+/Na} = -2.70$ V,
Answer: Yes

4-16- Can we keep copper sulfate ($CuSO_4$) solution in a nickel cup? Tell the reason.
Standard reduction potential: $E^0_{Ni^{2+}/Ni} = -0.24$ V, $E^0_{Cu^{2+}/Cu} = +0.34$ V
Answer: No

4-17- Calculate the concentration of zinc ions in the solution of zinc electrode. Non-standard zinc reduction potential is (-0.82 V). Standard Zinc reduction potential: $E^0_{Zn^{2+}/Zn} = -0.76$ V, $\ln^{-1}(4.6) = 100$
Answer: 0.01 mol/L

4-18- Calculate the Daniell cell potential as the concentration of zinc sulfate, $ZnSO_4$, solution is 0.1M and the concentration of copper sulfate, $CuSO_4$, solution is 0.01M at 25 °C. Standard cell potential is (1.10 V), ln10= 2.3
Answer: +1.07V

4-19- Which of the following is an oxidation-reduction reaction?

1) $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

2) $2Na + Cl_2 \rightarrow 2NaCl$

3) $2KClO_3 \rightarrow 2KCl + 3O_2$

4) $SiBr_4 + 3H_2O \rightarrow H_2SiO_3 + 4HBr$

5) $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

4-20- Calculate free energy change of a galvanic cell which has a standard potential of +0.74 V at 25 °C. (In10=2.3)

$Cu^{2+}_{(aq)}$ (0.01M) + $Cd_{(s)} \rightarrow Cu_{(s)} + Cd^{2+}_{(aq)}$ (0.1M)

Answer: -137030 J/mol

4-21- Calculate the free energy change of the following cell which has a standard reduction of $E^0_{Br_2/Br^-} = +1.07$ V, $E^0_{Mg^{2+}/Mg} = -2.37$ V, (In0.01 = -4.6)

Mg | Mg^{2+} (1M) || Br^- (0.1M) | Br_2 (1atm) | Pt

Answer: -675500 J/mol

4-22- Calculate the free energy change in the cell with $K_{eq} = 2.3\times10^4$ at 25 °C. The full reaction is given below.

$2H^+_{(aq)}$ (1M) + $Pb_{(s)} \rightarrow H_{2(g)} + Pb^{2+}_{(aq)}$ (0.01M) (In23000 = 10, In0.01 = -4.6)

Answer: -36515 J/mol

4-23- The following reaction occurs in a voltaic cell at 25 °C.

$Sn^{2+}_{(aq)} + Ni_{(s)} \rightarrow Sn_{(s)} + Ni^{2+}_{(aq)}$

$E^0_{Ni^{2+}/Ni} = -0.25$V, $E^0_{Sn^{2+}/Sn} = -0.14$V and the non - standard potential of the cell is +0.17 calculate the concentration of nickel ions. Sn electrode is under standard conditions with 1M solution. (In^{-1} (- 4.62)=0.01)

Answer: 0.01 mol/L

4-24- In this reaction; **Al | Al^{3+}(1M) || Cd^{2+}(1M) | Cd** Calculate the reduction potential of aluminum as standard cell potential is 1.26 V and standard reduction potential of cadmium: $E^0_{Cd^{2+}/Cd} = -0.40$ V

Answer: -1.66V

4-25- In a galvanic cell at 25°C at one pole there is hydrogen gas at 1 atm pressure and at the other pole there is 0.01 M solution containing nickel ions.

Calculate the pH of this cell as free energy for the cell reaction is -48.25 kJ/mol and the potential of standard nickel electrode is -0.25 V.

Answer: 1

4-26- If the potential of the following cell is 0.9992 V at 25 °C, calculate the concentration of tin (Sn^{2+}) ions in the electrode solution.

Sn | Sn^{2+} (?M) || Ag^+ (1M) | Ag

Silver electrode is under standard conditions. Standard reduction potential: $E^0_{Ag^+/Ag} = +0.80$ V, $E^0_{Sn^{2+}/Sn} = -0.14$ V

Answer: 0.01 mol/L

4-27- 10A of electric current is passed through an electrolysis cell containing copper sulfate, $CuSO_4$, solution for 965 seconds. Calculate the mass and number of atoms of copper accumulated at the electrode. (M_{Cu} = 63 g/mol)

Answer: 3.15 g; 0.3×10^{23} atoms

4-28- As a result of passing 3A of electric current through a metal salt with single valence for 3 min 13 seconds, 0.648 g of metal accumulated at the cathode. Calculate the atomic mass of the metal.

Answer: 108 g

4-29- In order to release 2 times of molar volume of oxygen gas under standard conditions (STP), what is the number of electrons needed. (Molar volume of a gas under standard conditions (STP) is 22.4 L)

Answer: 48.16×10^{23} e^-

4-30- What is the amount of electric current to be passed through (in ampere) an electrolysis cell for 2 hours 520 second necessary to release 36.12×10^{21} hydrogen and oxygen molecules at two poles?

Answer: 1A

4-31- A jeweler passed 10A of electric current through an electroplating cell containing gold salt in order to plate a ring. As 75% of electric current was consumed in 9.65 seconds, what is the mass of gold used in plating? Atomic mass of gold = 197 g/mol.
Answer: 0.05g

4-32- Calculate the equilibrium constant of the following reaction.

$$Sn_{(s)} + Pb^{2+}_{(aq)} \rightarrow Sn^{2+}_{(aq)} + Pb_{(s)}$$

Standard reduction potential = $E^0_{Pb^{2+}/Pb} = -0.13$ V, $E^0_{Sn^{2+}/Sn} = -0.14$ V , $(\ln^{-1}(0.769) = 2.16)$
Answer: 2.16

4-33- In water electrolysis cell at STP, electrical current was applied for 3 minutes and 13 seconds, hydrogen and oxygen gases were released at the cell electrodes. The volume of the two released gases equals 0.0672 L. Write down the equation of the two halves, and total equation, find out the volume of each gas and the electric current intensity.
Answer: 2 A

4-34- Standard cathode solution of daniell cell was diluted with water, the potential of electrode decreased by 0.0592 V than its standard potential, calculate the concentration of electrode ions. ($e^{4.6} = 100$)
Answer: 0.01 M

COORDINATION CHEMISTRY CHAPTER-5

cis-diamminedicholoroplatinum(II)
cis-$[Pt(NH_3)_2Cl_2]$

trans-diamminedicholoroplatinum(II)
trans-$[Pt(NH_3)_2Cl_2]$

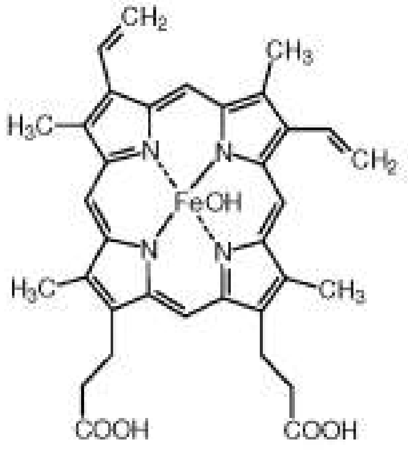
ACHIEVEMENTS

After completing this chapter, the student is expected to :

- Differentiate double salts and complex compounds.
- Learn the properties of coordination compounds and how coordination chemistry has developed.
- Calculate primary and secondary valences of coordination compounds.
- Learn special terms about coordination chemistry.
- Learn about different types of ligands.
- Learn central atom, ligands and they can calculate coordination numbers.
- Learn the theories describing the properties of bonds in complex coordination compounds and they can apply valence bond theory on coordination compounds.
- Find coordination numbers of coordination compounds and decide their geometrical shapes.

Chapter - 5

5-1 PREFACE

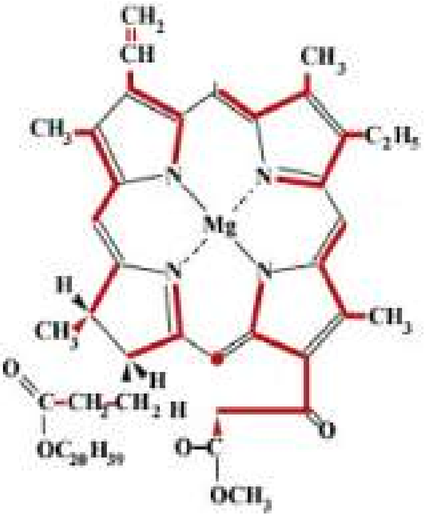


Hemoglobin

Coordination (complex) compounds have become one of main subjects of inorganic chemistry as in addition to different colors and magnetic properties they have, they also participate in many chemical structures and reactions. These compounds have an increasing importance in industry, agriculture, medicine, pharmacy, modern life and clean energy production. Hemoglobin, B12 vitamin and chlorophyll are examples for these compounds.

Most of the metallic elements in periodic table form complex compounds. But in this chapter, we will study mainly the complex compounds that transition elements form.

Elements that are situated between IIA and IIIA groups are called as transition elements (Figure 5-1). Where the element is considered transitional either in its free state or in one of its compounds, if it have d or f orbitals partially filled. Transition elements are divided into two:



Chlorophyll

1- d group elements are called as main transition elements. They are found in 3 periods and each period consists of 10 elements. These are called as first, second and third transition chains.

2- f group elements are called as inner transitions elements. This group consists of 2 periods, each period includes 14 elements. These elements are called as lanthanides and actinides.

Properties of Transition Elements

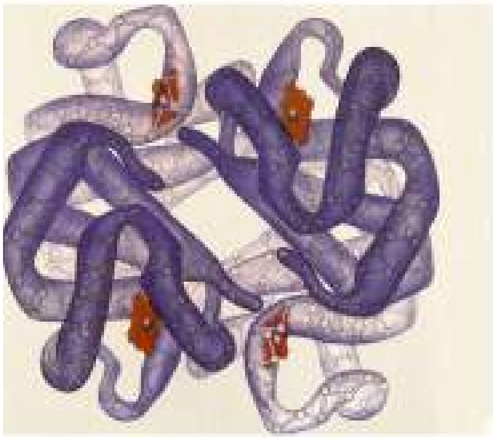
1- They have more than one oxidation states (valence).

2- In the last orbits of transition elements there are d and f orbitals. Those have unshared electrons. These single electrons give paramagnetism to atoms (attraction property in magnetic field).

3- Most of their compounds are colored.

4- Great tendency to form ions or complex compounds.

5-2 DOUBLE SALTS AND COORDINATION COMPOUND



Cage structure of hemoglobin

When two stable and simple salt solutions (ammonium sulfate and iron (III) sulfate) are mixed in mole amounts and if the resulting solution is vaporized, a new compound called as addition compound is obtained. This process is shown in the following equation:

$$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow \underset{\text{Mohr's salt}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

When copper sulfate, $CuSO_4$, is dissolved in a certain solution and with addition of ammonia, the following addition compound is obtained:

$$CuSO_4 + 4NH_3 \longrightarrow CuSO_4 \cdot 4NH_3 \quad \text{or} \quad [Cu(NH_3)_4]SO_4$$

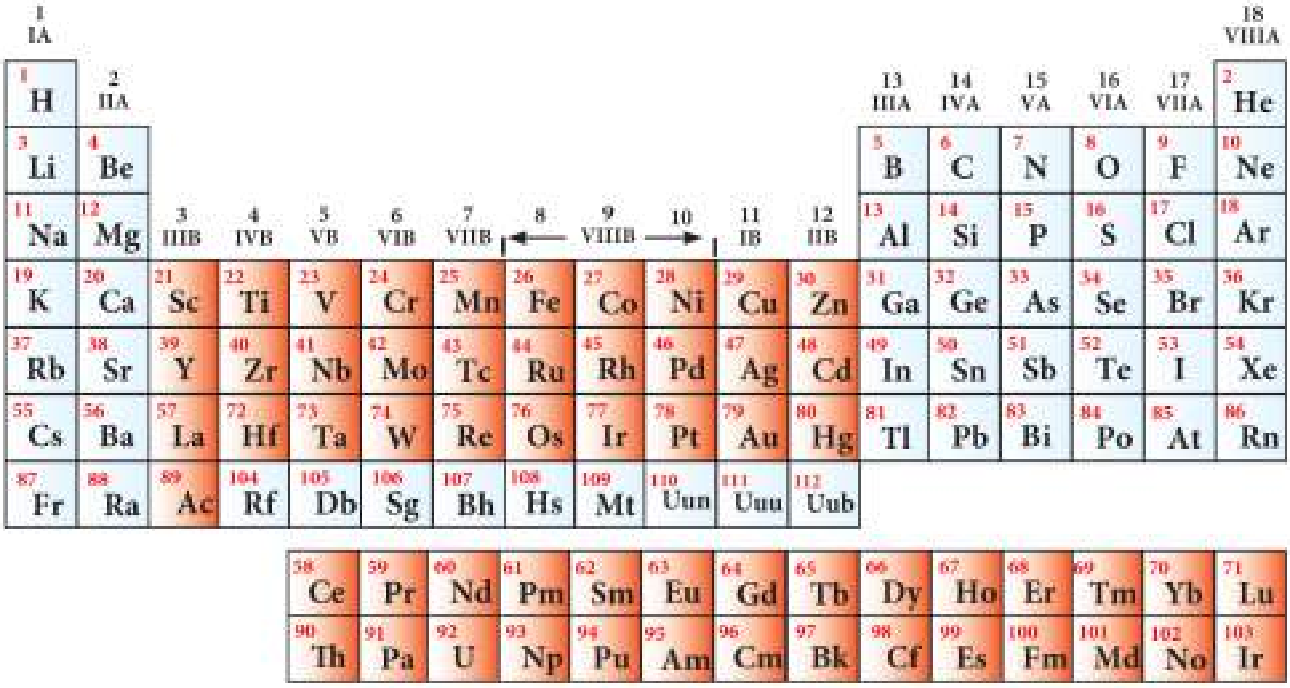


Figure 5-1 Location of the transition elements in the periodic table.

Therefore, we can divide addition compounds into two:

A- Double Salts

These are stable salts of addition compound. When they dissolve in water, they decompose to ions that form them. For example, Mohr's salt, prepared in the first equation above, gives Fe^{2+}, NH_4^+, SO_4^{2-} ions to the solution when it dissolves in water.

in this case, each ion keeps its own characteristics. They can be confirmed in the solution using common methods of detection.

B- Coordination Compound

These are stable addition compound. But they don't decompose to ions which form them completely when they dissolve in water. For example, the coordination compound $CuSO_4.4NH_3$ in the second equation above doesn't give Cu^{2+} ion to solution when it dissolves in water, but it gives only SO_4^{2-} ion. Cu^{2+} ion takes place in $[Cu(NH_3)_4]^{2+}$ complex ion according to the following equation:

$$CuSO_4.\ 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

Therefore, there is only SO_4^{2-} ion in the solution, but not Cu^{2+} ion. Thus, this complex salt is written as $[Cu(NH_3)_4]SO_4$. This coordination compound is formed from $[Cu(NH_3)_4]^{2+}$ positive complex ion and simple negative SO_4^{2-} ion. Coordination compounds can be formed from a complex negative ion and a simple positive ion or complex negative and complex positive ions, as shown in the following examples:

$$\underset{\text{Coordination compound}}{K_3[Fe(CN)_6]} \rightleftharpoons \underset{\text{Positive simple ion}}{3K^+} + \underset{\text{Negative complex ion}}{[Fe(CN)_6]^{3-}}$$

$$\underset{\text{Coordination compound}}{[Co(NH_3)_6]Cl_3} \rightleftharpoons \underset{\text{Positive complex ion}}{[Co(NH_3)_6]^{3+}} + \underset{\text{Negative simple ion}}{3Cl^-}$$

Some coordination compounds don't dissolve in water as they don't ionize completely. e.g. $[Ni(CO)_4]$ and $[Ni(dmg)_2]$ (dmg = dimethylglyoxime) and $[Co(NH_3)_3Cl_3]$

Example 5-1

Whereas $Fe(NH_4)_2(SO_4)_2$ is classified as a double salt, $K_3[Fe(CN)_6]$ is accepted as a coordination compound. Tell the reason for that.

Solution:

$Fe(NH_4)_2(SO_4)_2$ compound is formed from the mixture of iron (II) sulfate and ammonium sulfate solutions according to the equation below:

$$(NH_4)_2SO_4 + FeSO_4 \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4$$

The resulting compound is anhydrous(without water molecules) Mohr's salt. It gives Fe^{2+}, NH_4^+, SO_4^{2-} ions to solution when it dissolves in water. In order to make sure that those ions are present in the solution, each ion can be determined through known analysis methods.

When $K_3[Fe(CN)_6]$ compound dissolves in water, the following equation occurs:

$$K_3[Fe(CN)_6] \rightleftharpoons [Fe(CN)_6]^{3-} + 3K^+$$

As seen here, Fe^{3+} ions in free state have disappeared and these ions be within the structure of complex ion $[Fe(CN)_6]^{3-}$. Therefore, when dissolves in water, the solution gives detection for K^+ ions only but not Fe^{3+} or CN^- ions. That means whereas $Fe(NH_4)_2(SO_4)_2$ is a double salt, $K_3[Fe(CN)_6]$ is a complex compound (complex salt.)

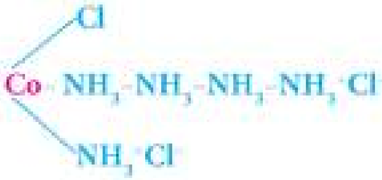
5-3 DEVELOPMENT OF COORDINATION CHEMISTRY

The preparation of hexaammine cobalt (III) chloride ($CoCl_3 \cdot 6NH_3$), in 1798 is accepted as the real beginning of coordination chemistry. The preparation of this compound was big news owing to its unprecedented properties. The reason is that forming a stable compound from two stable compounds (from mixture of ammonia and $CoCl_3$) could be explained only 100 years later. Within this time period, many theories were proposed upon formation of these compounds. But none of those theories were able to explain practical results.

One of those theories is the Chain Theory. The theory was submitted by a Swiss scientist.

The method followed in this theory is the same as the chain formation between carbon atoms in organic chemistry. Due to the general idea that atoms had only one valence (oxidation state) at that time, this scientist claimed that cobalt (III) formed 3 bonds in complex compounds. Therefore, chain structure was used in order to explain the shape where 6 ammonia molecules are bonded in $CoCl_3$. $6NH_3$ {Formula I} compound. According to this, chloride ions aren't bonded to cobalt directly, when silver nitrate solution is added to aqueous solution of this compound, it precipitates as silver chloride. This theory explains the structure of $CoCl_3.5NH_3$ {Formula II}. According to this, one single chloride ion that does not precipitate is directly-bonded to cobalt when silver nitrate is added. Meanwhile, other two chloride ions precipitate easily.

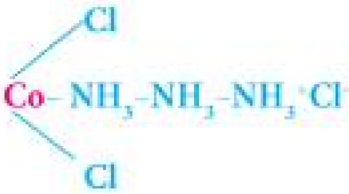
Formula (I)



Formula (II)

$CoCl_3.4NH_3$ compound is shown with {Formula III} that is compatible with scientific experiments. According to this formula, there are two ions which are bonded to cobalt directly. But third chloride ion is not bonded to cobalt directly. $CoCl_3.3NH_3$ compound is shown with Formula (IV).

Formula (III)



Formula (IV)

We might expect that the behavior of chloride ions in Formula (IV) is similar to that of $CoCl_3.4NH_3$ compound. But it is observed that there is no precipitation occurs when silver nitrate solution is added. Because of this and for other reasons, this theory couldn't explain all properties of this kind of compounds.

5-3-1 Werner's Coordination Theory

Werner proposed his theory which prepared a basis for modern theories based on the following hypotheses:

1- Most of the elements have two kinds of valences. One is primary ionization valence and it defines oxidation state that is shown with dashed line (----). The with other is unionized secondary valence. It is the coordination number that is shown continuous line (——) .

2- Each element which reacts to form a complex compound tries to satisfy both valences. First valence is satisfied with a negative ion, second valence is satisfied with negative ions or molecules.

3- Second valence is oriented to the fixed locations in the space called coordination sphere around the metal ion. This forms the basis of metal complex compounds (stereochemistry.)

Werner showed ($CoCl_3$. $6NH_3$) compound with formula (V). This can be shown with the molecular formula of $[Co(NH_3)_6]Cl_3$. Here, the oxidation state of cobalt is (+3). Therefore, 3 chloride ions try to satisfy the first valence (balancing of cobalt ion charge). Second valence or coordination number is satisfied with 6 ammonia molecules. According to this, second valence of cobalt (III) is 6 which is shown with coordination number.

Six (6) ammonia molecules in this situation are called as ligands. According to this theory, ligands are bonded to metal with coordinate covalent bonds. Chloride ions aren't accepted as ligands. Because these form ionic bonds with metal out of coordination area and all precipitate when silver nitrate solution is added.

Werner showed ($CoCl_3$. $5NH_3$) compound with formula (VI). Here, one of the chloride ions saturated both primary and secondary valences. And expressed the bond that connects it to the metal with the continuous and dashed lines. (----). Therefore, the chloride ion doesn't precipitate easily when silver nitrate solution is added as it is directly-bonded with cobalt atom inside coordination area.

Meanwhile, the charge of positive complex ion $[Co(NH_3)_5Cl]^{2+}$ is (+2). The reason is that $Co^{3+} + Cl^- = (+3) + (-1) = +2$. Therefore, the compound which is shown with ($CoCl_3.5NH_3$) is with the following molecular formula:

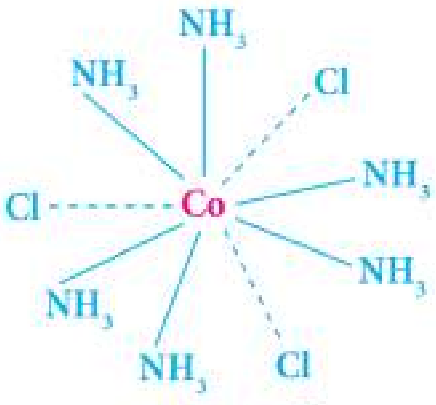
$[Co(NH_3)_5Cl]Cl_2$

According to this theory, ($CoCl_3.4NH_3$) compound is shown with formula (VII). According to this, two chloride ions satisfy both first and second valences. Therefore, these are bonded strongly in coordination area. When silver nitrate solution is added, only one chloride ion which is out of coordination area precipitates. As this compound decomposes to Cl^- and

$[Co(NH_3)_4Cl_2]^+$ ions, its molecular is shown as $[Co(NH_3)_4Cl_2]Cl$.

Do you know that?

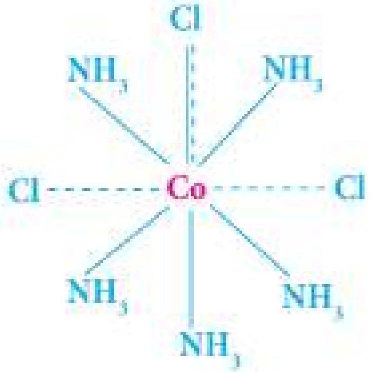
Today we can understand the properties of complex compounds owing to the perfect theory of Werner. He was 26 when he proposed his theory. He was the first chemist in inorganic chemistry field who won Nobel Prize in 1913.



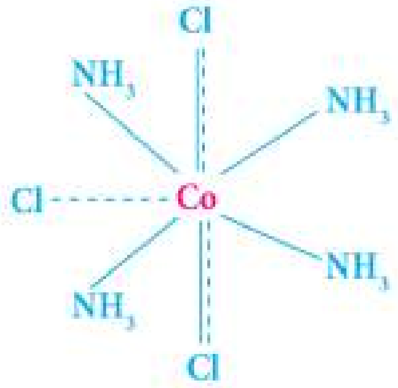
Formula (V)

According to the theory, the compound ($CoCl_3 . 3NH_3$) shown with formula (VIII) doesn't precipitate when silver nitrate solution is added and it can be shown with the chemical formula $[Co(NH_3)_3Cl_3]$.

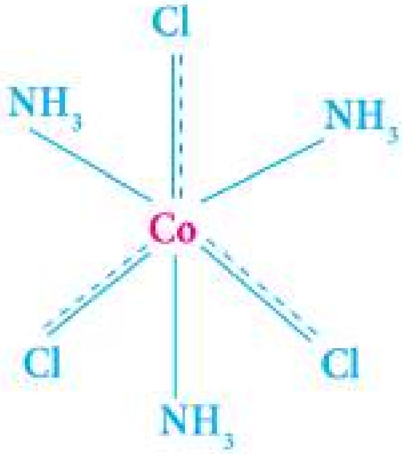
The absence of precipitation means that this compound doesn't ionize in this solution. This is the opposite of what is expected in the chain theory. According to practical results, this kind of compounds doesn't ionize in solution. This proved that the chain theory isn't correct and it supported the hypotheses of coordination theory.



Formula (VI)



Formula (VII)



Formula (VIII)

Example 5-2

What are the first (oxidation state) and second (coordination number) valences of the central metal atom in the two following compounds?

A- $K_4[Fe(CN)_6]$

B- $[Cr(NH_3)_6](NO_3)_3$

(Note: Cyanide ion (CN^-) in $K_4[Fe(CN)_6]$ compound behaves like a ligand.)

Solution:

A- We know that each potassium ion has +1 charge. Therefore, the negative ion is $[Fe(CN)_6]^{4-}$ which carries (-4) charge.

Thus: $Fe^{(x)} + (CN^-)_6 = -4$

$\Rightarrow x + 6 \times (-1) = -4$

$x = +2$

Therefore, primary valence of iron is equal to (+2) and secondary valence is equal to 6. Thus, this is the number of ligands which are directly related to metal and shown in brackets.

B- Each nitrate ion has (-1) charge and ammonia is neutral. Therefore, as positive ion is bonded to ammonia molecules it has +3 charge. $[Cr(NH_3)_6]^{3+}$

$Cr^{(x)} + (NH_3^{0})_6 = +3$

$\Rightarrow x + 0 \times 6 = +3$

$x = +3$

Therefore, primary valence of chromium is +3 and secondary valence is equal to 6.

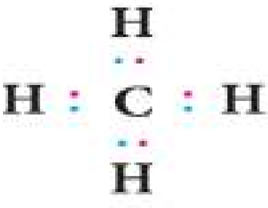
Exercise 5-1

What are the primary and secondary valences of iron in $K_3[Fe(CN)_6]$ compound?

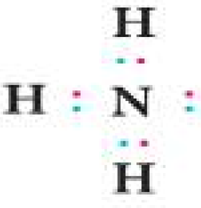
Answer: +3; 6

5-3-2 Lewis Acids and Bases

According to Lewis structure, methane (CH_4) and ammonia (NH_3) molecules are shown with the following formulas.

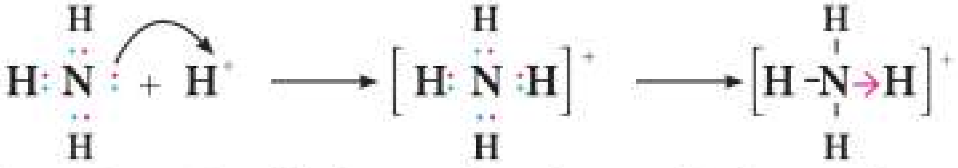


Methane



Ammonia

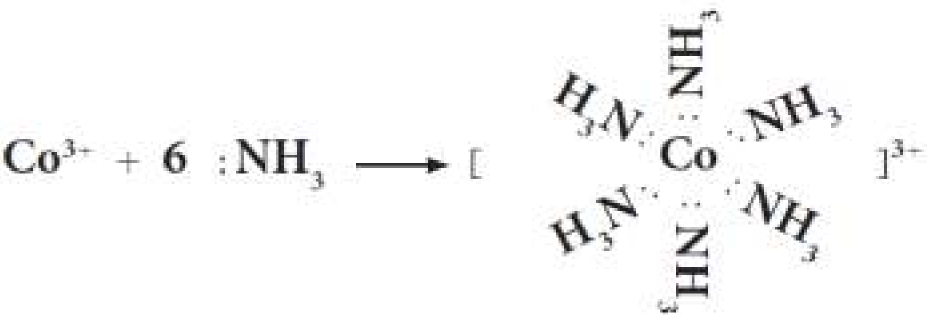
Lewis structures of methane and ammonia molecules show that there is a very important difference between them. This difference is that nitrogen atom has a pair of electrons which don't form a bond with hydrogen atom. As a result of this, ammonia molecule can react with other atoms using this electron pair. As in nitrogen atom, this pair of electrons is shared with another atom which has an empty orbital and a coordinate covalent bond is formed. This bond is shown with an arrow (→) showing the direction from donor atom to acceptor atom. As an example to this reaction, interaction of ammonia with proton in order to produce ammonium ion can be given.



Ammonia, can share this electron pair on nitrogen with other atoms just as with hydrogen. The following example reactions show using electron pair on nitrogen with metals.

$$Ag^{+} + 2\ :NH_3 \longrightarrow [H_3N:Ag:NH_3]^{+}$$

$$Cu^{2+} + 4\ :NH_3 \longrightarrow [H_3N:\underset{\underset{NH_3}{\cdot\cdot}}{\overset{\overset{NH_3}{\cdot\cdot}}{Cu}}:NH_3]^{2+}$$



These reactions are accepted as acid-base reactions according to Lewis structure. Ammonia is accepted as electron donor. Therefore, it is a base according to Lewis theory. The metal ion which accepts electron pair is an acid according to Lewis theory. As a result of this reaction, a coordinate covalent bond is formed. The resulting compounds are called as coordination complexes.

To summarize, this reaction occurs between a Lewis base which is called as a ligand and a Lewis acid which is called as central atom (metal).

As mentioned above, some terms are used about coordination compounds. Let's learn some other terms which we will see in this chapter later.

1- Ligands

They are molecules or negative or positive charged ions which are bonded to a central atom through one or more atom donor electronic pair. A ligand is called as a monodentate ligand if it donates a pair of electrons, it is called a bidentate ligand if it donates two pairs of electrons and if it donates more than two pairs of electrons, it is called as a multidentate ligand.

2- Central Atom

One of the properties of coordination compounds is that they have an metallic atom which is an electron pair acceptor. This atom is bonded to a ligand with a coordinate covalent bond. This atom is called as the central atom.

3- Coordination Complex

The compound which results from bonding of central atom and ligand molecules with coordinate covalent bonds.

4- Coordination Number

This number is the multiplication of number of ligands bonded to central atom with the number of dentate of ligand. In other words, it is equal to the number of covalent bonds. Most occurring coordination numbers are 2, 4 and 6. Odd coordination numbers are rarely seen. In coordination complexes, central atom has two valences. One is oxidation number and the other is coordination number. In simple compounds, there is only oxidation number. For example, the oxidation number of iron in $[Fe(CN)_6]^{4-}$ is (+2) and coordination number is 6. The sum of charges in the complex molecule gives the charge of it. Here, the charge of the complex ion is (-4). The charge of Fe(II) is (+2) and the sum of charges of six cyanide ions (CN^-) is (-6).

5- Complex Ion

They are compounds charged with positive or negative charges. They have a central metal atom and suitable number of ligands around metal atom bonded to it with covalent bonds. Central atom has an oxidation state as neutral, positive or negative. Ligands are usually neutral or negative or both.

For example: $[Co(NH_3)_6]^{3+}$ Neutral ligand

$[Ni(CN)_4]^{4-}$ Negative ligand

$[Fe(CN)_6]^{4-}$ Negative Ligand

$[Co(NH_3)_5Cl]^{2+}$ Negative and Neutral ligand

6- Neutral Complex Compound

The complex that doesnt carry charge called neutral complex, which doesnt ionize in water. Following compounds are examples for neutral complexes.

$[Co^{3+}(NH_3)_3Cl_3]$; $[Ni^{0}(CO)_4]$

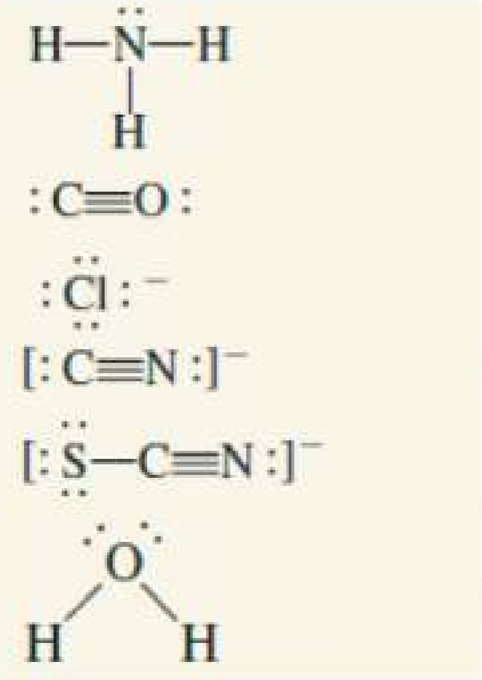
$[Pt^{2+}(NH_3)_2Cl_2]$; $[Ni^{2+}(dmg)_2]$

7- Coordination Sphere

While writing complex compounds, central atom and ligands are shown in brackets. These brackets show the coordination field and it is called as inner sphere. The part out of these brackets are called as ionization sphere or outer sphere. For example, inner sphere of $[Co(NH_3)_5Cl]Cl_2$ complex compound consists of central ion Co^{3+} and 6 ligands. These ligands are 5 ammonia molecules and one chloride ion Cl^-. The part which consists of 2 chloride ions is the outer sphere. Therefore, ions written inside ionization sphere can ionize in water. These ions can be precipitated through using suitable agents. Ions inside inner sphere cannot ionize thus, they cannot be precipitated. For example:

$$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

$$2Ag^+ + 2Cl^- \longrightarrow \underset{\text{White precipitate}}{2AgCl}$$

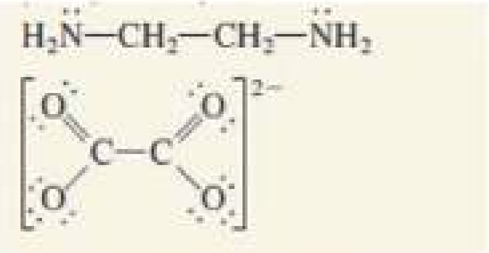


Monodentate ligand

Two (2) Cl^- ions inside ionization sphere can be precipitated as silver chloride(AgCl) (white precipitate) through addition of silver nitrate ($AgNO_3$). But Cl^- ion inside inner sphere doesn't ionize in water and therefore it cannot be precipitated.

8- Coordination Chemistry

It is the branch of inorganic chemistry which studies coordination compounds and their properties.

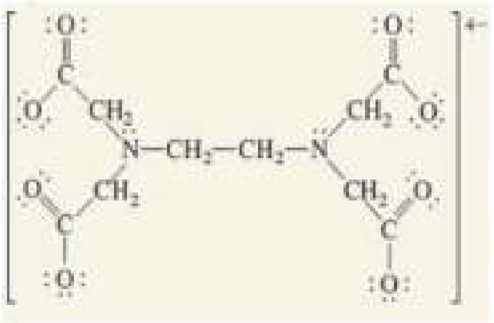


Bidentate ligand

5-4 TYPES OF LIGAND

A- Monodentate Ligands

Most of those ligands are negative ions or neutral molecules which can donate an electron pair to positive metal ion. In ligand chemical structure, there is a single atom which is bonded to central metal atom. For example, CN^-, Br^- ,F^- , and Cl^- ions and ammonia (NH_3), alkyl amine (RNH_2) and pyridine (C_5H_5N) and water (H_2O) molecules.



Multidentate ligand

B- Bidentate Ligands

Many ions or molecules form complex compounds through more than one atom (they have two pairs of electrons which don't take place in reaction). For example, oxalate ion $C_2O_4^{2-}$, and ethylene di amine $NH_2–CH_2\ CH_2\ –NH_2$ are bidentate ligands.

C- Multidentate Ligands

These are ligands which have 3, 4 or more atoms that can form covalent bonds. For example, ethylene diamine tetraacetic acid (EDTA).

EDTA is called as hexadentate ligand as it has six atoms which can form covalent bonds.

Ligands which are bonded to the same metal atom by two or more regions are called as chelating ligand. In Table 5-1 some examples are given for mono or bidentate ligand types. (Table in the end of this book can be used to solve chapter quations)

Table 5-1 Types and Names of Some Mono and Bidentate Ligands

Structure of ligand	Name of Ligand	Structure of ligand	Name of Ligand
Monodentate ligands			
NO	nitrosyl	CO	carbonyl
NH_3	ammine	H_2O	aqua
C_5H_5N	pyridine	CH_3NH_2	methyl amine
N_3^-	azido	CH_3COO^-	acetato
$\{(NH_2)_2CO\}$	urea	CN^-	cyano
Br^-	bromo	Cl^-	chloro
Bidentate ligands			
NH_2NH_2	hydrazine	$NH_2CH_2CH_2NH_2$	ethylenediamine (en)
CO_3^{2-}	carbonato	$C_2O_4^{2-}$	oxalato
$C_4N_2O_2H_7^-$	dimethylglyoximato $(dmg)^{1-}$	NO_3^-	nitrato

5-5 EFFECTIVE ATOMIC NUMBER RULE (EAN RULE)

The first attempt which explains the stable structures of complex compounds was made by Sidgwick who expanded Lewis' Theory. Sidgwick explained the stability of these compounds by their similarity to noble gas electron configuration. According to this theory, if the numbers of electrons donated by central ion or ligands is equal to atomic number of one of the noble gases ; $_{36}$Kr, $_{54}$Xe, or $_{86}$Rn, the complex compound will be stable. The total number of electrons on the central atom which are donated by ligands are called as effective atomic number (EAN). This rule is called as effective atomic number rule. Through this rule, the structure of many complex compounds could be explained.

Exercise 5-2

Calculate EAN for the following compounds. Then specify if EAN rule is valid for them.

($_{46}Pd$, $_{26}Fe$, $_{28}Ni$)

$[Pd(NH_3)_6]^{4+}$

$[Fe(CN)_6]^{3-}$

$[Ni(en)_3]^{2+}$

Answer: 35 not valid; 54 valid; 38 not valid

Exercise 5-3

Calculate EAN of $[Ag(NH_3)_4]^+$ and $[Ni(NH_3)_6]^{2+}$ complex compounds. (Atomic number of Ni = 28, atomic number of Ag = 47). Is EAN rule valid for these compounds?

Answer: 38 not valid; 54 valid

Attention:
Some complex compounds do not follow EAN rule; but they are stable complexs compound.

Example 5-3

What is the effective atomic number of $[Co(NH_3)_6]^{3+}$ compound? Is EAN rule valid in this compound? (Atomic number of cobalt = 27)

Solution: Calculation is as follows:

$$\begin{array}{l} Co = 27\ e^- \\ Co^{3+} = 24\ e^- \\ 6\ NH_3 = 12\ e^- \\ \hline [Co(NH_3)_6]^{3+} = 36\ e^- \end{array}$$

Here, the effective atomic number is 36. This number is equal to the atomic number of noble gas Krypton. Therefore, the complex compound is stable as it follows the EAN rule.

Example 5-4

What is the EAN of $[CoCl_4]^{2-}$ compound? Is EAN rule valid for it? (Atomic number of Cobalt = 27)

Solution:

$$\begin{array}{l} Co = 27\ e^- \\ Co^{2+} = 25\ e^- \\ 4\ Cl^- = 8\ e^- \\ \hline [CoCl_4]^{2-} = 33\ e^- \end{array}$$

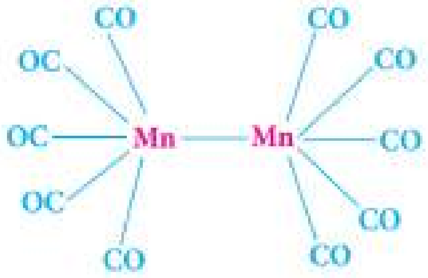
Here, the EAN is 33. This number isn't equal to atomic number of any noble gases. Therefore, it doesn't follow EAN rule. But despite the fact that it is a stable complex compound.

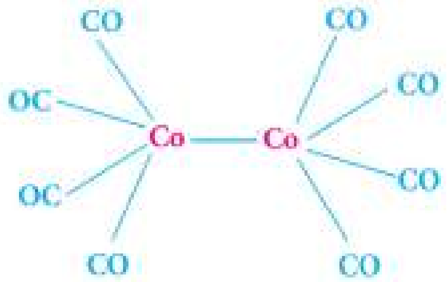
There are many exceptions of this rule. Although the rule explains the structure of metal carbonyl complex compounds, it is useful for only a limited part of coordination chemistry. For example:

$$\begin{array}{lll} Cr = 24\ e^- & Fe = 26\ e^- & Ni = 28\ e^- \\ 6\ CO = 12\ e^- & 5CO = 10\ e^- & 4CO = 8\ e^- \\ \hline [Cr(CO)_6] = 36\ e^- & [Fe(CO)_5] = 36\ e^- & [Ni(CO)_4] = 36\ e^- \end{array}$$

These complex compounds seem to follow EAN rule. On the other hand, metals with odd atomic numbers which make compounds with ligands like above don't follow EAN rule. Because the result is always an odd electron number. Therefore, whatever the added carbonyl number is, effective atomic number will never be equal to 36, 54 or 86. This kind of compounds are in dimer molecular or polymer structure.

The following two complex compounds $[Co_2(CO)_8]$, $[Mn_2(CO)_{10}]$ can be given as examples. EAN's of these compounds are calculated as follows:





Mn = 25 e^-

Mn – Mn = 1 e^-

5CO = 10 e^-

$[Mn_2(CO)_{10}]$ = 36 e^-

Co = 27 e^-

Co – Co = 1 e^-

4CO = 8 e^-

$[Co_2(CO)_8]$ = 36 e^-

Exercise 5-4

Calculate EAN of $[Re_2(CO)_{10}]$ complex compounds. Is EAN rule valid for this compound? (Atomic number of Re = 75)

Answer: Valid ;86

5-6 NOMENCLATURE OF COORDINATION COMPOUNDS

Rules assigned by (IUPAC) are as follows:

1- While naming an ionic compound, positive ion is named first and negative ion second. e.g. naming simple salt NaCl sodium chloride, complex compound $[Cr(NH_3)_6]Cl_3$ hexaamminechromium(III) chloride.

2- In coordination compounds, ligands are named first, then the metal comes. If there are more than one ligands, naming is done in alphabetical (English) order. For example:

$[Cr(H_2O)_4Cl_2]Cl$ Tetraaquadichlorochromium(III) chloride

3- Negative ligands' names finish with –o suffix. But neutral ligands assume molecule name without any change. As exceptions, water becomes aqua and ammonia becomes ammine. In order to differentiate ammonia from other amines, double m is used. Other amines are written with single m. Positive ligands (which are rare) finish with –ium suffix. In Table 5-2 , some positive and negative ligands are given.

Attention: While writing IUPAC names of positive or negative ions, no blank is left. But a blank is left between positive and negative ions.

Table 5-2

Name of ligands	Symbol of ligands
Chloro	Cl^-
Cyano	CN^-
Acetato	CH_3COO^-
Thiocyanato	SCN^-
Ethylenediamine	$NH_2CH_2CH_2NH_2$
Hydrazinium	$NH_2NH_3^+$

Exercise 5-5

Name the following coordination compounds.

1- $[Co(NH_3)_5H_2O]Cl_3$

2- $Na[Co(NH_3)_4Cl_2]$

3- $K_2[PtCl_6]$

4- $[Cr(NH_3)_6](NO_3)_3$

5- $[Cu(en)_2]Cl_2$

6- $(NH_4)_2[Cr(SCN)_6]$

4- If there are more than one of the same ligands in a complex compound, prefixes di-, tri-, tetra- etc. are mentioned before ligand name. But before complex ligands as ethylenediamine (en) and ethylenediaminetetraacetic acid (EDTA), prefixes bis-, tris- are used.

For example: $[Co(en)_2Cl_2]_2SO_4$ Dichlorobis(ethylenediamine)cobalt(III) sulfate.

5- The oxidation state of central atom is mentioned right after the name of the metal with Roman numerals. If the oxidation state is zero, "0" number is used.

For example: $[Ni(CO)_4]$ tetracarbonylnickel (0)

6- If complex compound is a negative ion, name of central atom finishes with suffix –ate. Most of the time, Latin names are used for metals (For example: iron = ferrum, lead= plumbum, etc.) But in positive ionic or neutral complex compounds, name of central metal atom remains unchanged. For example:

$Ca_2[Fe(CN)_6]$	Calcium hexacyanoferrate (II)
$[Fe(H_2O)_6]SO_4$	Hexaaquairon (II) Sulphate
$[Ni(dmg)_2]$	Bis(dimethylglyoximato)nickel (II)

5-7 BONDING THEORIES IN COORDINATION COMPOUNDS

Werner's coordination theory and chain theory were just simple introduction to understand the structures of coordination compounds. Today, there have been three theories proposed to explain the bond structures of coordination compounds. These are:

1- Valence Bond Theory (VBT)

2- Crystal Field Theory (CFT)

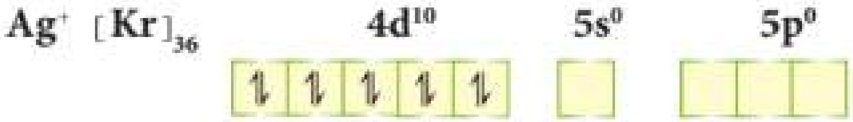
3- Molecular Orbital Theory (MOT)

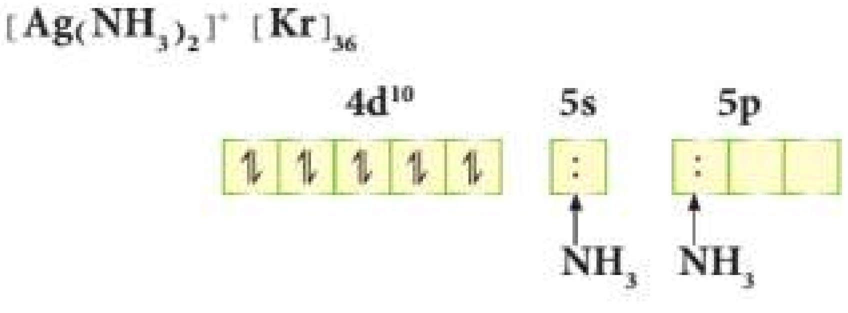
At this level, we will only give a simple explanation of Valence Bond Theory. You can study Crystal Field Theory and Molecule Orbital Theory at university.

5-7-1 Valence Bond Theory

This theory explains the bond structure of coordination compounds successfully. This theory is related to hybridization and geometrical shape of central atom. According to this theory, complex structure is formation of coordinate covalent bond between Lewis base (ligand) and Lewis acid (metal) reaction. In this theory, orbitals of metal are shown with squares (sometimes with circles). They show the electron configuration of metal in outer shell and also electrons of ligands. We will apply this theory to compounds with coordination number of 2, 3 or 4. We will leave the application of this theory to compounds with bigger coordination numbers to upper classes.

For example, in diamminesilver (I) complex ion $[Ag(NH_3)_2]^+$, electron configuration in outer shell of silver and electron configuration of complex compound is as follows:



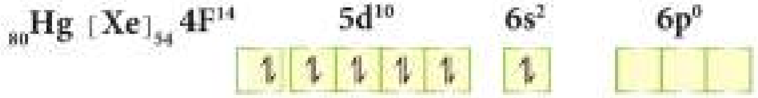


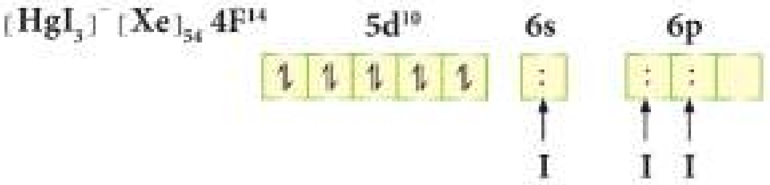
- 4 electrons from 2 ligands
- Hybridization type is sp (while forming a bond, one s orbital and one p orbital are used).
- The shape of complex ion is linear.
- As there are no unpaired electrons, complex ion shows diamagnetic property (all electrons are paired).

Exercise 5-6

Show electron configuration of metal and ligand in $[Cu(CN)_2]^-$ complex compound according to Valence Bond Theory. ($_{29}Cu$)

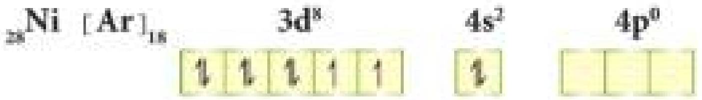
In $[HgI_3]^-$ triiodomercurate (II) complex compound, the configuration of electrons in outer shell and electron configuration of complex compound is as follows:

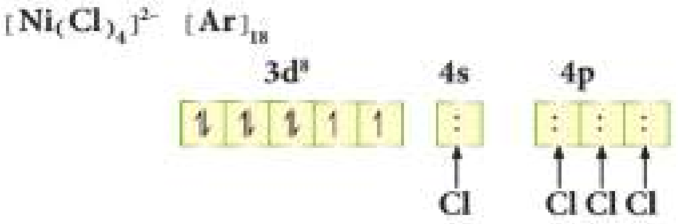




- 6 electrons from 3 ligands
- Hybridization type is sp^2 (in bond formation one s orbital and 2 p orbitals are used).
- Geometrical shape is trigonal planar.
- It shows diamagnetic property as all electrons are paired.

The electron configuration of outer shell nickel and complex compound in tetrachloronickelate (II) $[Ni(Cl)_4]^{2-}$ complex ion is as follows:



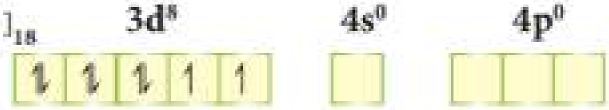


- 8 electrons from 4 ligands
- Hybridization type is sp^3 (In bond formation, one s orbital and 3 p orbitals are used).
- Geometrical shape is tetrahedral.
- It is paramagnetic as it has 2 unpaired electrons.

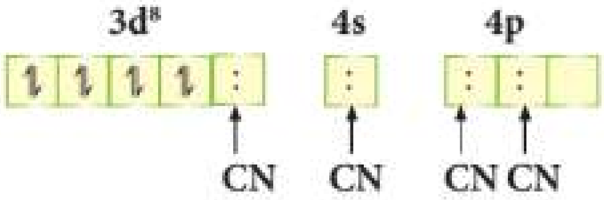
The electron configuration of outer shell of nickel and complex compound in tetracyanonickelate $[Ni(CN)_4]^{2-}$ complex compound is as follows:

$_{28}Ni$ $[Ar]_{18}$

$[Ni^{2+}]$ $[Ar]_{18}$



$[Ni(CN)_4]^{2-}$ $[Ar]_{18}$



- 8 electrons from 4 ligands
- Hybridization type is dsp^2 (in bond formation, one d orbital, one s orbital and 2p orbitals are used).
- Geometrical shape is square planar.
- It shows diamagnetic property as all electrons are paired.

As it is seen in the previous 2 examples, single d electrons remained as they are in $[Ni(CN)_4]^{2-}$ compound. But in $[Ni(Cl)_4]^{2-}$ compound, it (d electron) became an electron pair. In formation of complex compound, type of ligand has an important role. CN^- is accepted as a strong ligand. Because it causes unpaired single electrons to become paired in forming complex. But Cl^- doesn't have such capability. Therefore it is accepted as a weak ligand. Ligands are accepted as weak or strong according to chemical spectrum. Table 5-3 shows those weak and strong ligands.

Table 5-3 SOME STRONG AND WEAK LIGANDS

Weak Ligands		Strong Ligands	
Symbol	Name	Symbol	Name
I^-	Iodide ion	CN^-	Cyanide ion
Br^-	Bromide ion	NH_3	Ammine (ammonnia)
Cl^-	Chloride ion	$NH_2CH_2CH_2NH_2$	Ethylene diamine
F^-	Fluoride ion	NO_2^-	Nitrite ion
OH^-	Hydroxide ion	CO	Carbonyl
H_2O	Aqua	C_5H_5N	pyridine

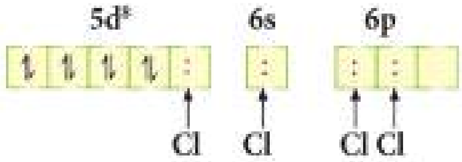
The elements of the second and third transitional chains, their complexes are tetragonal.

If complex compound undergoes dsp^2 hybridization, ligand's geometrical shape is square planar, no matter ligand is strong or weak. The reason for that is volume expansion after hybridization. Therefore, the configuration of electrons in outer shell of platinum metal and complex compound in $[PtCl_4]^{2-}$ compound.

$_{78}Pt\ [Xe]_{54}\ 4F^{14}$

$Pt^{2-}\ [Xe]_{54}\ 4F^{14}$

$[PtCl_4]^{2-}\ [Xe]_{54}\ 4F^{14}$



- 8 electrons from 4 ligands.

- Hybridization type is dsp^2. In bond formation, one d orbital, one s orbital and 2p orbitals are used.

- Geometrical shape is square planar.

- It shows diamagnetic property as there are no single electrons (all electrons are paired).

To learn the geometrical shape of complex compounds with single central atom due to hybridization is possible by calculating their number of single electrons (unpaired electrons). This calculation is made by the following equation. It depends on magnetic momentum resulting from electron movement.

Exercise 5-7

Why $[NiCl_4]^{2-}$ complex compound is paramagnetic while $[PtCl_4]^{2-}$ complex compound is diamagnetic. Explain the reason according to Valence Bond Theory. ($_{28}Ni$, $_{78}Pt$)

$$\mu\ (B.M) = [e(e+2)]^{1/2}$$

In this equation, e = number of single electrons. B.M= Bohr Magneton (magnetic momentum unit).

Let's study Example 5-5 to explain this equation.

Example 5-5

If "L" is a monodentate ligand in $[Co(L)_4]^{2+}$ complex ion of cobalt (II), explain the type of hybridization of the complex compound.

Solution:

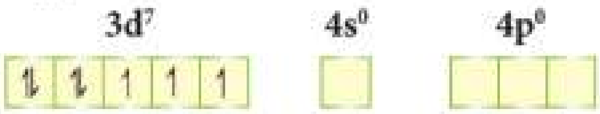
Hybridization can be decided as follows:

1- First Case

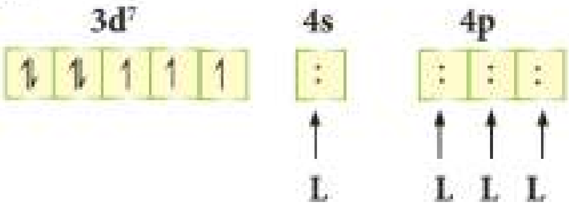
The electron configuration in outer shell of cobalt element and complex compound is as follows:

$_{27}Co\ [Ar]_{18}$

$Co^{2+}\ [Ar]_{18}$



$[Co(L)_4]^{2+}$



If we consider this configuration, we see that the number of unpaired electrons is 3. Therefore, magnetic moment is as follows:

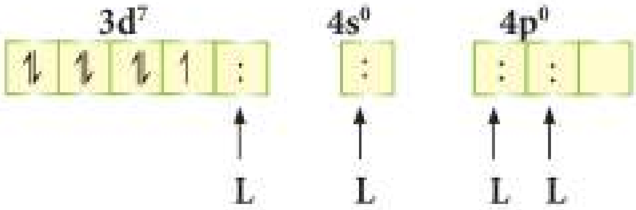
$\mu = [e(e+2)]^{1/2}$

$\mu = [3\ (3 + 2)\ ]^{1/2}$

$= 3.87$ B.M

2- Second Case

The electron configuration of the complex is as follows: $[Co(L)_4]^{2+}$



According to this configuration, the number of unpaired (single) electrons is 1. Therefore, magnetic moment is as follows:

$\mu = [1(1 + 2\ )]^{1/2} = 1.73$ B.M

If we know magnetic moment, we can guess the type of hybridization. In this complex compound, if magnetic moment were 3.87 BM, the type of hybridization would be sp^3 as in the first example. But its magnetic moment is 1.73 B.M, therefore its hybridization type is dsp^2.

Do you know that?

The magnetic momentum value of complexes can be practically measured using a special device called magnetometer.

Exercise 5-8

According to Valence Bond Theory, what are the types of hybridizations, geometrical shapes and magnetic properties of the following two complex compounds? ($_{46}Pd$, $_{27}Co$)

$[PdCl_4]^{2-}$, $[Co(H_2O)_4]^{2+}$

After that calculate the magnetic moment (μ) of each.

Answer:

dsp^2, diamagnetic, square planar
sp^3, tetrahedral, paramagnetic

5-8 COORDINATION NUMBERS AND EXPECTED GEOMETRICAL SHAPES (view only)

Previously, we have learnt that coordination number shows the number of atoms directly bonded to the central metal atom. Besides, we have learnt this number is related to the expected geometrical shape of complex compound. The values of coordination numbers are between 2 and 9. The most common ones are 4 and 6. Now, we will mention coordination numbers from 2 to 4 in coordination compounds. Besides, we will tell the most common geometrical shape of each number.

1- Coordination Number 2

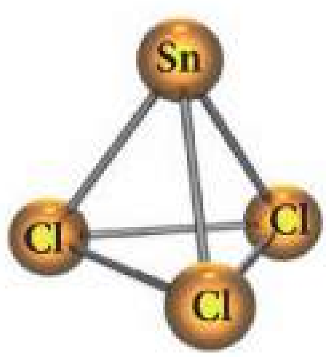
Compounds with coordination number 2 is rare. The best example to this complex compound [Ag(NH$_3$)$_2$]$^+$. As expected, this complex ion has a linear structure, [H$_3$N-Ag-NH$_3$]$^+$. This coordination number is seen in complex compounds of copper (I), silver(I) and gold(I) as in the following examples.

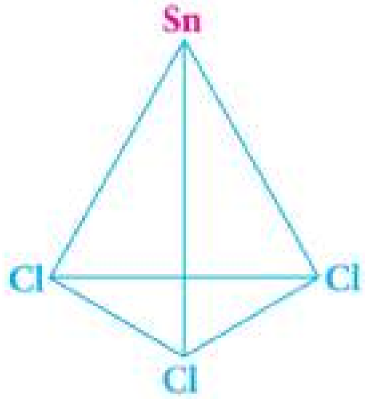
[NC-Ag- CN]$^-$; [Cl – Au – Cl]$^-$; [CN – Cu – CN]$^-$

2- Coordination Number 3

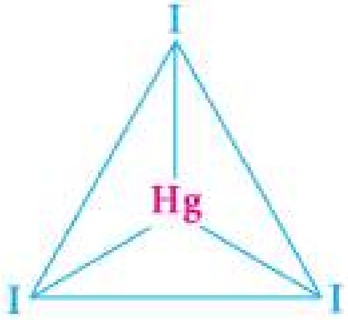
This type of compounds are also rare. Examples of them are few. Negative complex ion [HgI$_3$]$^-$ is the best example of this. In this kind of complexes, two geometrical shapes are expected. The first is trigonal planar and the other is trigonal pyramid shape. [HgI$_3$]$^-$ has trigonal planar shape whereas

SnCl$_3^-$ is trigonal pyramid.





SnCl$_3^-$

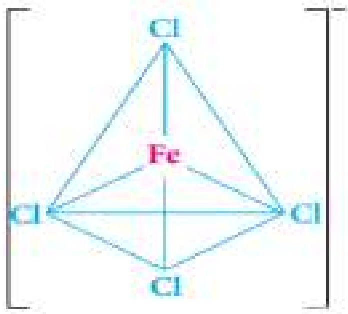


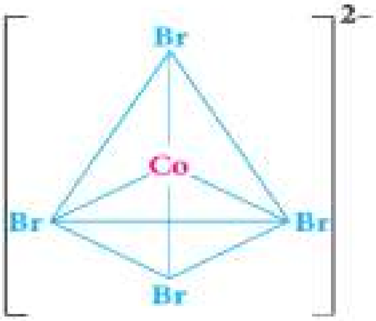
[HgI$_3$]$^-$

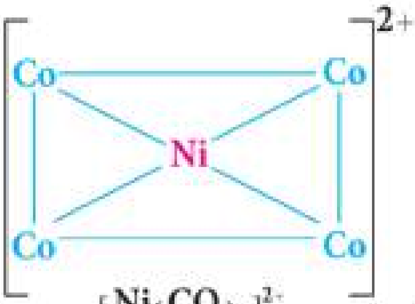
3- Coordination Number 4

This is the most common coordination number. Coordination compounds with this number have great importance in coordination chemistry. This coordination number causes formation of coordination compounds in which ligands are coordinated around the central metal atom in tetrahedral or square planar shapes. Examples of tetrahedral complex compounds are:

[CoBr$_4$]$^{2-}$; [FeCl$_4$]$^-$







[Ni(CO)$_4$]$^{2-}$

Square planar shaped complex compounds are formed by especially ions. For example,

Au^{3+} , Pt^{2+}, Pd^{2+}, Cu^{2+}, Ni^{2+}, [PtCl$_4$]$^{2-}$, [Pd(CN)$_4$]$^{2-}$, [Ni(CO)$_4$]$^{2+}$

QUESTIONS OF CHAPTER-5

5-1- What are the distinctive properties of transition elements?

5-2- What is the difference between double salts and complex compounds?

5-3- When $FeSO_4$ and $(NH_4)_2SO_4$ solutions are mixed in 1:1 mole ratio, Fe^{2+} ion appears in the resulting solution. But when $CuSO_4$ solution is mixed with ammonia solution in 4:1 ratio, no Cu^{2+} ion is observed. Explain this by giving reason(s).

5-4- Define effective atomic number. Then calculate this number in the following complexes:

1- $[PtCl_6]^{2-}$

2- $[Pt(NH_3)_6]$

3- $[FeCl_4]^-$

4- $[Cr(NH_3)_6]^{3+}$

5- $[Ag(NH_3)_2]^+$

Answers: 1) 86, 2) 90, 3) 31 ,4) 33 , 5) 50

5-5- What are the oxidation states (first valence) of iron in the following compounds?

1- $[Fe(CO)_5]$

2- $[Fe(C_2O_4)_3]^{3-}$

3- $K_3[Fe(CN)_6]$

4- $[Fe(H_2O)_5(NO)]SO_4$

Answers: 1) 0 2) (+3) 3) (+3) 4) (+2)

5-6- Name the following complex compounds:

1- $[Fe(H_2O)_5(NO)]^{2+}$

2- $Na_2[Fe(CN)_5(NO)]$

3- $[Co(N_3)(NH_3)_5]SO_4$

4- $K_4[Ni(CN)_4]$

5- $[Cr(H_2O)_4Cl_2]^+$

6- $[Ni(en)_2Cl_2]^{2+}$

7- $[Co(NO_2)_3(NH_3)_3]$

8- $K_2[PtCl_6]$

5-7- Write down structural formulas for the following complex compounds:

A- Tris(ethylenediamine)cobalt(III) nitrate

B- Potassium tetracyanonickelate(0)

C- Aquabis(oxalato)chromate(III) ion

D- Potassium tetrachloronickelate (II)

E- Potassium tetrachloromanganate (II)

F- Hexaaquatitanium(III) chloride

G- Tetracarbonylnickel (0)

H- (Ethylenediamine)tetraiodochromate (III) ion

I- Aquacyanobis(ethylenediamine)cobalt (III) ion

J- Tetraamminecopper (II) ion

5-8- Answer the following questions for the 3 given coordination compounds.

$[Cr(H_2O)_5Cl]Cl_2.H_2O$, $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

A- What is the oxidation number (first valence) of chromium in each compound?

B- What is the coordination number of chromium in each compound?

5-9- Circle the right answer in the following questions.

1- What is the oxidation number (first valence) of $[Cr(H_2O)_4Cl_2]^+$?

A) 3 B) 1 C) 6 D) 5

2- What is the structural formula for dichlorobis(urea)copper(II) compound?

A) $[Cu\{(NH_2)_2CO\}_2]Cl_2$

B) $[Cu\{(NH_2)_2CO\}Cl]Cl$

C) $[CuCl_2\{(NH_2)_2CO\}_2]$

D) None of the above

3- According to IUPAC system, what is the name of the $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ compound?

A) triamminechlorobromonitroplatinum(IV) chloride

B) chlorotriamminebromonitroplatinum(IV) chloride

C) triamminebromochloronitroplatinum(IV) chloride

D) triamminenitrochlorobromoplatinum(IV) chloride

5-10- Reply the questions about the following coordination compounds according to Valence Bond Theory (VBT).

$[PtCl_4]^{2-}$; $[Pd(CN)_4]^{2-}$; $[Ni(dmg)_2]$; $[CoCl_4]^{2-}$; $[Zn(CN)_4]^{2-}$; $[Co(CN)_4]^{2-}$; $[ZnCl_2(NH_3)_2]$

A- What is the type of hybridization of central atom?

B- What is the geometrical shape of complex compound?

C- What is the magnetic property of complex compound? Why?

5-11- What are the numbers of single (unpaired) electrons in the following coordination compounds according to Valence Bond Theory? What is the value of magnetic moment value (**μ**) in each?

$[Ni(H_2O)_4]^{2+}$; $[Ni(NH_3)_4]^{2+}$

5-12- Suppose that $[NiL_4]^{2-}$ complex ion contains Ni (II) and L monodentate ligand which is weak. Answer the following questions according to the complex ion. ($_{28}Ni$)

1- What is the charge of the ligand?

2- What is the hybridization type of the central atom?

3- What is the value of magnetic momentum (μ)?

5-13- Define the following terms:

Coordination compound, ligand, donor atom, coordination number, chelating ligand

CHEMICAL ANALYSIS

CHAPTER-6

ACHIEVEMENTS

After completing this chapter, the student is expected to :

* Learn different methods of chemical analysis.
* Differentiate qualitative and quantitative analysis.
* Have information about some positive ions.
* Understand the importance of quantitative analysis method in determining the amounts of unknown compounds.
* Learn steps of quantitative analysis and how to do it.
* Perform necessary calculations in quantitative analysis.
* Understand the importance of volumetric analysis in determining the amount of substance dissolved and concentration of unknown solution.
* Learn calculation of equivalent mass of different substances and relationship between chemical reactions.
* Learn some laboratory equipments which are used in volumetric analysis.

Chapter - 6

6-1 PREFACE

Chemical analysis has wide applications in industry, chemistry, biology, geology and in other science fields. For example, while analyzing air pollution, it is necessary to measure the amounts of hydrocarbons, nitrogen oxides and carbon monoxide from exhaust fumes. To diagnose goiter illness, it is necessary to find out calcium amount in human blood. The amount of nitrogen from food we consume gives the amount of protein. In industry, by regular mass analysis, the strength of iron and its resistance to corrosion can be checked. As it is understood from those examples, chemical analysis has an important place in life.

The chemical analysis which is used to find out the components (elements or compounds) which form a substance is called as qualitative analysis and the analysis which is used to find out the percentage of the components of a substance is called as quantitative analysis.

6-2 METHODS OF QUALITATIVE ANALYSIS

The aim of qualitative analysis of a sample is to find out what the component(s) is/are in a mixture or solution and how these components (elements or a group of elements) are bonded to each other. The substance which is wanted to be analyzed is usually transformed to a known compound by a substance called as **detector**.

For example, a mixture of common positive ions can be analyzed. In this case, qualitative analysis is a two-step process. In the first step, ions are separated. In the second step, through some certain chemical reactions, ions are detected. To apply qualitative analysis, the sample is divided into groups. The reaction of each group against different precipitants is examined. When the right precipitant is added to solution, it precipitates the target ion and the resulting solid is extracted from other ions by filtering method.

Common positive ions in nature are divided into 5 groups according to the precipitation factor (Table 6-1). In other words, the ions in the same group are precipitated with the same substance. The analysis process starts from the first group and continues to the last group by addition of precipitant until the precipitate is formed.

First, dilute hydrochloric acid (HCl) is added to solution and (Ag^+, Pb^{2+}, Hg_2^{2+}) from 1st group ions are separated from the solution in the form of chlorides of these ions with filter paper. In order to precipitate 2nd group ions (Hg^{2+},Cu^{2+},Bi^{3+},Cd^{2+},Pb^{2+},Sn^{2+} , As^{3+},Sb^{3+}) hydrogen sulfide gas (H_2S) is passed through the solution. In the remaining solution, upon addition of ammonium chloride (NH_4Cl) and ammonium hydroxide (NH_4OH) solution, IIIA group positive ions are precipitated. Separation process goes on like this.

After positive ions are separated according to their groups, precipitate of each group is analyzed to learn the presence of ions.

In the following experiment, the separation of first group ions from other groups and methods of detection will be given.

Table 6-1 Group of positive ions, precipitants and chemical formula of precipitates

Group		Precipitants	Ions	Precipitates
I		Dilute Hydrochloric acid (HCl)	Ag^+, Hg_2^{2+}, Pb^{2+}	$AgCl$, Hg_2Cl_2, $PbCl_2$
II		Dilute Hydrochloric acid upon addition of hydrogen sulfide gas (H_2S)	Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Pb^{2+}, Sn^{2+}, As^{3+}, Sb^{3+}	HgS, CuS, Bi_2S_3, CdS, PbS, As_2S_3, Sb_2S_3, SnS
III	A	Ammonium hydroxide + ammonium chloride (NH_4Cl, NH_4OH)	Al^{3+}, Cr^{3+}, Fe^{3+}	$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$
	B	By passing hydrogen sulfide gas (H_2S) into (NH_4Cl, NH_4OH)	Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}	NiS, ZnS, CoS, MnS
IV		Addition of $(NH_4)_2CO_3$ into NH_4Cl, NH_4OH	Ca^{2+}, Ba^{2+}, Sr^{2+}	$CaCO_3$, $BaCO_3$, $SrCO_3$
V		Substance remaining in final solution without precipitation	Mg^{2+}, Na^+, K^+, NH_4^+	

6-2-1 Separation of Group (I) Ions and Detection

As mentioned above, first group positive ions (Ag^+, Pb^{2+}, Hg_2^{2+}) are separated from solution by precipitation as chloride compounds. In the second step, each positive ion is detected according to the following principles.

1. $PbCl_2$ precipitate dissolves in hot water but $AgCl$ and Hg_2Cl_2 don't dissolve in hot water. Dissolved $PbCl_2$ is separated by filtering from other precipitates upon addition of hot water. In order to detect lead, K_2CrO_4 detector is added to the filtered substance. If there is lead, yellowish $PbCrO_4$ precipitates according to the following equation.

$$PbCl_2 + K_2CrO_4 \rightarrow \underset{\text{yellow precipitate}}{PbCrO_4\downarrow} + 2KCl$$

2. After separation of lead chloride, dilute ammonia solution is added to the remaining solution (Hg_2Cl_2, $AgCl$). Silver chloride $AgCl$ forms a complex compound diamminesilver(I) chloride $[Ag(NH_3)_2]Cl$ which dissolves in ammonia solution and passes filter. To detect silver, dilute nitric acid (HNO_3) is added and a white precipitate forms or potassium iodide (KI) solution is added and a yellow precipitate forms.

$$AgCl + 2NH_3 \rightarrow \underset{\text{diamminesilver(I) chloride}}{[Ag(NH_3)_2]Cl}$$

$$[Ag(NH_3)_2]Cl + 2HNO_3 \rightarrow \underset{\text{white precipitate}}{AgCl\downarrow} + 2NH_4NO_3$$

$$[Ag(NH_3)_2]Cl + KI \rightarrow \underset{\text{yellow precipitate}}{AgI\downarrow} + KCl + 2NH_3$$

Attention:

Pb^{+2} is in both groups I and II, because solubility of lead ion is high and some may not precipitate when dilute HCl is added.

Exercise 6-1

Complete the following reactions.

$$Hg_2^{2+} + \underset{\text{dilute}}{HCl} \rightarrow$$

$$Bi^{3+} + H_2S \xrightarrow[\text{dilute}]{HCl}$$

$$Al^{3+} + NH_4OH \xrightarrow{NH_4Cl}$$

$$Mn^{2+} + H_2S \xrightarrow[NH_4Cl]{NH_4OH}$$

Mercury (I) chloride (Hg_2Cl_2) reacts with ammonia solution and forms a black precipitate according to the following equation.

$$Hg_2Cl_2 + 2NH_3 \rightarrow \underset{\text{white precipitate}}{Hg(NH_2)Cl \downarrow} + \underset{\text{Black precipitate}}{Hg \downarrow} + NH_4Cl$$

Upon addition of king's water (HNO_3+3HCl), a soluble salt $HgCl_2$ is formed. To detect mercury, tin (II) chloride ($SnCl_2$) is added to the solution and a precipitate is obtained which is white in the beginning then turns into black.

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + \underset{\text{white precipitate}}{Hg_2Cl_2 \downarrow}$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + \underset{\text{Black precipitate}}{2Hg \downarrow}$$

Example 6-1

How are silver, cadmium and iron (III) ions separated?

Solution:

Silver (Ag^+) ion is in Group I, cadmium (Cd^{2+}) is Group II and iron (III) (Fe^{3+}) is in Group III. Therefore, we need to add precipitants in order.

1. When dilute hydrochloric acid solution is added, only silver ion precipitates as AgCl. Cadmium and iron ions remain as dissolved. We can separate silver chloride from other components of solution by filtering.

2. H_2S gas is passed through the solution. As a result, cadmium ions precipitate as cadmium sulfide and are separated from solution by filtering method.

3. Only iron (III) ions remain in the solution. We can precipitate iron in iron(III) hydroxide ($Fe(OH)_3$) form by adding ammonium hydroxide and ammonium chloride solutions.

6-3 QUANTITATIVE ANALYSIS

Quantitative analysis aims to determine the amount of target substance in a sample. For example, calculation of percentage of iron in a rock is an application of quantitative analysis. The amount of substance can be expressed as percentage and also in a ratio of thousand, million or even billion. Besides, the amount of substance is expressed as the mass or volume of matter found in a certain volume of the sample or described as molar ratio.

Quantitative analysis process is applied through two measurements. The first is the amount of the subject sample, and the second is the amount of the component which we want to measure in the sample. Mass, volume, strength of color, absorption intensity, electric intensity or any physical or chemical property about the amount of matter can be given as examples to measurements during analysis. But, in this book, we will cover measurements of number of moles, equivalent mass, mass and volume which show amount of matter.

Before applying quantitative analysis, the following are the steps to be made.

1. **Exemplifying:** It is the method of obtaining the sample which represents the substance in a right way.

2. **Preparing the sample:** The sample undergoes a preparation process for analysis in laboratory. It includes processes as grinding the solid sample, mixing, making it homogeneous and removing the moisture in it.

3. **Measuring the sample:** In order to determine the amount of matter correctly, the mass and volume of the sample to be analyzed needs to be known precisely.

4. **Dissolving the sample:** Chemical analysis is usually made on solutions. Therefore, a solution of the sample needs to be prepared. This solution is prepared with a solvent which can dissolve not only the target component in the sample but all of the components. The solvent normally doesn't change the amount of the sample.

5. **Separating the mixed substances:** There are certain substances which have physical and chemical properties with which correct measurement processes can be made in quantitative analysis. In this case, measurements can be estimated directly. But in many cases, by measuring one of properties directly, it may not be possible to identify the substance. To make measurements in quantitative analysis, chemical reactions with the target compound are necessary. Those reactions used in chemical analysis and measured properties may be common for some elements and compounds in the sample. This situation affects results of analysis and some problems may arise in chemical analysis processes. For this reason, the target substance needs to be separated from other components in the sample which affect analysis. The other elements in the sample which affect the results of the target substance are called as interferents. Separating those before measurement is important for analysis.

Practically, the person working in quantitative analysis field may apply many different analysis methods to get results. In order to choose the most suitable method, many factors need to be considered. The urgency of analysis, suitability and degree of correctness, supplying tools and devices, number of samples, amount of samples and concentration of target substance in sample, cost of analysis are some of those factors. Therefore, the success of analysis depends on choosing the suitable method.

Quantitative analysis includes many methods with respect to their uses and significance. Those are usually considered in two titles:

6-3-1-Quantitative Chemical Analysis

Under this title, classical analysis methods are placed. Those are:

1- Gravimetric analysis methods: depend on measurement of mass.

2- Volumetric analysis methods: depend on measurement of volume.

6-3-2-Instrumental Analysis

Different instruments are used in analysis. In this chapter, classical analysis methods will be studied.

6-4-GRAVIMETRIC ANALYSIS

In gravimetric analysis, a substance related to another substance with a known chemical structure is separated and its mass is measured correctly. Separation process is made from a sample with a known amount. In gravimetric analysis, the target substance is usually transformed into a pure and a chemically stable compound. This compound has a shape and formula which enables measuring its weight precisely. After measurement, as the chemical formula of the substance is known, its mass can be calculated.

In gravimetric analysis, the target substance is separated through different methods. The most important of those are:

1- Volatilization method

2- Precipitation method

3- Electrical precipitation method

4- Other physical methods

6-4-1-Volatilization Methods

These methods depend on removal of the volatile substance in the sample. This process is applied through different methods below:

A-Sample burning method in air at high temperature Figure (6 – 1)

B- The method in which the sample undergoes reactions with chemical indicators and volatilize its components and target substance residues. Afterwards, volatilized substances are collected in a suitable medium and their mass is calculated. This method is called direct volatilization. In indirect volatilization, the mass of volatile substance is calculated through the loss in mass of the sample. For example, we can determine the percentage of crystal water in aqueous barium chloride
($BaCl_2 .2H_2O$) by direct volatilization method through heating.

$$BaCl_2.2H_2O \xrightarrow{\text{heating}} BaCl_2 + 2H_2O\uparrow$$

(volatile substance)

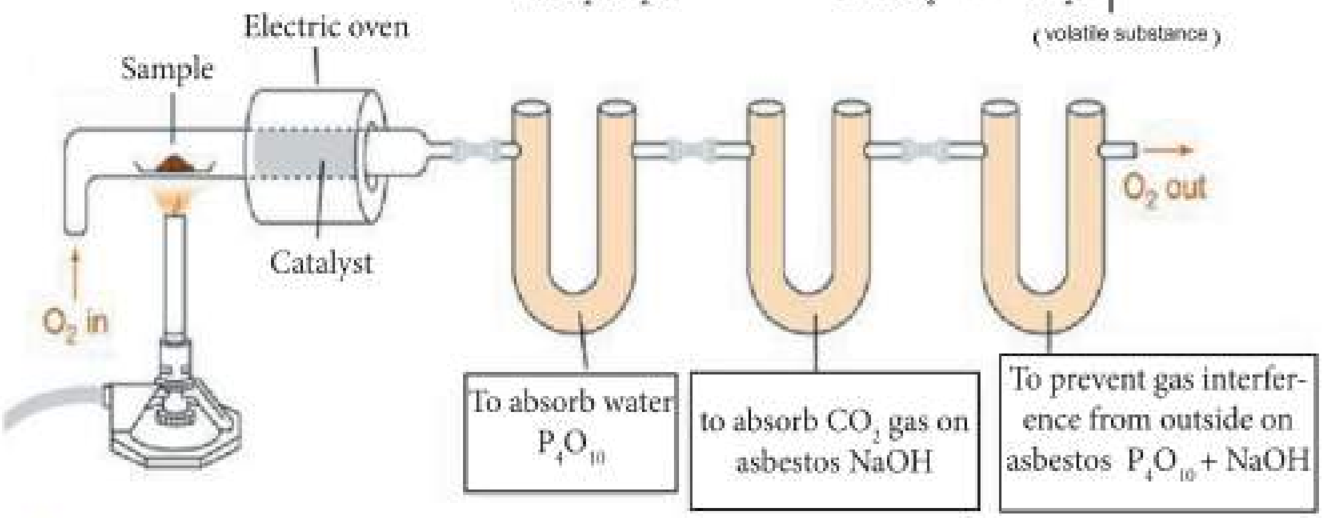


Figure (6 – 1)

The vapor is absorbed on a suitable medium and its weight is measured. To determine crystal water in aqueous barium chloride by indirect volatilization method, it is heated in open air and this causes water to vaporize. The mass of residue $BaCl_2$ is measured and the mass of crystal water is determined by subtracting this mass from the sample's mass.

In another example, to determine the mass of carbon dioxide CO_2 in calcium carbonate sample, hydrochloric acid HCl is added to it.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + \underset{\text{volatile substance}}{CO_2\uparrow} + H_2O$$

Carbon dioxide gas is passed through a drying substance to remove its moisture, and then it is absorbed by a suitable medium (asbestos immersed in sodium hydroxide solution). The mass of carbon dioxide is calculated through the mass increase in absorbent medium.

Example 6-2

1.451 g of aqueous barium chloride ($BaCl_2.2H_2O$) sample was analyzed through indirect volatilization method to determine the mass of crystal water. The sample was heated at 125 °C for some time and then it was cooled in a dry medium. As the mass of solid substance is 1.236 g, what is the mass percentage of crystal water in the sample?

Solution:

$$\text{Percentage of crystal water} = \frac{\text{Mass of crystal water}}{\text{Mass of the sample}} \times 100\%$$

The mass of crystal water lost during volatilization is calculated through the following equation:

$$\underset{\text{before heating}}{BaCl_2.2H_2O} \xrightarrow{\text{heating}} \underset{\text{after heating}}{BaCl_2} + \underset{\text{volatile substance}}{2H_2O}$$

Mass of crystal water = mass of the sample before heating - mass of the sample after heating

$$m_{H_2O}(g) = m_{BaCl_2.2H_2O} - m_{BaCl_2}$$

$$m_{H_2O}(g) = 1.451\ (g) - 1.236\ (g) = 0.215\ g$$

Percentage of crystal water:

$$H_2O\ \% = \frac{m_{H_2O}(g)}{m_{BaCl_2.2H_2O}(g)} \times 100\%$$

$$H_2O\ \% = \frac{0.215\,(g)}{1.451\,(g)} \times 100\% = 14.81\%$$

Example 6-3

A sample of organic matter was analyzed through direct volatilization method to determine its carbon percentage. 15.24 mg sample was burnt in aerobic conditions and CO_2 gas was absorbed on a suitable medium. As the mass of carbon dioxide is 22.36 mg, calculate the percentage of carbon element in the compound.

Solution:

$$\text{Percentage of carbon} = \frac{\text{Mass of carbon}}{\text{Mass of the sample}} \times 100\%$$

We can calculate the mass of carbon from evolved CO_2 gas. Because this gas was emitted through burning of carbon in the sample.

$$C \xrightarrow{\text{burning with oxygen}} CO_2\uparrow$$

$$m_C = m_{CO_2}\,(\text{mg}) \times \frac{M_C\,(\text{g/mol})}{M_{CO_2}\,(\text{g/mol})}$$

$$m_C = 22.36\,(\text{mg}) \times \frac{12\,(\text{g/mol})}{44\,(\text{g/mol})} = 6.1\text{ mg}$$

$$C\,\% = \frac{m_C}{m_{\text{sample}}} \times 100\% = \frac{6.1\,(\text{mg})}{15.24\,(\text{mg})} \times 100\% = 40\%$$

Exercise 6-2

Alloy containing nickel, chromium and a small amount of carbon was analyzed gravimetrically by volatilization method. 1.4 g of mixture was burnt in aerobic conditions and emitted CO_2 gas was collected. As the mass of CO_2 gas is 2.2 mg, find the percentage of carbon in the Alloy.

(C:12 g/mol, CO_2: 44 g/mol)

Answer: 0.043%

6-5 PRECIPITATION METHODS

Gravimetric analysis method which depends on precipitation reactions consist of some steps that need to be made quantitatively (that means in a way without any increase or decrease in amount of matter).

These steps are as follows:

1- Dissolving a known, accurate mass from the sample in a suitable solvent. weighing is done using scales that vary in accuracy from one to another. some of them are accurate (sensitive), with an accuracy of four decimal places for gram, and one with one decimal place for gram.

2- To precipitate a sample in a solution as in the form of a compound which is slightly-soluble a precipitate is formed with a known chemical formula. By using a suitable (chemical reagent) precipitating agent.

3- Separating and removing precipitate from a solution by filtering.

Some scales (micro-balances) to weigh samples

4- Washing the precipitate: The precipitate separated from its solution remains on the filter paper. To remove the impurities on the precipitate, it needs to be washed with a suitable solvent. The solvent used for washing needs to have some properties. These are:

a- It shouldn't affect the solubility of the precipitate; it should only help to dissolve impurities.
b- It shouldn't form a volatile compound with the precipitate.
c- It should be volatile to be removed from the precipitate easily.

Addition of chemical reagent to the sample solution and formation of the precipitate

5- Drying the precipitate: This step means that precipitation formula (the chemical formula of the formed precipitate) is transformed to a suitable mass formula. This process is done through drying (sometimes at a temperature over 100 °C) or burning (temperature reaching 1000 °C.)

Thus, the precipitate is removed from any type of moisture (base water, retained water, crystal water)

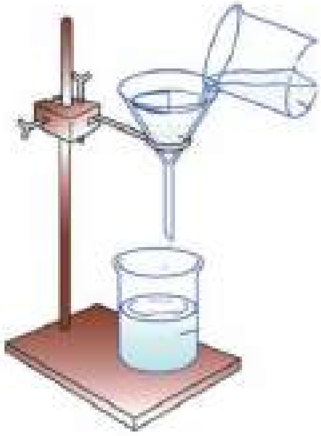
$$\underset{\text{precipitate formula}}{CaC_2O_4.H_2O} \xrightarrow{\text{drying at 130 °C}} \underset{\text{mass formula}}{CaC_2O_4} + H_2O\uparrow$$

$$\underset{\text{precipitate formula}}{Al_2O_3.xH_2O} \xrightarrow{\text{drying at 130 °C}} \underset{\text{mass formula}}{Al_2O_3} + xH_2O\uparrow$$

Burning process causes removal of water from the structure of the precipitate and also decomposition of the precipitate through thermal reactions.

$$CaC_2O_4.H_2O \xrightarrow[\text{130 - 225 °C}]{\text{drying}} CaC_2O_4 + H_2O \xrightarrow[\text{400 - 490 °C}]{\text{burning}}$$

$$CaCO_3 + CO\uparrow \xrightarrow{\text{burning at 840 °C}} CaO + CO_2\uparrow$$



Removal of substance by precipitation and then washing with a suitable solvent.

6- The precipitate is weighed for accurate calculation of its mass through mass formula. To achieve mass analysis and get accurate results, there are factors need attention:

1- In order to prevent loss of mass in precipitate, it should have a very slight solubility.

2- The precipitate needs to have some physical properties to be separated from solution quantitatively and removed from impurities. The crystals of the precipitate must be at suitable sizes. Thus, impurity possibility is low, the precipitate cannot pass through the filter paper and the size of the particles isn't affected from washing process.

3- The precipitate must be suitable to be dried, burnt or to be processed with suitable chemical reagents in order to be converted to a pure substance with a stable chemical formula.

6-5-1- Separating the precipitate by filtering and purifying

Separating the precipitate principally depends on the particle size of the precipitate. The precipitates with bigger particle sizes can be separated fully, quickly and easily. If the precipitate has a small particle size, a filter paper with smaller pores needs to be used for separation. In this case, separation takes more time and it is more difficult. On the other hand, the relationship between particle size and purity of the precipitate isn't clear. But, generally precipitates with bigger particle sizes can be obtained in a purer form.

Drying oven: It is used to dry precipitates at hight temperature. (It can reach 100°C temperature)

6-5-2- The factors affecting the particle size of the precipitate

There are some factors affecting the size of particles of the precipitate during precipitation process. Some of those depend on the type of the precipitate while some depend on the conditions under which precipitation is made. If the precipitate is in the form of colloidal form (the volume of the particles in this precipitate is nearly 10^{-4}-10^{-6} mm.) this kind of particles cannot be separated by filtering. The other type of precipitate has comparably bigger sized particles. These particles can be separated from solution easily. The aim of the precipitation process is to have a crystallized precipitate. This is a preferred property for a precipitate. The most significant conditions affecting the precipitation are as follows:

1- The characteristic and chemical structure of the precipitate: Compounds like $BaSO_4$ dissolve slightly. This kind of substances form crystallized precipitates when they are comparing with substances as AgCl at the same condition for precipitation.

2- Solubility of the precipitate: precipitates with relatively high solubility in the precipitation environment (relatively much soluble) form crystallized precipitates and vice versa.

3- Temperature: During precipitation, generally the solubility of most precipitates increases with temperature and a crystallized precipitate forms as a result of precipitation at high temperatures. Because, by slowing the precipitation process, necessary time for crystallization is supplied.

4- The concentrations of substances involved in precipitation process: In precipitation process, dilute solutions (valid for the target component and the solvent) are preferred. During the process, the precipitating agent must be added slowly and solution must be mixed continuously. Under these conditions, necessary time for the formation of precipitate crystals is supplied and therefore a crystallized precipitate is formed.

Muffle furnace: It is used to burn precipitates over 1000 °C temperature.

6-5-3- Chemical structure of precipitate and calculations in Gravimetric Analysis

After drying and burning steps, the last step in gravimetric analysis is weighing the precipitate correctly. Because the resulting substance isn't exactly the substance to be measured itself but usually another substance containing it. For example, in order to measure barium in a sample by gravimetric analysis, it is precipitated as $BaSO_4$. At the end of the precipitation process, the precipitate is weighed as $BaSO_4$ after separation, washing and drying processes finished. (mass formula):

$$\underset{\text{precipitating agent}}{Ba^{2+} + SO_4^{2-}} \rightleftharpoons \underset{\text{precipitating formula}}{BaSO_4} \xrightarrow{\text{separation and drying}} \underset{\text{mass formula}}{BaSO_4}$$

In the following example, calcium is weighed as calcium oxide:

$$\underset{\text{precipitating agent}}{Ca^{2+} + C_2O_4^{2-}} \rightleftharpoons \underset{\text{precipitating formula}}{CaC_2O_4} \xrightarrow{\text{separation and burning}} \underset{\text{mass formula}}{CaO + CO\uparrow + CO_2\uparrow}$$

Therefore, at the end of each gravimetric analysis, after determining the net weight of mass formula by a micro-balance, some calculations are necessary to learn the amount of substance to be measured (sought substance). These calculations depend basically on equilibrium reactions (or reaction groups) and include application of percentage and ratio rules.

$$\frac{\text{Molar mass of sought substance (atomic or molecular)}}{\text{Molar mass of gravimetric formula}} = \frac{\text{Mass of sought substance}}{\text{Mass of gravimetric formula (mass of precipitate)}}$$

- The ratio of molar mass of the sought substance to molar mass of gravimetric formula is called as Gravimetric factor, G_f (G: First letter of word gravimetric and F: first letter of word factor.) (For the component in mass formula)
- But in both formulas, contain the same number of atoms of the element or molecules of the compenent to be estimated.

$$G_f = \frac{a}{b} \times \frac{M_{\text{sought substance}}\ (g/mol)}{M_{\text{Mass formula}}\ (g/mol)}$$

In this formula, a and b shows the lowest numbers for two compounds to have the same sought substance in numerator and denominator. Below are examples on how gravimetric factor is calculated.

Example 6-4

Calculate the gravimetric factor of chloride (sought substance) in AgCl (mass formula) precipitate. (M_{AgCl}= 143.5 g/mol), (M_{Cl}= 35.5 g/mol)

Solution:

In this example, chloride is the sought substance. AgCl is accepted as gravimetric formula.

$$G_f = \frac{a}{b} \times \frac{M_{Cl}\ \cancel{(g/mol)}}{M_{AgCl}\ \cancel{(g/mol)}}$$

As both formulas contain the same number of chloride atoms, a and b are both equal to 1. Therefore, G_f which is gravimetric factor of silver chloride is calculated as follows:

$$G_f = \frac{1}{1} \times \frac{35.5\ \cancel{(g/mol)}}{143.5\ \cancel{(g/mol)}} = 0.25$$

If the result is examined, it is seen that gravimetric formula is a numeric value and therefore, it doesn't have a unit.

Gravimetric factor is used in calculating the mass of the sought component. This is done practically by the mass of precipitate as shown in the following formula. For this, gravimetric factor is multiplied by mass of precipitate (mass formula).

(1) $$m_{\text{sought substance}}\ (g) = G_f \times m_{\text{mass formula}}\ (g)$$

Or the following equation is used to calculate the percentage of the sought substance found in sample.

(2) $$\text{Percentage of sought substance }\% = \frac{M_{\text{sought substance}}\ (g/mol)}{M_{\text{sample}}\ (g/mol)} \times 100\%$$

If we insert m from Equation 1 in Equation 2, we get the following:

$$\text{Percentage of sought substance }\% = \frac{G_f \times m_{\text{mass formula}}\ (g)}{m_{\text{sample}}\ (g)} \times 100\%$$

Exercise 6-3

Calculate gravimetric factor of iron in Fe_2O_3 compound. (M_{Fe}= 56 g/mol; $M_{Fe_2O_3}$=160 g/mol)

Answer: 0.7

Example 6-5

What is the mass of calcium oxide (CaO) formed by complete burning of 3.164 g of calcium oxalate (CaC_2O_4) ?

Solution:

Firstly, the equilibrium reaction showing the burning is written.

$$CaC_2O_{4(solid)} \xrightarrow{\text{burning}} CaO_{(solid)} + CO_2\uparrow + CO\uparrow$$

Then, gravimetric factor of CaO (M = 56 g/mol) in calcium oxalate CaC_2O_4 (M=128 g/mol) is calculated. a and b is determined as 1. (Because the number of calcium atoms in both formulas are equal)

$$G_f = \frac{a}{b} \times \frac{M_{CaO}}{M_{CaC_2O_4}}$$

$$G_f = \frac{1}{1} \times \frac{56\ g/mol}{128\ g/mol} = 0.4375$$

In order to get the mass of CaO, gravimetric factor is multiplied with mass of CaC_2O_4 according to the following equation:

$$m_{CaO}\ (g) = G_f \times m_{CaC_2O_4}\ (g)$$

The mass of calcium oxide is found as follows:

$$m_{CaO}\ (g) = 0.4375 \times 3.164\ g = 1.384\ g$$

Exercise 6-4

120 mg of an organic substance was treated with nitric acid. Then, in order to precipitate the chloride content of the compound quantitatively as silver chloride, some silver nitrate was added to the resulting solution above. As the mass of the precipitated silver chloride is 153 mg, calculate the percentage of chloride (M_{Cl} =35.5 g/mol) in the sample.

(AgCl: 143.5 g/mol)

Answer: 31.5%

6-6 VOLUMETRIC ANALYSIS

Volumetric analysis is a quantitative analysis method. It is based on the volume measurement of a chemical reagent with unknown concentration with the help of another solution with known concentration. The solution with known concentration is called as standard solution. Therefore, this solution is defined as follows: It is a solution which contains a known and certain amount of reagent in a certain volume. (Equivalent grams, number of moles or grams etc.) After volumetric analysis process is finished, from the volume of standard solution, the amount of sought component can be calculated according to chemical valence rules.

In order to obtain standard solutions, direct preparation method of solution is used. This is done through dissolving a certain amount of standard substance in a certain volume of solvent (distilled water is usually used as solvent.) The solution prepared through this method is called as **primary standard solution**.

On the other hand, most of the time standard solutions are prepared through standardization method. In this method, it is done through precise measurement of volume of solution which reacts with a certain amount of standard substance in order to determine precise concentration of solution. In this case, standard solution is called as **secondary standard solution**.

As known, not all chemical substances which are used to prepare solutions are standard substances. Standard substances to be used must have the conditions listed below:

1- need to be **stable with high purity.**
2- mustn't react or absorb air components (moisture, oxygen, or carbon dioxide) and are not affected by light.
3- must have a big equivalent mass in order to minimize mistakes which can occur at weighing process while preparing solution.

4- need to have the capability of dissolving in the solvent (mostly distilled water) which is used in analysis.

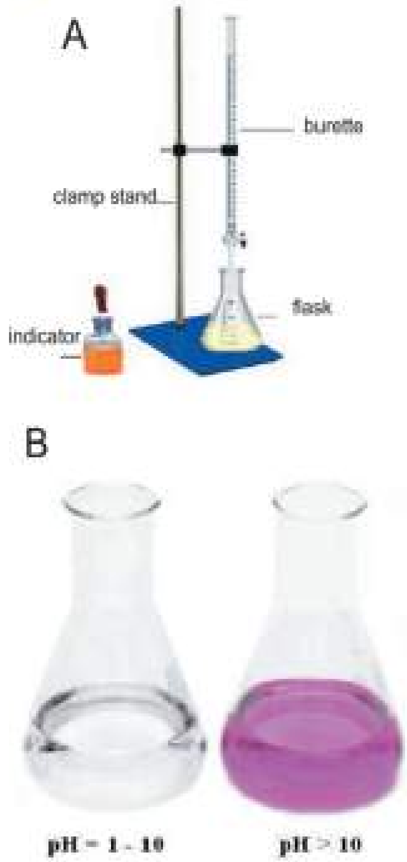
5- Non-poisonous substances are preferred.

6- Preferably, need to be cheap and found abundantly.

6-6-1 Titration

Most of the time, volumetric analysis is done at laboratory. This is done through quantitative volume measurement of one of the solutions (e.g. standard solution) which is necessary to react with a certain amount of unknown solution. Then, the concentration of the unknown solution is calculated. This process is performed by sending standard solution drop by drop from a burette to a flask which contains the unknown solution. (Figure 6-2)

Figure 6-2



A) Instruments used in titration

B) Colorless phenolphthalein turns into pink at pH = 10 point

This addition process which continues until the reaction between chemical reactant and sought component completes is called as **titration**. In titration process, the point at which the reactions end is called as **equivalent point**. This point is practically can be observed with naked eye easily through a change in a property of the solution (e.g. change in the color of solution or formation of precipitate.) For this purpose, usually chemical substances called as **indicators** are added to the solution. Indicators are substances whose colors or one of their physical properties change clearly at/near equivalent point although they don't react in the reaction. Therefore, this point at which change occurs and addition from burette is stopped is called as **end point**. This point needs to coincide with equivalent point. But between two points (theoretically and practically) a small difference can occur. This is a result of an error in titration. As titration is the most common and most used process, mostly, instead of the volumetric analysis term, the titration analysis term is used. But the volumetric analysis term is more extensive. Because it includes quantitative processes used in analysis of gases in addition to titration analysis.

The reactions between standard reagents and compounds to be measured need to follow some conditions.

1- The reactions need to be simple and expressed with balanced chemical equations. represent the reaction of the component to be quantified with the standard reagent.

2- They need to be one way but not equilibrium reactions.

3- The reaction need to be complete and fast. In some cases, a catalyst can be used to increase the reaction rate.

4- Practically, the end point of the reaction needs to be determined. This is possible via a change in a property of solution at or near equivalent point.

According to this, we can divide chemical reactions which have the conditions above and can be used successfully in titration processes into 4.

These are:

1-Neutralization Reactions: (reaction of Acides and Bases)

These reactions include titration of a strong base with a standard solution of a strong acid or the opposite as the titration of a strong acid solution with a standard solution of a strong base. Because hydrogen ion reacts with hydroxide ion and water is formed.

Attention: In the following chapters, we will study the hydrolysis of salts derived from weak acids and bases. Besides, we will study what oxidation and reduction reactions are and how they are used in chemical analysis.

2-Oxidation and Reduction Reactions:

This includes the reactions of all substances of which a change occurs in oxidation numbers. The standard solution in these reactions is either a reducing or an oxidizing agent.

3-Precipitation Reactions:

These reactions include interaction of ions (except H^+ and OH^-) to form simple precipitates. For example, the reaction between silver and chloride ions.

$$Ag^+ + Cl^- \longrightarrow \underset{\text{precipitate}}{AgCl\downarrow}$$

4-The Formation Reactions of Complex Ions:

In these reactions, polyatomic anions or cations are bonded to other ions or molecules and they form coordination compounds. These compounds dissolve in solutions but as shown below, they decompose little.

$$2\,CN^- + Ag^+ \longrightarrow \underset{\text{Dissolved complex compound}}{[Ag(CN)_2]^-}$$

6-6-2-Methods of Defining Concentrations of Solutions Used in Titration:

As we have studied before, standard solution is a solution formed by dissolving a certain amount of reagent in a certain volume of solution. There are many methods which define the concentration of solution. The following are the most commonly used in volumetric analysis:

Molarity (M):

A solution with 1 molar concentration is formed by dissolving 1 mole of substance in 1 liter solution. In other words:

$$M\ (mol/L) = \frac{n(mol)}{V(L)} = \frac{n\,(mmol)}{V(mL)} = \frac{\dfrac{m\,(g)}{M\,(g/mol)}}{V(L)}$$

The symbols in the equation are: n is number of moles; M is molar mass of dissolved substance; V is volume of solution.

Normality (N):

You have seen different ways to define the concentration of a dissolved substance in a solution. Now you will see a new method called as normality to define concentration. Also there are other terms you will meet later.

1 normal solution is formed by dissolving 1 equivalent gram of substance in 1 liter of solution.

$$N(eq/L) = \frac{Eq\,(eq)}{V(L)} = \frac{Eq\,(m\,eq)}{V(mL)} = \frac{\frac{m\,(g)}{EM\,(g/eq)}}{V(L)}$$

Eq in the equation is equivalent gram, EM is equivalent mass.

As known, the molar mass of any substance is equal to the sum of atomic masses forming this substance. This amount is constant and shown as gram/mol (g/mol). Equivalent mass of any substance is the mass of substance which produces or consumes 1 mole of active component (reactant). This amount isn't constant. It can change with respect to the reaction type in which the substance participates. According to this, a single compound may have more than one equivalent mass with respect to the reaction type in which it takes place. This value is shown with (g/eq) unit.

Standard concentration (Normality) is usually used to prevent confusion which may arise as in one mole of substance, one or more moles of active (reactant) substance is found. Therefore, it is preferred in calculations of quantitative analysis methods which depend on titration.

6-6-3-Calculation of Equivalent Mass (EM)

Attention: Here, as you can see, instead of molar mass M, equivalent mass EM (g/eq) is used.

Calculation of equivalent mass of any compound changes with respect to the reaction type in which the compound participates. These calculations are:

1-Neutralization Reactions:

The equivalent mass of an acid is defined as the mass of acid which has one mole of hydrogen atom (1.008 g hydrogen) that can change (participate) in the reaction. We can define this mathematically as follows:

$$\text{Equivalent mass of acid} = \frac{\text{Molar mass of acid}}{\text{Number of ionized } H^+ \text{ ions}}$$

$$EM = \frac{M_a}{\text{Number of ionized } H^+ \text{ ions}}$$

a in the equation is the first letter of the word acid.

The equivalent mass of a base is defined as the mass of base which has one mole of hydroxide group (17.0081 g of ionized hydroxide group) that can change (participate) in the reaction.

$$EM = \frac{M_b}{\text{Number of ionized } OH^- \text{ ions}}$$

b in the equation is the first letter of the word base.

When salts obtained from hydrolysis of weak acids and strong bases or vice versa participate in this kind of reactions, their equivalent masses can be calculated. For this, a balanced chemical equation of acid-base reaction is written.

The mole number which is equivalent to acid or base is found and this number is used to calculate equivalent mass as shown in the following example.

$$\underset{\text{Salt of weak acid}}{Na_2CO_3} + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

$$\text{Equivalent mass of } Na_2CO_3 = \frac{\text{Molar mass of } Na_2CO_3}{\underbrace{\text{Mole number of active part of acid}}_{\text{Number of moles of } H^+}} = \frac{\text{Molar mass of } Na_2CO_3}{2}$$

$$EM_{Na_2CO_3} = \frac{M_{Na_2CO_3}}{2}$$

2-Precipitation and Complex Component Reactions

The equivalent mass of a substance which participates a precipitation reaction is equal to a substance which includes a mole of single positive ion (equivalent to 1.008 g hydrogen) or a substance which reacts with it.

$$\text{Equivalent mass} = \frac{\text{Molar mass of substance}}{\text{Positive ion} \times \text{number of valence}}$$

$$EM = \frac{M}{\text{Positive ion} \times \text{number of valence}}$$

The equivalent mass of a substance which participates a reaction to form a complex component (which has electron pairs as active part) shows the mass of the substance which donates or takes electron pair.

$$EM = \frac{M}{\text{Number of donated or taken electrons pairs}}$$

3-Oxidation and Reduction Reactions:

The equivalent mass of oxidation or reduction factor is the mass of the reagent which includes or reacts with 1.008 g hydrogen or 8.000 g oxygen. For example, equivalent masses of potassium permanganate and potassium dichromate which participate oxidation and reduction reactions can be calculated.

In order to calculate the equivalent masses of potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$), virtual reactions are written to determine amount of oxygen in each molecule.

$$\mathbf{2KMnO_4 \longrightarrow K_2O + 2MnO + 5O}$$

$$\mathbf{K_2Cr_2O_7 \longrightarrow K_2O + Cr_2O_3 + 3O}$$

According to those above, 2 molecules of potassium permanganate yield 5 oxygen atoms. Therefore, the equivalent mass of this substance can be calculated through the following equation.

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molar mass} \times 2}{10}$$

With the same method, the equivalent mass of $K_2Cr_2O_7$ is calculated as follows:

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Molar mass}}{6}$$

In order to simplify the subject, we can calculate the equivalent mass of any substance which participate oxidation and reduction reactions according to the following 2 reactions.

$$\text{Equivalent mass of oxidation factor} = \frac{\text{Molar mass}}{\text{Number of taken electrons}}$$

$$\text{Equivalent mass of reduction factor} = \frac{\text{Molar mass}}{\text{Number of donated electrons}}$$

As stated above, the equivalent mass of a substance is equal to the ratio of molar mass of substance to **η** (eta) number. This number shows the number of moles of active part (the part participating reaction) of the substance. Therefore, number of **η** can be determined while deciding the active part of the substance (according to the reaction type that substance undergoes). Because this value is ≥ 1. We can write the general relationship between equivalent mass of substance with its molar mass.

$$\mathbf{EM} = \frac{\mathbf{M(g/mol)}}{\mathbf{\eta(eq/mol)}} = \frac{\mathbf{M}}{\mathbf{\eta}}\ \mathbf{(g/eq)}$$

$$= \frac{\mathbf{M}}{\mathbf{\eta}}\ \mathbf{(mg/meq)}$$

Attention: In order to differentiate number of moles of active part of substance from number of moles, η (eta) symbol is used.

η = number of positive salt ions replaced amount of charge of a metallic ion.

Example 6-6

Calculate equivalent mass of each substance which participate reactions below.

1. $Pb(NO_3)_{2(aq)} + 2KI_{(aq)} \rightarrow PbI_{2(s)} + 2K^+_{(aq)} + 2NO^-_{3(aq)}$

2. $H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow 2H_2O_{(l)} + 2Na^+_{(aq)} + SO^{2-}_{4\,(aq)}$

3. $5Fe^{2+}_{(aq)} + MnO^-_{4(aq)} + 8H_3O^+_{(aq)} \rightarrow 5Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 12H_2O_{(l)}$

4. $AgNO_{3(aq)} + 2KCN_{(aq)} \rightarrow [Ag(CN)_2]^-_{(aq)} + 2K^+_{(aq)} + NO^-_{3(aq)}$

Solution:

1- In order to calculate equivalent mass of a substance with respect to the type of the reaction, value of molar mass and η are needed to be known.

$$EM_{Pb(NO_3)_2} = \frac{M_{Pb(NO_3)_2}}{\eta}$$

To calculate molar mass of $Pb(NO_3)_2$, atomic masses of atoms forming this substance are summed up.

$$M\,[Pb(NO_3)_2] = 1\times207+[2\times1\times14]+[2\times3\times16]$$
$$= 331\ g/mol$$

Then, according to the reaction equation below, value of η is calculated.

$Pb(NO_3)_{2(aq)} + 2KI_{(aq)} \rightarrow PbI_{2(s)} + 2K^+_{(aq)} + 2NO^-_{3(aq)}$

The equation shows that $Pb(NO_3)_2$ participated a precipitation reaction as PbI_2 salt was formed. Therefore, the value of η is calculated as follows:

η = valence of positive ion x number of positive ions = 2x1 = 2 eq/mol

$$EM_{Pb(NO_3)_2} = \frac{M_{Pb(NO_3)_2}}{\eta} = \frac{331\ (g/\cancel{mol})}{2\ (eq/\cancel{mol})} = 165.5\ g/eq$$

With the same method, equivalent mass of KI salt is calculated.

$$M(KI) = 1\times39+1\times127 = 166\ g/mol$$

η = valence of positive ion x number of positive ions =1x1=1 eq/mol

$$EM_{KI} = \frac{M_{KI}}{\eta} = \frac{166(g/\cancel{mol})}{1(eq/\cancel{mol})} = 166\ g/eq$$

2- The following is an acid-base reaction.

$H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow 2H_2O_{(l)} + 2Na^+_{(aq)} + SO^{2-}_{4\,(aq)}$

Equivalent mass of sulfuric acid

η = number hydrogen ions = 2 eq/mol

$$EM_{H_2SO_4} = \frac{M_{H_2SO_4}}{\eta} = \frac{98\ (g/\cancel{mol})}{2\ (eq/\cancel{mol})} = 49\ g/eq$$

Exercise 6-5

In order to prepare a solution of 2L volume and 0.12 N concentrations, how many grams of potassium dichromate $K_2Cr_2O_7$ is needed according to the following oxidation reduction reaction? (M=294 g/mol)

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

Answer: 11.76 g

Exercise 6-6

What is the mass of sodium hydroxide, NaOH (M= 40 g/mol), necessary to prepare a solution of 0.2 M 500 mL?

Answer: 4 g

Exercise 6-7

Calculate the mass of dissolved substance in each of the following solutions.

1- 350 mL, 0.125 M silver nitrate, $AgNO_3$ (M = 170 g/mol)

2- 250 mL, 0.1 N borax,

$Na_2B_4O_7.10H_2O$, (M=381 g/mol) solution according to the following reaction.

$$B_4O_7^{2-} + 2H_3O^+ + 3H_2O \rightarrow 4H_3BO_3$$

Answer:

1) 7.44 g

2) 4.76 g

The equivalent mass of sodium hydroxide

$$M\,(NaOH) = 1 \times 23 + 1 \times 16 + 1 \times 1 = 40\ g/mol$$

η = number of hydroxide ions = 1 eq/mol

$$EM_{NaOH} = \frac{M_{NaOH}}{\eta} = \frac{40\,(g/\cancel{mol})}{1\,(eq/\cancel{mol})} = 40\ g/eq$$

3- The following is an oxidation and reduction reaction.

$$5Fe^{2+}_{(aq)} + MnO^-_{4(aq)}\ 8H_3O^+_{(aq)} \rightarrow 5Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 12H_2O_{(l)}$$

The equivalent mass of Fe^{2+} ion is (This ion is the reducing agent in this reaction)

$M_{Fe} = 56$ g/mol

η = number of donated electrons = 1 eq/mol

Number of lost electrons is calculated from the difference between oxidation states (valences) of Fe^{2+} and Fe^{3+} ions.

$$EM_{Fe} = \frac{M_{Fe}}{\eta} = \frac{56\,(g/\cancel{mol})}{1\,(eq/\cancel{mol})} = 56\ g/eq$$

The equivalent mass of MnO_4^- ion (This ion is the oxidizing agent in the reaction.)

$$M\,(MnO_4) = 1 \times 55 + 4 \times 16 = 119\ g/mol$$

η = number of taken electrons = 5 eq/mol

Number of accepted (taken) electrons are calculated from the difference between the oxidation states of Mn^{-2} and MnO_4^-

$$EM_{MnO_4} = \frac{M_{MnO4}}{\eta} = \frac{119\,(g/\cancel{mol})}{5\,(eq/\cancel{mol})} = 23.8\ g/eq$$

4- The following is a complex ion formation reaction.

$$AgNO_{3(aq)} + 2KCN_{(aq)} \rightarrow [Ag(CN)_2]^-_{(aq)} + 2K^+_{(aq)} + NO^-_{3(aq)}$$

The equivalent mass of silver nitrate $AgNO_3$

$$M\,(AgNO_3) = 1 \times 108 + 1 \times 14 + 3 \times 16 = 170\ g/mol$$

η = number of accepted electron pair = 2 eq/mol

$$EM_{AgNO_3} = \frac{M_{AgNO_3}}{\eta} = \frac{170\ (g/\cancel{mol})}{2\ (eq/\cancel{mol})} = 85\ g/eq$$

The equivalent mass of potassium cyanide KCN

$$M(KCN) = 1\times39+1\times12+1\times14 = 65\ g/mol$$

η = number of donated electrons= 1x1 = 1 eq/mol

$$\frac{M_{KCN}}{\eta} = \frac{65\ (g/\cancel{mol})}{1\ (eq/\cancel{mol})} = 65\ \ g/eq$$

Volumetric flask

Example 6-7

η value of 0.23 mol/L sulfuric acid is found to be 2 eq/mol in a neutralization reaction. Calculate the normality of this acid solution.

Solution:

If we consider the two mathematical equations about standardization of solutions and their molarities, with the condition of their molarities and η (eq/mol) values are known, it is possible to calculate its standardization (normality) by the following equation.

$$N\ (eq/L) = \eta\ (eq/mol) \times M\ (mol/L)$$

$$N = 2\ (eq/\cancel{mol}) \times 0.23\ (\cancel{mol}/L) = 0.46\ eq/L.$$

6-6-4-Instruments Used in Volumetric Analysis

We should express that liter (L) is a principal unit to measure volumes of solutions used in volumetric analysis processes. Also milliliter which is a thousandth of liter is used in volumetric analysis. While making sensitive measurements with solutions, only some glass instruments are used. These are:

1-**Volumetric flask:** It is used to measure the volume of solution during its preparation.

2- **Burette:** During titration, it is used to measure the volume of consumed solution accurately.

3- **Pipette:** It is used to transfer a certain volume of solution from one container to another.

Pipettes Burette

Figure 6-3
Laboratory equipment used to measure volumes of solution

6-6-5-Calculation of Volumetric Analysis Results

The aim of any volumetric analysis with titration method is to add chemically equivalent amount of standard solution on the substance with an unknown amount. This condition occurs in titration process. (Equivalent point is the point at which the amount of standard substance becomes equivalent with the

amount of substance which is to be guessed in titration process.) Practically, this point is determined at the end of the reaction (practical equivalent point). At this point, one of the properties of the solution changes (e.g. color change).

In titration processes, chemists usually use standard concentration to define concentrations during preparation of solutions.

Therefore; As we have mentioned before, standard concentration (normality) is basically used to calculate the equivalent masses of substances in volumetric analysis calculations.

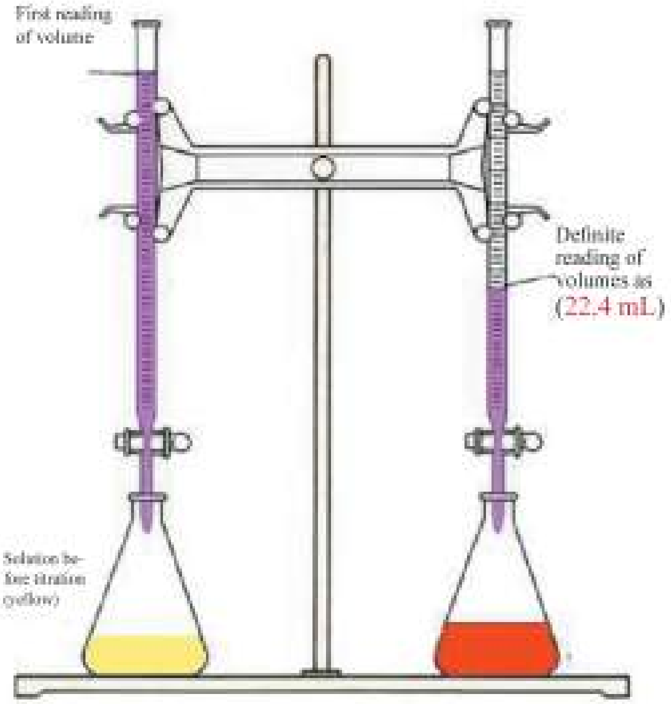
The following titration experiment shows the calculations necessary to find out the mass of barium hydroxide $Ba(OH)_2$ (M=171 g/mol) using volumetric analysis processes. For this, we follow the steps below:

1- We dissolve the sample in distilled water. Then, we complete the volume of the solution to 25 mL by adding distilled water in a flask.

2- By a pipette, 20 mL from sample solution is taken. It is transferred to a volumetric flask with appropriate volume.

3- A few drops of organic indicator methyl red is added to the solution. This substance doesn't reacte in the reaction. But, at the end point of the reaction, as a result of change in the pH value of solution, its color turns red from yellow. Therefore, the solution turns red at the end point.

4- With the barium hydroxide solution in the beaker, titration starts against standard hydrochloric acid (with 0.098 M or 0.098 N concentration) solution. For this, acid solution in the burette is added drop by drop to the sample solution in the beaker. Meanwhile, the solution in the beaker is swirled continuously. At the end, for the color change from yellow to red (at the end point), 22.4 mL of acid solution is measured to be added.



Attention: The unit mmol/mL is equivalent of mol/L. Both are molarity (M) units.

5- Calculations: As known, at the end point of the reaction (practically equivalent point), the amount of unknown substance (substance to be measured) is equal to the amount of standard substance. In order to calculate the amount (amount of substance is defined with number of moles or equivalent grams etc.) of substance dissolved in a solution, the volume of solution (mL) is multiplied with the concentration of solution (mol/L or eq/L respectively).

Amount of substance dissolved in solution $\text{(mmol)} = V_{\text{solution}}\text{(mL)} \times \text{M (mmol/mL)}$

or

Amount of substance dissolved in solution $\text{(meq)} = V_{\text{solution}}\text{(mL)} \times \text{N (meq/mL)}$

Generally, the following relationship can be written when reaction has reached end point in any titration process.

Amount of unknown substance = Amount of standard substance

Amount of equivalent grams of unknown substance (meq) = amount of equivalent grams of standard substance(meq) $(N \times V)_{HCl} = (N \times V)_{Ba(OH)_2}$

$$N_{HCl} \times V_{HCl} = N_{Ba(OH)_2} \times V_{Ba(OH)_2}$$

$$0.098\ \text{(meq/mL)} \times 22.4\ \text{(mL)} = N_{Ba(OH)_2} \times 20\ \text{(mL)}$$

From this relationship, standard concentration (normality) of $Ba(OH)_2$ solution can be calculated.

$$N_{Ba(OH)_2} = \frac{0.098\ \text{(meq/mL)} \times 22.4\ \text{(mL)}}{20\ \text{(mL)}} = 0.1097\ \text{meq/mL} = 0.1097\ \text{eq/L}$$

In order to calculate the amount of dissolved substance in a certain volume of solution (25 mL), equivalent mass of barium hydroxide is calculated as follows:
The reaction is used in titration;

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$

According to this reaction, $\eta = 2$ eq/mol. Therefore,

$$EM_{Ba(OH)_2} = \frac{M_{Ba(OH)_2}}{\eta} = \frac{171\ \text{(g/mol)}}{2\ \text{(eq/mol)}} = 85.5\ \text{g/eq}$$

$$N\ \text{(eq/L)} = \frac{Eq\ \text{(eq)}}{V\ \text{(L)}} = \frac{\dfrac{m\ \text{(g)}}{EM\ \text{(g/eq)}}}{\dfrac{V\ \text{(mL)}}{1000\ \text{(mL/L)}}}$$

We get the following formula if we re-arrange the equation:

$$m\ \text{(g)} = \frac{N\ \text{(eq/L)} \times V\ \text{(mL)} \times EM\ \text{(g/eq)}}{1000\ \text{(mL/L)}}$$

$$m\ \text{(g)} = \frac{0.1097\ \text{(eq/L)} \times 25\ \text{(mL)} \times 85.5\ \text{(g/eq)}}{1000\ \text{(mL/L)}}$$

$$m\ \text{(g)} = 0.235\ \text{g}$$

Attention:

In titration process, when relying on the use of molar concentrations to prepare solutions, the balanced chemical equation is relied upon to determine the equivalent amounts of the standard solution and the solution of the component to be estimated. However, when using the titrant concentration for the same purpose, the following relation ship can be directly applied at the end point of the reaction without having to write the balanced chemical equation for the reaction:

$$N_1 \times V_1 = N_2 \times V_2$$

For this reason, it is preferable to use the titrant concentration to express the concentration of the solutions used in titration processes.

Exercise 6-8

Potassium permanganate, $KMnO_4$, is a widely used substance in reduction-oxidation reactions. What is the η value of a chemical reaction in which potassium permanganate is used to produce MnO_2? What is the normality of the solution with a molarity of 0.05M?

Answer: 3; 0.15 eq/L

Exercise 6-9

The amount of nickel was measured in a sample with titration process according to the reaction below.

$$Ni^{2+} + 4CN^{-} \rightarrow Ni(CN)_4^{2-}$$

160 mg of sample was titrated against 0.137 N KCN standard solution. As 38.3 mL of KCN was used when the end point was reached, calculate the percentage of Ni_2O_3 (M = 165 g/mol) in the sample.

Answer: 67.5%

Exercise 6-10

0.958 g of a sample containing acetic acid, CH_3COOH, (M = 60 g/mol) was standardized with titration of 0.225 N standard sodium hydroxide solution. As the volume of solution needed to reach the end point was 33.6 mL, calculate the percentage of acetic acid in the sample.

Answer: 47.34%

Example 6-8

0.1743 g of impure oxalic acid ($H_2C_2O_4$) (M=90 g/mol) was titrated with sodium hydroxide solution. 39.82 mL of 0.09 M base solution was used at the end point. What is the percentage of oxalic acid in the sample?

Solution:

The reaction equation:

$$2NaOH + H_2C_2O_4 \rightarrow Na_2C_2O_4 + 2H_2O$$

According to the neutralization reaction, 1 mole of acid reacted with 2 moles of base. That means, at the end point of the reaction;

$$(mmol)\ H_2C_2O_4 = \frac{1}{2} \times (mmol)\ NaOH$$

The amount (mmol) of used sodium hydroxide is calculated:

$$(mmol_{NaOH}) = V_{solution}(mL) \times M\ (mmol/mL)$$

$$mmol_{NaOH} = 39.82\ (mL) \times 0.09\ (mmol/mL)$$

$$mmol_{NaOH} = 3.584\ mmol$$

From the amount of sodium hydroxide, the amount of reacting oxalic acid can be calculated.

At the end point of the reaction (practically the equivalent point)

Half of the amount of sodium hydroxide = the amount of oxalic acid

$$(mmol)\ H_2C_2O_4 = \frac{\text{the amount of reacting sodium hydroxide}}{2}$$

$$\frac{3.584\ mmol}{2} = 1.79\ mmol = 1.79 \times 10^{-3}\ mol$$

$$M\ (mol/L) = \frac{\frac{m\ (g)}{M\ (g/mol)}}{V\ (L)}$$

From the re-arrangement of the equation, the following formula is obtained.

$$m\ (g) = M\ (mol/L) \times V\ (L) \times M\ (g/mol)$$

In this equation, into the result of multiplication of volume and molarity, the amount of acid defined with number of moles is inserted.

$$m\ (g) = 1.79 \times 10^{-3}\ (mol) \times 90\ (g/mol) = 0.16\ g$$

Then, the percentage of impure oxalic acid in the sample is calculated according to the following relationship.

$$H_2C_2O_4\% = \frac{m_{H_2C_2O_4}\ (g)}{m_{sample}\ (g)} \times 100$$

$$H_2C_2O_4\% = \frac{0.16\ (g)}{0.1743\ (g)} \times 100 = 91.8\%$$

QUESTIONS OF CHAPTER-6

6-1- How can we separate common positive ions (cations) from each other?

6-2- Name the positive ions in the second group of the table 6-1. Name the factors causing those to precipitate. How can copper ion and iron ion in the same solution be separated? Explain.

6-3- Complete the following reactions and tell the properties of products.

$$PCl_2 \xrightarrow{K_2CrO_4 \text{ and boiling water}}$$

$$AgCl \xrightarrow{NH_3} \qquad \xrightarrow{HNO_3}$$

$$Hg_2^{2+} \xrightarrow{\text{dilute } HCl} \qquad \xrightarrow{NH_3} \qquad \xrightarrow{\text{Royal water}} \qquad \xrightarrow{SnCl_2} \qquad \xrightarrow{SnCl_2}$$

6-4- How is the separation process of Hg^{2+} and Hg_2^{2+} ions made?

6-5- Fill in the blanks.

1- Cr^{3+} is one of……………..group of positive ions and it precipitates as ....form after addition of ……………………..and ………………… precipitants.

2- Precipitants of IV group positives ions are …………………… , ……………………….. and ……………………..

3- Molarity of 0.3 N $Al_2(SO_4)_3$ solution is ………………..

4- Value of η of a solution which is 0.2M and 1N is ……………

6-6- In order to precipitate 1.67 g of lead iodate $Pb(IO_3)_2$, how many grams of potassium iodate KIO_3 is needed? (KIO_3 = 214 g/mol, $Pb(IO_3)_2$ = 557 g/mol)

Answer: 1.283 g

6-7- 14.4 mg of carbon dioxide gas and 2.5 mg of water vapor were produced from burning of an 5.7 mg organic compound . Calculate the percentages of carbon and hydrogen in the compound.

(C:12 g/mol, O:16 g/mol, H:1 g/mol)

Answer: 68.9%; 4.9%

6-8- As 36.7 mL hydrochloric acid solution is equivalent to 43.2 mL 0.236 M sodium hydroxide solution, what is the molarity of hydrochloric acid?

Answer: 0.278 M

6-9- 2 L solution of 9.5 g of barium hydroxide is prepared to be used in an acid-base reaction. What is the molarity and normality of barium hydroxide $Ba(OH)_2$? ($Ba(OH)_2$: 171 g/mol)

Answer: 0.027 M; 0.054 eq/L

6-10- If 15.675 mg of carbon dioxide, CO_2, gas is released from combustion of 5.7 mg of a hydrocarbon of organic compound, what is ratio of hydrogen in the compound ? (M_C = 12 g /mol, M_{O_2}= 32 g/mol)

6-11- What is the volume of 0.2 M potassium permanganate solution which is necessary to titrate (oxidation -reduction reaction) 40 mL 0.1 M iron (II) sulfate in acidic medium ? Titration reaction equation is given below. $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$

Answer: 4 mL

6-12- Circle the correct answer in the following questions.

1- What is the η value of iron (III) sulfate, $Fe_2(SO_4)_3$, salt used to precipitate lead ion?

A- 4 eq/mol

B- 5 eq/mol

C- 6 eq/mol

2- How can Cu^{2+} ion be separated from Ca^{2+} ion by addition of one of the following?

A- Dilute HCl acid

B- passing H_2S gas in NH_4OH and NH_4Cl through solution

C- passing H_2S gas in dilute HCl through solution

3- What percent of 0.74 g of impure pesticide $C_{14}H_9Cl_5$ (DDT) is pure which is needed to obtain 0.253 g of AgCl?

A- 17%

B- 19%

C- 21%

4- What is the name of the gravimetric method which is used to determine the mass of a volatile component from mass difference occurring after a certain amount of sample is heated or burnt in open air?

A- Direct volatilization method

B- Indirect volatilization method

C- Precipitation Method

5- In gravimetric analysis processes which depend on precipitation reactions,

A- formation of colloidal precipitate is preferred.

B- formation of crystallized precipitate is preferred.

C- type of precipitate has no significance.

6- What does the ratio of molecular mass of sought substance to molecular mass of gravimetric formula show (with the condition of both formulas contain the sought element or molecules)?

A- Precipitation formula

B- Molar mass

C- Gravimetric factor

7- What is the definition of mass of the substance which produces or consumes 1 mole of active component?

A- Equivalent Mass

B- Molar Mass

C- Standard Mass

8- The normality of solution obtained by dissolving 13 g of $K_2Cr_2O_7$ in 500 mL of distilled water:

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

A- 0.53 mol/L

B- 0.53 eq/L

C- 3.18 eq/L

6-13- Calculate the gravimetric factor of $Na_5P_3O_{10}$ (M=368 g/mol) in $Mg_2P_2O_7$ (M=222 g/mol).

Answer: 1.11

6-14- 50 mL HIO_3 (M = 176 g/mol) acid solution was titrated against 0.145 N standard sodium hydroxide solution. As the volume of the base solution added from burette to reach end point was 45.8 mL, calculate the following :

A- Normality of HIO_3 acid
B- According to the following reaction, if the same acid was used to obtain iron, what would be the normality of the acid? $HIO_3 + 4FeCl_2 + 5H_3O^+ + 6Cl^- \rightarrow 4FeCl_3 + ICl_2^- + 8H_2O$
Answer: A: 0.13 N; B: 0.52 N

6-15- In order to find the concentration of 25 mL NaOH solution, it was titrated against 0.08 M sulfuric acid, 47.1 mL of acid was added to reach the end point. Calculate the molar concentration of sodium hydroxide solution, and then find out the mass of NaOH dissolved in 500 mL of this solution. (NaOH = 40 g/mol).

Answer: 0.3 M; 6 g

6-16- 0.5 g of impure sodium iodide, NaI, (M = 150 g/mol) salt was dissolved in water. To precipitate iodide ions, silver nitrate, $AgNO_3$, solution was added to the solution. At the end of the reaction, 0.744 g of silver iodide AgI (M = 235 g/mol) precipitate was obtained. Calculate the percentage of sodium iodide found in impure salt.

Answer: 95%

6-17- 4.29 g of sodium carbonate crystals $Na_2CO_3.xH_2O$ is dissolved in pure water then the volume is completed to 250 mL. 15 mL of 0.2N HCl solution is needed to neutralize 25 mL of the same solution completely. What is the number of water molecule (x) in the formula of $Na_2CO_3.xH_2O$? (Na: 23 g/mol, C: 12 g/mol, O: 16 g/mol, H: 1 g/mol)

Answer: $Na_2CO_3.10H_2O$

6-18- Potassium iodide solution was added to 0.3 N 20 mL potassium permanganate ($KMnO_4$) solution in acidic conditions. At the end of the reaction, some iodine (I_2) was produced. Produced iodine was titrated with sodium thiosulfate, $Na_2S_2O_3$ (M=158 g/mol).

$$I_2 + 2Na_2S_2O_3 \rightleftharpoons 2NaI + Na_2S_4O_6$$

To reach the end point, 25 mL of $Na_2S_2O_3$ was consumed. According to this, calculate the following:

A- The normality of $Na_2S_2O_3$ solution

B- How many grams of sodium thiosulfate is needed to prepare 1 L solution?

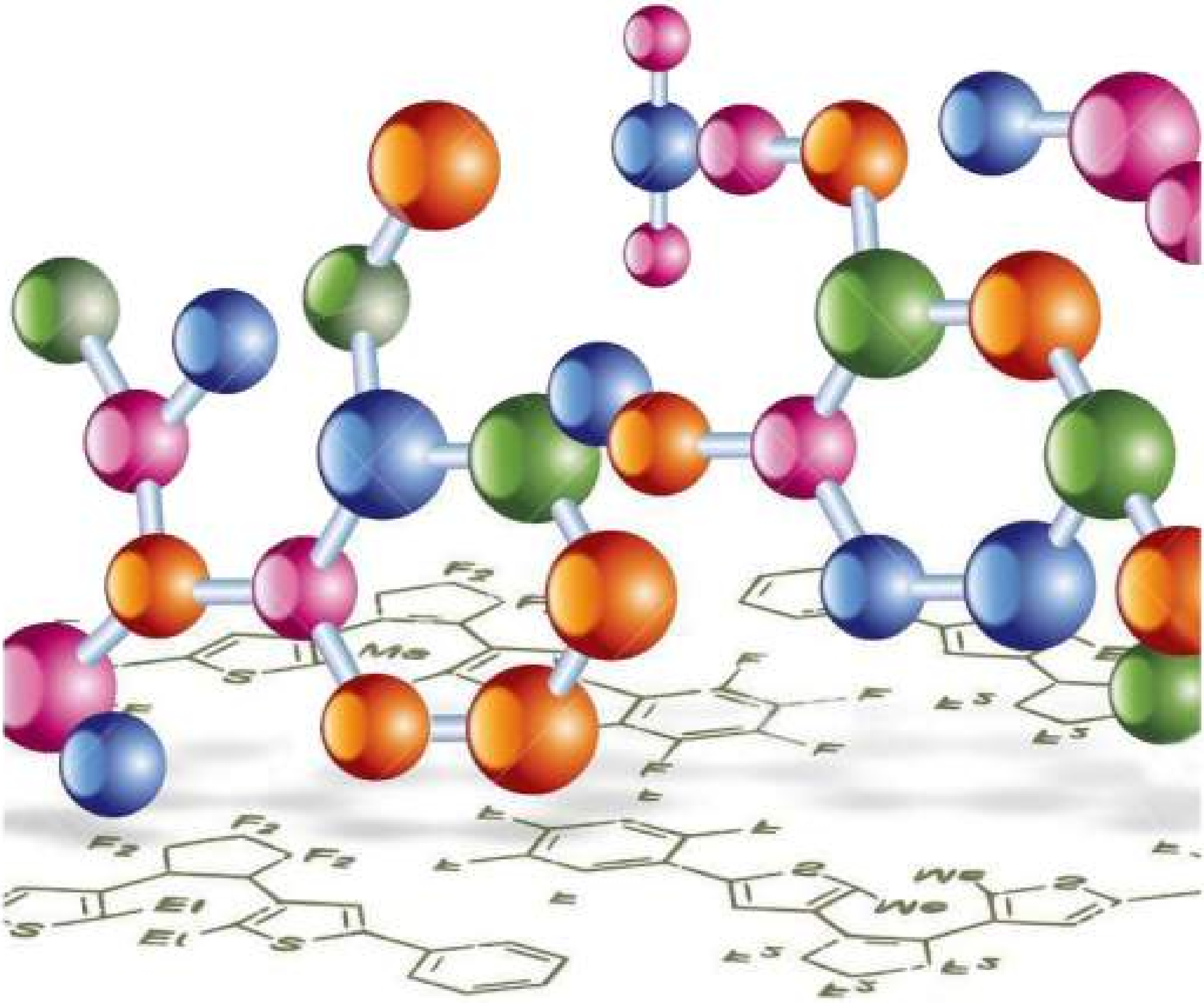
Answer: A) 0.24 N; B) 37.92 g

6-19- What is the mass of barium sulfate, $BaSO_4$, (M=233 g/mol) that precipitates completely when a sufficient amount of barium chloride, $BaCl_2$, (M=208 g/mol) is mixed with 100 mL of sulfuric acid solution, H_2SO_4, (M=98 g/mol). 16 mL of 0.10 M NaOH is needed to neutralize 20 mL of sulfuric acid.

Answer: 0.932 g

ORGANIC CHEMISTRY FOR SUBSTITUTED HYDROCARBONS

CHAPTER-7



ACHIEVEMENTS

After completing this chapter, the student is expected to :

- Differentiate the class of a compound from its structural formula.
- Apply the IUPAC system to name organic compounds (hydrocarbons).
- Learn the physical and chemical properties and reactions of aromatic hydrocarbons.
- Learn methods of production of these compounds.
- Separate alcohols, ketones and aldehydes using analysis methods.
- Learn the significance of these compounds in our daily lives and their usages.

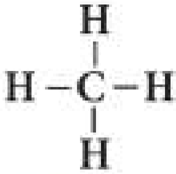
Chapter - 7

7-1 PREFACE

Previously, we have learnt that one of the branches of chemistry is organic chemistry which studies properties and reactions of some compounds that have carbon as the basic element besides other elements.

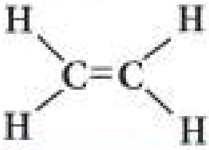
Hydrocarbons are considered as the simplest part of organic chemistry as they consist of carbon and hydrogen elements. Hydrocarbon compounds are divided into two as aliphatic hydrocarbons and aromatic hydrocarbons. In hydrocarbons, covalent bonds which are formed by electron sharing exist between carbon atoms. If there is one bond between two carbon atoms, the compound is called as **ALKANE**. Alkanes are saturated aliphatic hydrocarbon compounds. If there are two bonds between carbons, the compound is an **ALKENE**, if there are three bonds, it is an **ALKYNE**. Alkenes and alkynes are unsaturated aliphatic hydrocarbons. They can be either in open-chain structure or in cyclic structure. Benzene and its derivatives form aromatic hydrocarbons. These compounds have cyclic structures.

The compounds which have the same molecular formulas but different structural formulas are called as isomeric compounds. They have different physical properties such as different boiling and melting points. We have learnt how to differentiate this kind of compounds.



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

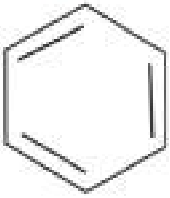
Methane
(saturated hydrocarbon)
single bond



Ethylene or ethene
(Unsaturated hydrocarbon)
double bond

$H-C\equiv C-H$

Acetylene
(unsaturated hydrocarbon)
triple bond



Benzene
(aromatic cyclic, unsaturated hydrocarbon)

Table 7-1

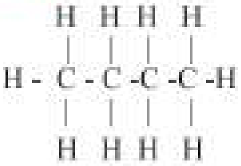
IUPAC Nomenclature of Hydrocarbons

Number of carbon	Name in Latin	Alkane -ane	Alkene -ene	Alkyne -yne
C_1	meth	methane	-	-
C_2	eth	ethane	ethene	ethyne
C_3	prop	propane	propene	propyne
C_4	but	butane	butene	batyne
C_5	pent	pentane	pentene	pentyne
C_6	hex	hexane	hexene	hexyne
C_7	hept	heptane	heptene	heptyne
C_8	oct	octane	octene	octyne
C_9	non	nonane	nonene	nonyne
C_{10}	dec	decane	decene	decyne

Example 7-1

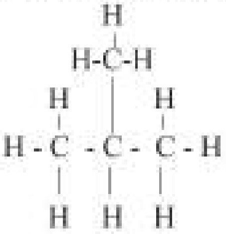
Write down the structural formulas of n-butane and 2-methylpropane (isobutane) which have the same molecular formula C_4H_{10}.

Solution:



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & - & C & - & C & - & C & - & C & -H \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array}$$

n-butane



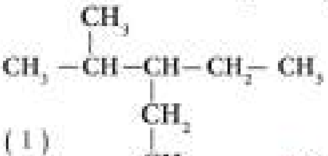
$$\begin{array}{ccccccc} & & & H & & & \\ & & & | & & & \\ & & & H-C-H & & & \\ & & H & | & H & & \\ & & | & | & | & & \\ H & - & C & -C- & C & - & H \\ & & | & | & | & & \\ & & H & H & H & & \end{array}$$

2-methylpropane

As you see, although these two compounds have the same molecular formula, they have different physical and chemical properties.

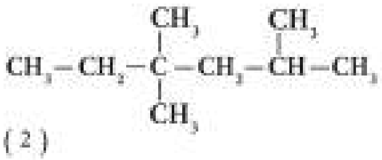
Example 7-2

Name the following compounds according to IUPAC.



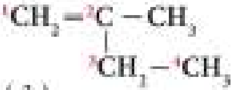
$$\begin{array}{l} CH_3 \\ | \\ CH_3-CH-CH-CH_2-CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

(1)



$$\begin{array}{l} CH_3CH_3 \\ || \\ CH_3-CH_2-C-CH_2-CH-CH_3 \\ | \\ CH_3 \end{array}$$

(2)



$$\begin{array}{l} {}^1CH_2={}^2C-CH_3 \\ \phantom{{}^1CH_2=}| \\ \phantom{{}^1CH_2=}{}^3CH_2-{}^4CH_3 \end{array}$$

(3)

Solution:

(1) 3-ethyl-2-methylpentane

(2) 2,4,4 –trimethylhexane

(3) 2-methyl-1-butene

The basic structure of all hydrocarbons consist of carbon and hydrogen. But many hydrocarbon compounds also include oxygen, nitrogen, halogens, sulfur and other elements. What are those compounds types? What are their properties? What are the relationship between those and hydrocarbons?

Exercise 7-1

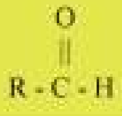
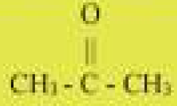
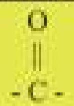
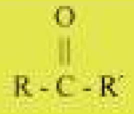
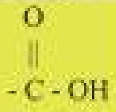
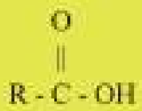
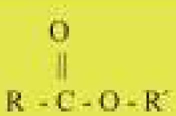
Write down structural formulas for C_5H_{12} compound with their names.

The presence of elements other than carbon and hydrogen in hydrocarbon compounds give them some distinctive properties. These elements and element groups which give organic compound distinctive properties are called as functional groups.

Functional groups are attached to carbon atoms. Table 7-2 shows those functional groups.

Functional Group: They are atoms or atom groups which are bonded to the carbon atom that differentiate organic compounds and give them different physical and chemical properties.

Table 7-2 **Functional Groups**

Example	General Formula	Suffix	Active Group	General structure	Name of Compound
CH_3Br Methyl bromide	$C_nH_{2n+1}X$	yl	-X	R-X (X= Cl, Br, I)	Alkyl Halides
CH_3CH_2-OH Ethanol	$C_nH_{2n+2}O$	ol	-OH	R-OH	Alcohols
CH_3-O-CH_3 Dimethyl ether	$C_nH_{2n+2}O$	ether	-OR´ Alkoxy	R-O-R´	Ethers
 $CH_3-\overset{\overset{O}{\Vert}}{C}-H$ Ethanal	$C_nH_{2n}O$	al	 $-\overset{\overset{O}{\Vert}}{C}-$ carbonyl	 $R-\overset{\overset{O}{\Vert}}{C}-H$	Aldehydes
 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_3$ Propanone	$C_nH_{2n}O$	one	 $-\overset{\overset{O}{\Vert}}{C}-$ carbonyl	 $R-\overset{\overset{O}{\Vert}}{C}-R´$	Ketones
 $CH_3-\overset{\overset{O}{\Vert}}{C}-OH$ Ethanoic acid	$C_nH_{2n}O_2$	oic	 $-\overset{\overset{O}{\Vert}}{C}-OH$ carboxyl	 $R-\overset{\overset{O}{\Vert}}{C}-OH$	Carboxylic acid
 $CH_3-\overset{\overset{O}{\Vert}}{C}-O-CH_3$ Methyl ethanoate	$C_nH_{2n}O_2$	Alkyle + oate	 $-\overset{\overset{O}{\Vert}}{C}-O-R´$ Ester	 $R-\overset{\overset{O}{\Vert}}{C}-O-R´$	Esters
$CH_3CH_2-NH_2$ Ethyl amine	$C_nH_{2n+3}N$	Amine	$-NH_2$	Primary  $R-\overset{\overset{H}{\vert}}{N}-H$ Secondary  $R-\overset{\overset{H}{\vert}}{N}-R´$ Tertiary  $R-\overset{\overset{R´´}{\vert}}{N}-R´$	Amines

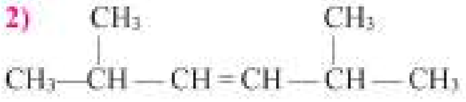
Exercise 7-2

Name the following compounds according to IUPAC.

1)

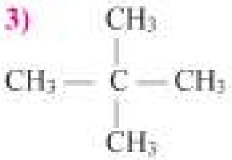
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-C\equiv C-CH_3$

2)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH=CH-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$

3)



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$

Attention:

mono = one

Primary = the carbon is attached to one other carbon.

Secondary = the carbon atom is attached to two other carbon atoms.

Tertiary = the carbon atom is attached to three other carbon atoms.

7-2 ALKYL HALIDES

By cleavage of one hydrogen atom from an alkane, an alkyl group forms. Table 7-3 shows some alkyl groups derived from alkanes.

$$\underset{\text{alkane}}{(R-H)}\xrightarrow{-H}\underset{\text{alkyl}}{R-}$$

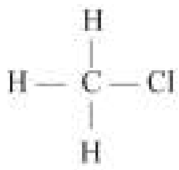
Table 7-3 Some Alkyl Groups derived from Alkanes

Name of group	Alkyls	Formula	Alkane
Methyl	CH_3-	CH_4	Methane
Ethyl	C_2H_5-	C_2H_6	Ethane
n-propyl	$CH_3-CH_2-CH_2-$	C_3H_8	Propane
Isopropyl	$CH_3-\overset{|}{C}H-CH_3$	C_3H_8	Propane

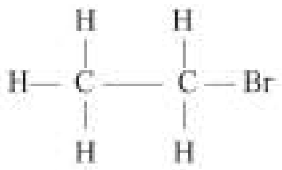
When a halogen atom (X−) is bonded to an alkyl group(R−), the resulting compound is called as an alkyl halide.

These compounds are derivatives of alkanes. The functional groups in those compounds are $-\overset{|}{\underset{|}{C}}-X$ or $R-X$ groups.

Here, R represents alkyl group and X represents halogens as I, Br, Cl.

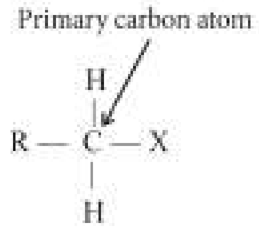


Methyl chloride

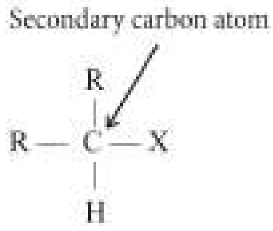


Ethyl bromide

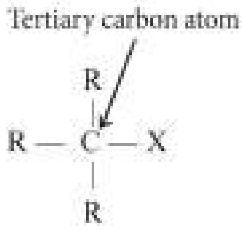
Alkyl halides are divided into three according to the carbon atom that halogen is attached to: primary (1°), secondary (2°) and tertiary (3°)



Primary alkyl halide (1°)

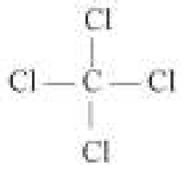


Secondary alkyl halide (2°)

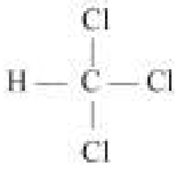


Tertiary alkyl halide (3°)

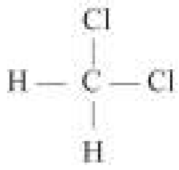
While forming alkyl halides, halogen atoms can replace more than one hydrogen atoms either on the same carbon or different ones.



Tetrachloromethane



trichloromethane
Chloroform



dichloromethane

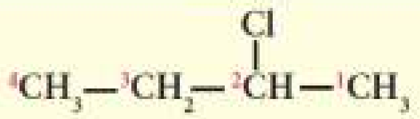
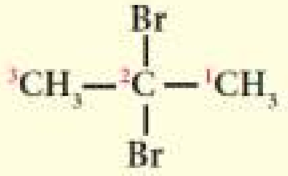
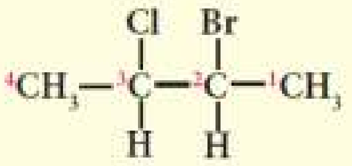
7-2-1 The Nomenclature of Alkyl Halides

Alkyl halides are named according to IUPAC nomenclature system as follows:

1- The longest carbon chain which has halogen atom is chosen. It is numbered starting from the halogen atom.

2- Firstly, the number of the carbon atom attached to halogen atom is written. Then, following the (-) hyphen symbol, halogen's name is written with –o suffix added (chloro, bromo, iodo). If there are other halogens, first the (-) symbol, then the names of those halogens are written in the same way. Halogens' names are written in alphabetical order in the compound. For example, bromo, chloro, iodo respectively. You can see those orders in Table 7-4.

Table 7-4 Systematic Names of Some Alkyl halides

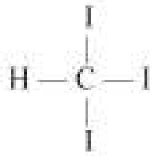
Compound	Systemic name of compound
 $^{4}CH_3-{}^{3}CH_2-{}^{2}\overset{Cl}{\overset{\vert}{C}}H-{}^{1}CH_3$	2-chlorobutane
 $^{3}CH_3-{}^{2}\underset{Br}{\underset{\vert}{\overset{Br}{\overset{\vert}{C}}}}-{}^{1}CH_3$	2,2- dibromopropane
 $^{4}CH_3-{}^{3}\underset{H}{\underset{\vert}{\overset{Cl}{\overset{\vert}{C}}}}-{}^{2}\underset{H}{\underset{\vert}{\overset{Br}{\overset{\vert}{C}}}}-{}^{1}CH_3$	2-bromo-3-chlorobutane
 $^{4}CH_3-{}^{3}\overset{CH_3}{\overset{\vert}{C}}H-{}^{2}CH_2-{}^{1}CH_2-Br$	1-bromo-3-methylbutane

7-2-2 The Synthesis of Alkyl Halides

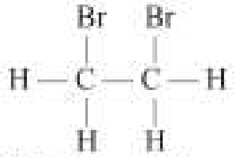
Alkyl halides are synthesized through many methods in industry and laboratories. We will explain some of those laboratory methods.

Addition of Hydrogen Halides to Alkenes

In case of the reaction of hydrogen halides HX such as (HBr, HCl, HI) with an alkene, hydrogen atom is attached to one of the carbons around the double bond, halogen atom is attached to the other carbon and alkyl halide is obtained. This reaction is called electrophilic addition reaction (searching for electrons).


$H-\underset{I}{\underset{\vert}{\overset{I}{\overset{\vert}{C}}}}-I$

Triiodomethane
Iodoform


$H-\underset{H}{\underset{\vert}{\overset{Br}{\overset{\vert}{C}}}}-\underset{H}{\underset{\vert}{\overset{Br}{\overset{\vert}{C}}}}-H$

1,2-dibromoethane

Attention:
While writing name of compound, does not leave space.

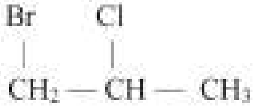
Exercise 7-3

1- Write down the structural formulas for the following compounds:

a- 1,1- dichloroethane
b- 2-bromo-2-iodohexane
c- 2-iodo-2-methylbutane

2- Write down the systematic names of the following compounds.

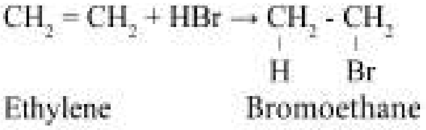
a) $CHCl_3$
b)


$\overset{Br}{\overset{\vert}{CH_2}}-\overset{Cl}{\overset{\vert}{CH}}-CH_3$

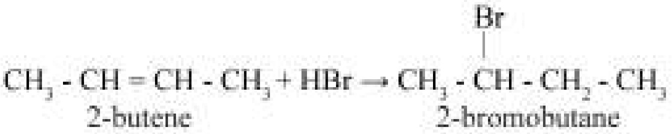
This kind of reactions occur in compounds which have double or triple bonds between carbon atoms. The reaction of hydrogen bromide with ethylene and 2-butene can be given as examples.

Note

Mechanism of reactions wherever found for information only



$$\underset{\text{Ethylene}}{CH_2=CH_2} + HBr \rightarrow \underset{\text{Bromoethane}}{\underset{H}{CH_2}-\underset{Br}{CH_2}}$$



$$\underset{\text{2-butene}}{CH_3-CH=CH-CH_3} + HBr \rightarrow \underset{\text{2-bromobutane}}{CH_3-\overset{Br}{CH}-CH_2-CH_3}$$

Attention:

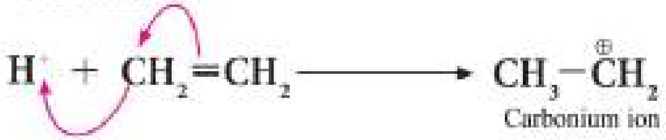
As nucleophile groups are free electron-rich (they have two or more electrons), they are named as nucleus loving. As electrophile groups have empty orbitals, they are named as electron loving. The steps of this mechanism apply to all alkenes which are symmetrical around the double bond. Therefore, it does not matter which carbon atom adds hydrogen and halide. The result is always the same, the same compound is obtained.

The mechanism of the reaction is as follows:

1- Hydrogen bromide contains positive proton (H^+) and negative bromide (Br^-) ions.

$$H-Br \longrightarrow \underset{\text{Electrophile}}{H^+} + \underset{\text{Nucleophile}}{Br^-}$$

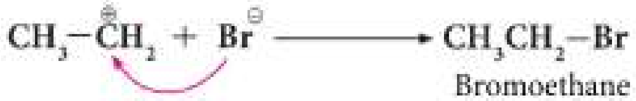
2- Proton (Electrophile) is added to the double bond of ethylene and carbonium ion forms.



$$H^+ + CH_2=CH_2 \longrightarrow CH_3-\overset{\oplus}{C}H_2$$

Carbonium ion

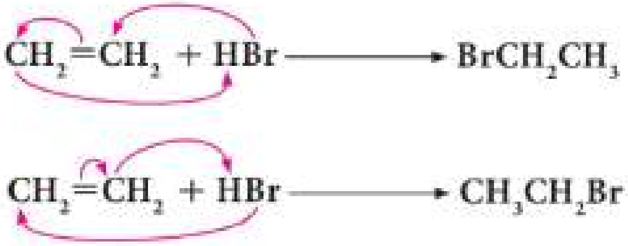
3- Negative bromide ion (Nucleophile) adds to positive carbonium ion and forms ethyl bromide (alkyl halide).



$$CH_3-\overset{\oplus}{C}H_2 + Br^{\ominus} \longrightarrow CH_3CH_2-Br$$

Bromoethane

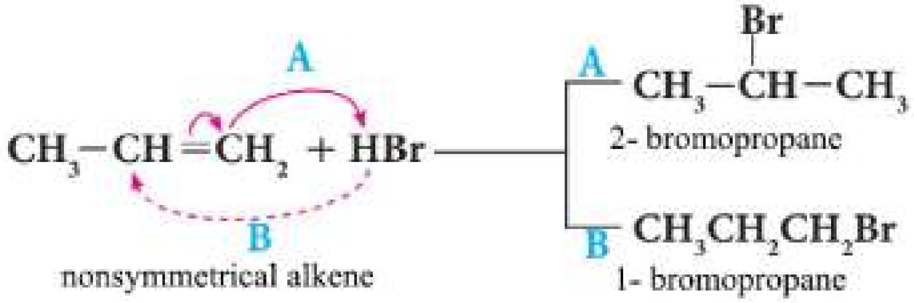
The steps of this mechanism apply to all alkenes which are symmetrical around the double bond. Therefore, it does not matter which carbon atom adds hydrogen and halide. The result is always the same, the same compound is obtained.



$$CH_2=CH_2 + HBr \longrightarrow BrCH_2CH_3$$

$$CH_2=CH_2 + HBr \longrightarrow CH_3CH_2Br$$

But if the groups around the double bond are not symmetrical, the reaction mechanism follows Markovnikov's rule.



According to Markovnikov's rule, 2-bromopropane is favored instead of 1-bromopropane.

Vladimir Markovnikov assigned the following rule after so many experiments. When a compound is added to a double bonded compound with asymmetric groups, the positive ion of the compound adds to the carbon with greater number of hydrogen atoms around the double bond. Negative ion adds to the other carbon (with less hydrogen) of the double bond.

Tertiary (3°) carbonium ion the most stable among the secondary (2°) and primary (1°) carbonium ions, whereas secondary carbonium is more stable than the primary one.

In the example above, Compound A is more stable therefore it is formed more than Compound B.

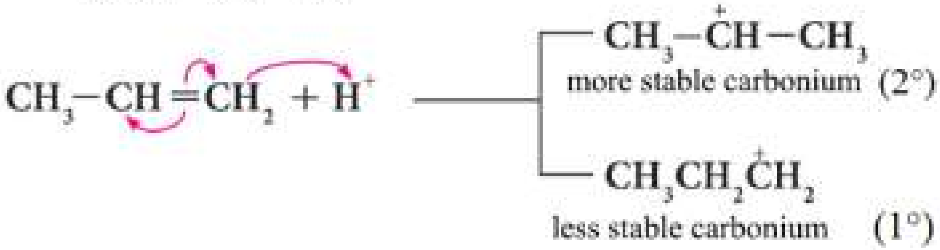
Exercise 7-4

Write down the reactions of the following with HCl.

a- 1-butene

b- 2-butene

$$H\text{-}Br \rightarrow H^+ + Br^-$$



$$\underset{\text{secondary carbonium ion}}{CH_3-\overset{+}{C}H-CH_3} + Br^- \longrightarrow \underset{\text{2- bromopropane}}{CH_3-\overset{\displaystyle Br}{\overset{|}{C}H}-CH_3}$$

Example 7-3

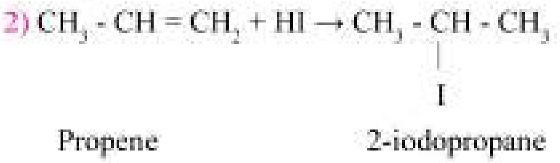
Prepare the compounds below:

1) ethyl chloride (chloroethane) from ethylene

2) 2-iodopropane from propene

Solution:

1) $\underset{\text{Ethylene}}{CH_2 = CH_2} + HCl \rightarrow \underset{\text{Chloroethane}}{CH_3 - CH_2 - Cl}$



2) $$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HI \rightarrow \underset{\text{2-iodopropane}}{CH_3 - \underset{\underset{\displaystyle I}{|}}{CH} - CH_3}$$

Exercise 7-5

Write down the chemical formulas for the following reactions:

1- Prepare 2-bromobutane using proper alkene

2- Add HCl to 2-methyl- propene

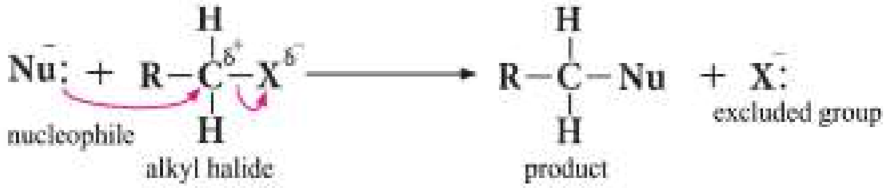
7-2-3-Properties of Alkyl Halides

1- Physical Properties

Alkyl halides like CH_3CH_2Cl, CH_3Br, CH_3Cl are in gas form at room temperature. Alkyl halides up to C_{18} are in liquid form and colorless. Alkyl halides that have more than 18 carbons are colorless and solid. They do not dissolve in water but dissolve in organic solvents. The reason for their water-insolubility is that they cannot form hydrogen bonds with water.

2- Chemical Properties

On the carbon which halogen is attached, the bond between carbon and hydrogen atoms is polarized as the halogen of alkyl halides has more electrons than carbon. The poles of this bond vary according to the type of halogen atom. For example, in alkyl iodide, the polarization is very low. The carbon which has the halogen atom becomes a good target for addition by the nucleophile group. The most significant reactions of alkyl halides are nucleophilic substitution reactions.



$$\bar{Nu}: + R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C^{\delta^+}}}-X^{\delta^-} \longrightarrow R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Nu + \bar{X}:$$

For this type of reactions, the following can be given as examples:

A- The reaction of alkyl halides with aqueous potassium hydroxide (KOH) solution

In this reaction, as shown in the following equation, halogen atom substitutes with hydroxyl group (-OH) and alcohol is formed.

$$\underset{\text{Iodomethane}}{CH_3I} + KOH \xrightarrow[\Delta]{H_2O} \underset{\text{Methanol}}{CH_3OH} + KI$$

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + KOH \xrightarrow[\Delta]{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + KBr$$

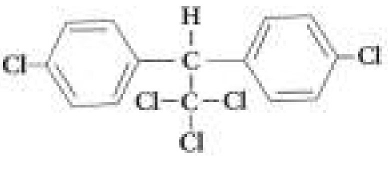
B- The reaction of alkyl halides with alcoholic potassium hydroxide (KOH)

When an alkyl halide reacts with alcoholic KOH, an alkene is obtained. In this reaction, HX molecule is lost from alkyl halide. This is a method of production of alkenes. For example:

$$\underset{\text{Bromoethane}}{\overset{H}{\overset{|}{CH_2}}-\overset{Br}{\overset{|}{CH_2}}} + KOH \xrightarrow[\Delta]{C_2H_5OH} \underset{\text{Ethylene}}{CH_2=CH_2} + KBr + H_2O$$

$$\underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br} + KOH \xrightarrow[\Delta]{C_2H_5OH} \underset{\text{propene}}{CH_3CH=CH_2} + KBr + H_2O$$

Do you know that?
Some alkyl halides such as CCl_4 are used in fire-extinguishers. Because they are so dense that they form a layer over fire. But due to the pollution they cause, they are used less nowadays. Alkyl halides are also used as pesticides, e.g DDT. But they were banned because they are dangerous.



D.D.T

C- The reaction of alkyl halide with magnesium metal in dry ether

Alkyl halides react with Mg metal in dry ether (free from moisture) to produce Grignard reagent to form methyl magnesium iodide (electrophile). from which alkanes are prepared.
For example:

$$CH_3I + Mg \xrightarrow{\text{dry ether}} CH_3MgI$$

Iodomethane Methyl magnesium iodide
(Grignard reagent)

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

Bromomethane Ethyl magnesium bromide
(Grignard reagent)

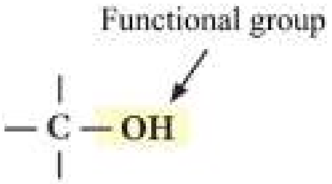
Exercise 7-6

Write down chemical equations for the following reactions:

1- The reaction of 2-chloro-2-methylpropane with aqueous KOH solution

2- The reaction of 1-bromo-3-ethylpentane with KOH in alcohol

7-3 ALCOHOLS

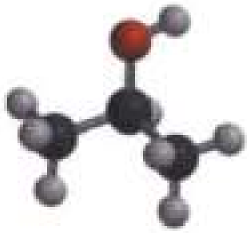


Alcohols are hydrocarbon compounds which have hydroxyl group bonded to saturated carbon atom. (-OH) is defined as the functional group in these compounds. Their general formula is R-OH or ($C_nH_{2n+2}O$).

CH_3OH
methanol

CH_3CH_2OH

ethanol



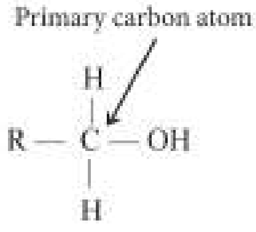
$$\underset{\displaystyle OH}{CH_3-\underset{|}{CH}-CH_3}$$

2- propanol

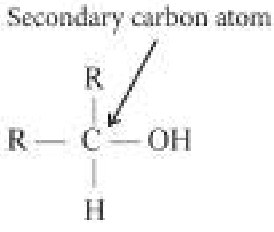
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH$$

2- methyl 2 propanol

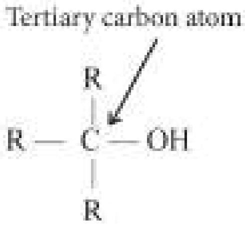
Alcohols are classified according to the hydroxyl group that is attached to carbon atom. If the carbon atom with hydroxyl group is attached to another carbon atom, it is a primary (1°) alcohol; if the carbon with the hydroxyl group is attached to two carbon atoms, it's a secondary (2°) alcohol; if the carbon with the hydroxyl group is attached to three carbon atoms, it is called as a tertiary (3°) alcohol.



Primary alcohol
(1°)



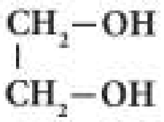
Secondary alcohol
(2°)



Tertiary alcohol
(3°)

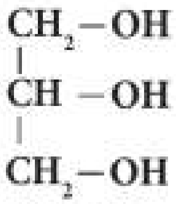
Do you know that?

Alcohols also include compounds that have 2 hydroxyl groups such as ethylene glycol or three hydroxyl groups such as glycerine. These compounds are called as polyalcohols.



$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

Ethylene glycol
Di-hidroxide

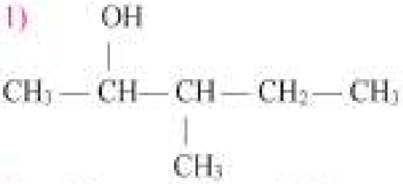


$$\begin{array}{l} CH_2-OH \\ | \\ CH\ -OH \\ | \\ CH_2-OH \end{array}$$

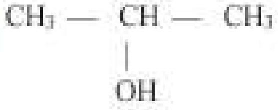
Glycerine
Tri-hidroxide

Exercise 7-7

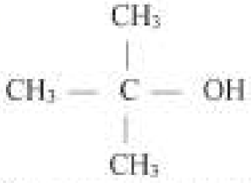
A- Name the following compounds systematically:

1) 

$$CH_3-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

2) 

$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

3) 

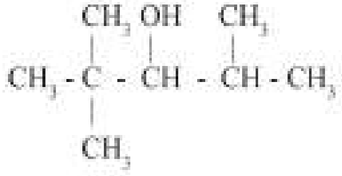
$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$$

B- Write down the structural formulas for the compounds below:
1) 2-methyl-2-hexanol
2) 2,2-dimethyl-1-butanol
3) 3-methyl-3-pentanol

7-3-1 Nomenclature of Alcohols

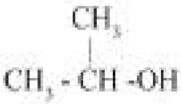
Alcohols are named according to IUPAC system as follows:
1- The longest chain which has the hydroxyl group is chosen. The carbon with the hydroxyl group is given the lowest number.
2- Naming is done according to the number of carbons. The –ol suffix is added to the end of the corresponding alkane.
3- The number and place of the alkyl groups on the chain is mentioned.

$CH_3-CH_2-CH_2-OH$
1- propanol



$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

2,2,4-trimethyl-3-pentanol



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-OH$$

2- propanol

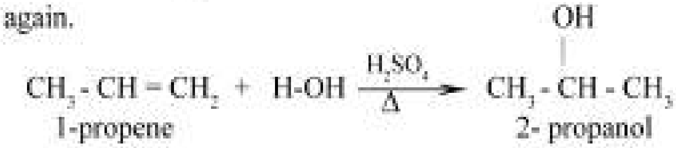
$Cl-CH_2-CH_2-CH_2-OH$
3-chloro-1- propanol

7-3-2 Synthesis of Alcohols

Alcohols can be synthesized through many methods in industry and laboratories. Here we will explain one of the laboratory methods.

Addition of Water to Alkenes

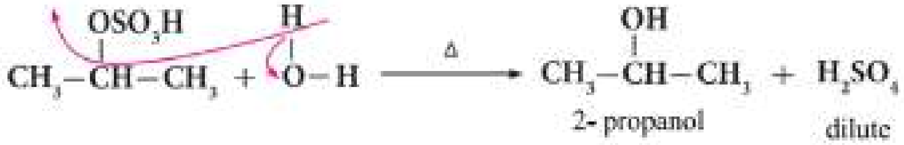
Addition of water to alkenes is achieved via hot concentrated sulfuric acid used as a catalyst. Alkene reacts first to produce alkyl sulfonic acid (Markovnikov's rule). This compound reacts with water and forms alcohol and sulfuric acid again.



$$CH_3-CH=CH_2 + H-OH \xrightarrow[\Delta]{H_2SO_4} CH_3-\overset{OH}{\overset{|}{CH}}-CH_3$$

According to reaction mechanism;

$$CH_3-CH=CH_2 + H\,OSO_3H \xrightarrow{\Delta} CH_3-\overset{OSO_3H}{\overset{|}{CH}}-CH_3$$



$$CH_3-\overset{OSO_3H}{\overset{|}{CH}}-CH_3 + \overset{H}{\overset{|}{O}}-H \xrightarrow{\Delta} CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 + H_2SO_4$$

Example 7-4

What are the probable structural formulas for alcohols that have a molecular weight of 74 g/mol?

Solution:

General formula for alcohols ($C_nH_{2n+2}O$)

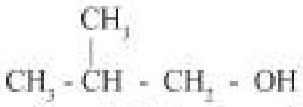
$C_nH_{2n+2}O = (n \times 12) + [(2n + 2) \times 1] + (1 \times 16)$

$C_nH_{2n+2}O = 12n + 2n + 2 + 16 = 74$ g/mol

$14n = 74 - 18 \Rightarrow n = 4$

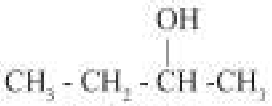
Molecular formula is $C_4H_{10}O$

$CH_3 - CH_2 - CH_2 - CH_2 - OH$
1- butanol
Primary alcohol



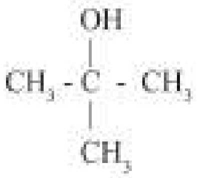
$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_2 - OH$$

2-methyl-1- propanol
Primary alcohol



$$CH_3 - CH_2 - \overset{\displaystyle OH}{\overset{|}{CH}} - CH_3$$

2- butanol
Secondary alcohol



$$CH_3 - \overset{\displaystyle OH}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}} - CH_3$$

2-methyl-2-propanol
Tertiary alcohol

7-3-3 Properties of Alcohols

1- Physical Properties

Alcohols have got low molecular weights. They are colorless and poisonous and they have sharp odors. They have strong intermolecular bonds. Therefore, their boiling points are much higher than of corresponding alkanes (Figure 7-1). Besides, alcohols can form hydrogen bonds between their molecules and with water molecules. Therefore, alcohols between (C_1-C_3) dissolve in water very well.

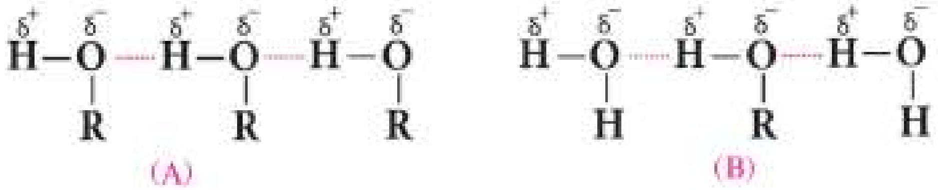


Figure 7-1

A) hydrogen bonds between alcohol molecules

B) hydrogen bonds between water and alcohol molecules

2- Chemical Properties

Alcohols are compounds that tend to react. They react with polarized or ionic compounds. Some important reactions of alcohols are given below:

A) Alcohols react with sodium or potassium metals to produce Alkoxides and hydrogen gas.

$$2CH_3 - CH_2 - OH + 2Na \longrightarrow 2CH_3 - CH_2 - O^- Na^+ + H_2 \uparrow$$

Ethanol → Sodium ethoxide

Attention:

OH^- group replaces OSO_3H^- in transition compound because OH^- is more basic and concentrated than OSO_3H^-. This method is used in preparation of alcohols in industry.

Exercise 7-8

What are the probable formulas for alcohols with a molar mass of 88 g/mol?

Exercise 7-9

Prepare the following compounds:

1) 2-butanol from 1-butene

2) ethanol from ethylene

B) They react with phosphorous trichloride (PCl_3) or phosphorous pentachloride (PCl_5) and form alkyl halides.

$$\underset{\text{Ethanol}}{CH_3 - CH_2 - OH} + PCl_5 \xrightarrow{\text{pyridine}} \underset{\text{Chloroethane}}{CH_3 - CH_2 - Cl} + POCl_3 + HCl$$

$$\underset{\text{Methanol}}{3CH_3 - OH} + PCl_3 \xrightarrow{\text{pyridine}} \underset{\text{Chloromethane}}{3CH_3 - Cl} + H_3PO_3$$

C) Reactions of Alcohols with (hydrogenhalide) Acids

Alcohols react with acid halides (HX) and form alkyl halides.

$$\underset{\text{2-propanol}}{CH_3 - \overset{\overset{OH}{|}}{CH} - CH_3} + HCl \xrightarrow{ZnCl_2} \underset{\text{2- chloropropane}}{CH_3 - \overset{\overset{Cl}{|}}{CH} - CH_3} + H_2O$$

This reaction occurs fast with tertiary alcohols especially when concentrated hydrochloric acid is used. But with primary and secondary alcohols, it is quite slow. And the reaction rate also depends on the type of acid.

HI > HBr > HCl

In the reaction, solution of zinc chloride in hydrochloric acid is used. This mixture is called as Lucas' reagent. It is used to differentiate primary, secondary and tertiary alcohols. Tertiary alcohols readily react with this cation and form alkyl halides which does not dissolve in the solution. While secondary alcohols react with Lucas' reagent after 5 minutes, primary alcohols do no react with it at room temperature.

Attention: As alcohols cannot donate hydroxyl OH^- ion to the solution, they are not accepted as strong bases.

Example 7-5

Differentiate 1-propanol, 2-propanol and 2-methyl-2-propanol chemically.

Solution:

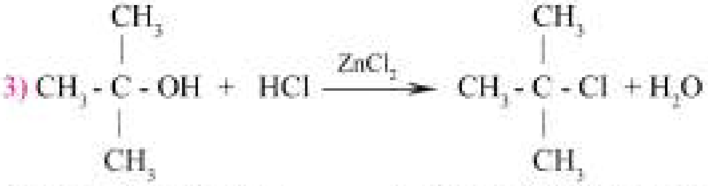
We can differentiate those compounds using dry $ZnCl_2/HCl$ Lucas' reagent. In this process, it is mixed with 2-propanol (secondary alcohol) and 5 minutes later, a layer of 2- chloropropane forms. While it reacts with 2-methyl-2-propanol (tertiary alcohol) readily, 1-propanol (primary alcohol) does not react with Lucas' reagent at room temperature.

1) $CH_3-CH_2-CH_2-OH + HCl \xrightarrow{ZnCl_2} N.R$

1-propanol

2) $CH_3-\overset{\overset{CH_3}{|}}{C}H-OH + HCl \xrightarrow{ZnCl_2} CH_3-\overset{\overset{CH_3}{|}}{C}H-Cl + H_2O$

2-propanol 2- chloropropane



3) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + HCl \xrightarrow{ZnCl_2} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + H_2O$

2-methyl-2-propanol 2-chloro-2-methylpropane

This way we can differentiate primary, secondary and tertiary alcohols using Lucas' reagent.

1- For primary alcohols to react with Lucas' reagent, high temperature is necessary and they do not react at room temperature. Therefore, no turbidity is visible in solution.

2- In secondary alcohols, turbidity appears 2-5 minutes later.

3- Through reaction of tertiary alcohol with Lucas' reagent, slightly water soluble alkyl halide forms and it causes turbidity in solution.

D) Dehydration of Alcohols

Ethyl alcohol reacts with concentrated sulfuric acid at 170 °C and ethylene forms.

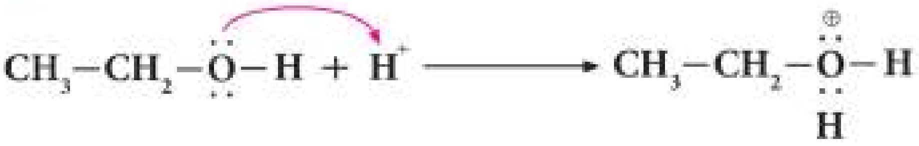
$CH_3-CH_2-OH \xrightarrow[(170°C)]{H_2SO_4\ Cond.} CH_2=CH_2 + H_2O$

Ethanol Ethylene

Mechanism:

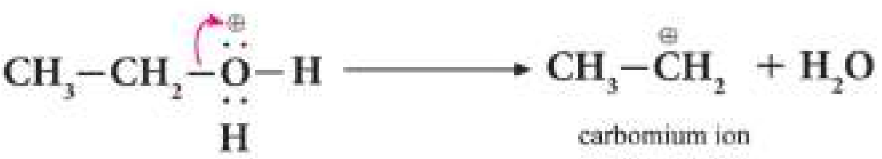
The mechanism of the reaction above follows the following steps:

1- Addition of proton to alcohol molecule:



$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\oplus}{\ddot{O}}}-H$

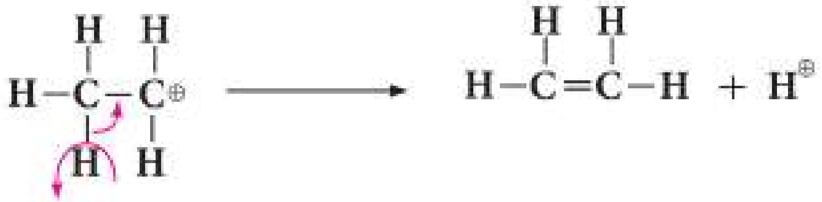
2- The cleavage of water molecule from the compound above and formation of more stable carbonium ion:



$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\oplus}{\ddot{O}}}-H \longrightarrow CH_3-\overset{\oplus}{C}H_2 + H_2O$

carbomium ion

3- The cleavage of proton from carbonium ion and formation of double bond and cation:



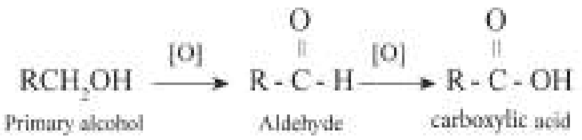
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}^{\oplus} \longrightarrow H-\overset{H}{C}=\overset{H}{C}-H + H^{\oplus}$$

According to Saytzeff's rule, The positive ion (H^+) is withdrawn from the carrier carbon atom the smallest number of hydrogen atom that adjacent to the carbon atom from which the negative ion (OH^-) is withdrawn.

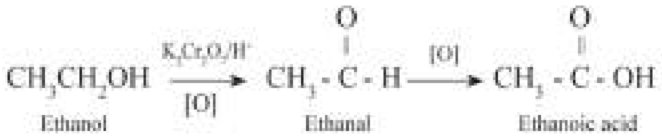
E) Oxidation

The structure of products which form when alcohols are oxidized depends on the type of alcohol and reaction conditions. Substances widely used in oxidation reactions are $K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/H_2SO_4$ mixtures. This reaction is a method used to differentiate alcohols.

Primary alcohols (1°) oxidize first to aldehydes then to carboxylic acids.

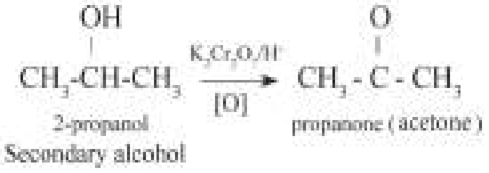


$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH}$$



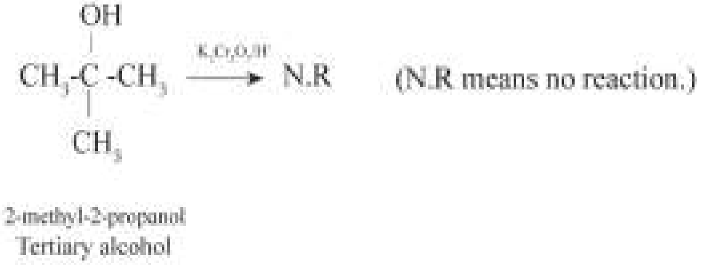
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} \underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

Secondary alcohols (2°) oxidize to ketones.



$$\underset{\substack{\text{2-propanol}\\ \text{Secondary alcohol}}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_3} \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} \underset{\text{propanone (acetone)}}{CH_3-\overset{O}{\overset{|}{C}}-CH_3}$$

Tertiary alcohols (3°) do not oxidize as the carbon atom which carries the OH^- group does not have any hydrogen atoms.



$$\underset{\substack{\text{2-methyl-2-propanol}\\ \text{Tertiary alcohol}}}{CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3} \xrightarrow{K_2Cr_2O_7/H^+} N.R \quad \text{(N.R means no reaction.)}$$

Exercise 7-10

When water molecule is removed from 2-butanol, why 2-butene is formed instead of 1-butene?

Exercise 7-11

Write the oxidation reaction of following compounds.

1) 1- butanol
2) 2- butanol
3) 2- methyl -2- propanol

Exercise 7-12

An organic compound which has 4 carbon atoms responses with Lucas' reagent. As a result of oxidation, a ketone compound forms. Write down the reaction equation. Guess the organic compound.

7-4 ETHERS

Ethers are shown as R'-O-R. Although they have a general formula as ($C_nH_{2n+2}O$) that is similar to that of alcohols, ethers have two alkyl groups and an oxygen atom. If alkyl groups are the same (R=R'), they are called as symmetric ethers, if alkyl groups are different (R≠R'), they are called as Asymmetric ethers. The functional group of ether is C-O-C.

symmetric ether

$CH_3 - O - CH_3$
Methoxy methane

Asymmetric ether

$CH_3 - O - CH_2CH_3$
Meythoxy ethane

Functional group in ethers is
C - O - C

7-4-1 Nomenclature of Ethers

Ethers (alkoxy alkanes) are named according to IUPAC system as shown in the following steps:

1- From alkyl groups which are bonded to oxygen atom, one with the longer chain is chosen and accepted as the main chain.

2- Main chain is numbered starting from the closest carbon to oxygen with the lowest number.

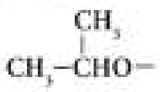
3- The –oxy suffix is added to name of the main chain.

4- Other alkyl groups are written with their numbers and place mentioned.

Number of branches + name of the branch + number of carbon atoms bonded to RO group + name of the RO group + name of the alkane corresponding to the longest chain

You can see the names of some –oxy (RO-) groups below:

1) Methoxy CH_3O-
2) Ethoxy CH_3CH_2O-
3) Propoxy $CH_3CH_2CH_2O$-
4) Izo -propoxy

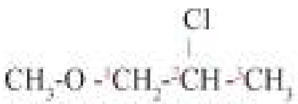


$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}HO-$

Example 7-6

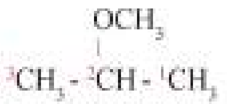
Write down systematic names for the following compounds:

Solution:



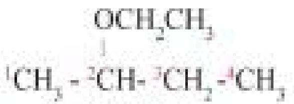
$CH_3\text{-}O\text{-}{}^1CH_2\text{-}{}^2\overset{\overset{\displaystyle Cl}{|}}{C}H\text{-}{}^3CH_3$

2-chloromethoxypropane



${}^3CH_3 - {}^2\overset{\overset{\displaystyle OCH_3}{|}}{C}H - {}^1CH_3$

2-methoxypropane



${}^1CH_3 - {}^2\overset{\overset{\displaystyle OCH_2CH_3}{|}}{C}H\text{-}\,{}^3CH_2 - {}^4CH_3$

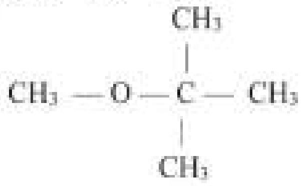
2-ethoxybutane

Exercise 7-13

A) Write down systematic names for the following compounds.

1) $CH_3 — O — CH_3$

2)



$CH_3 — O — \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} — CH_3$

B) Write down structural formulas for the following compounds.
1) 2,2-diethylmethoxyhexane
2) 2-chloro-2-methylpropoxypentane

7-4-2 Synthesis of Ethers

Ethers can be synthesized through many methods in industry and laboratories. We will explain one of the laboratory methods here.

Williamson Method

Ethers are prepared by the method which took the name of the scientist Williamson. In this method, sodium alkoxide forms from mixing of sodium metal with a suitable alcohol.

$$ROH + Na \longrightarrow \underset{\text{sodium alkoxide}}{RONa} + 1/2H_2$$

Then alkyl halide and sodium alkoxide reacts and target ether is obtained.

$$\underset{\text{Sodium alkoxide}}{R\text{-}ONa} + \underset{\text{alkyl halide}}{R' - X} \longrightarrow \underset{\text{ether}}{R\text{-}O\text{-}R'} + NaX$$

Exercise 7-14

1) Write the synthesis reaction of ethoxybutane from ethanol.

2) Write the produce of the following reaction.

$$\underset{\text{Bromopropane}}{CH_3CH_2CH_2\text{-}Br} + \underset{\text{Sodium methoxide}}{CH_3\text{-}ONa}$$

In order to synthesize methoxyethane and ethoxyethane, sodium reacts with methanol and ethanol. Formed sodium methoxide and sodium ethoxide react with bromoethane and following ethers are produced:

$$\underset{\text{Sodium methoxide}}{CH_3\text{-}ONa} + \underset{\text{bromoethane}}{C_2H_5 - Br} \longrightarrow \underset{\text{methoxyethane}}{CH_3\text{-}O\text{-}C_2H_5} + NaBr$$

$$\underset{\text{Sodium ethoxide}}{C_2H_5\text{-}ONa} + \underset{\text{bromoethane}}{C_2H_5 - Br} \longrightarrow \underset{\text{ethoxyethane}}{C_2H_5\text{-}O\text{-}C_2H_5} + NaBr$$

In these reactions, always primary alcohols are used. Secondary and tertiary alcohols cause formation of unwanted compounds.

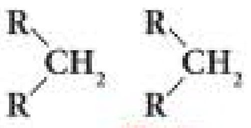
7-4-3 Properties of Ethers

1-Physical Properties

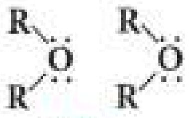
Methoxymethane and methoxyethane are in gas form at room temperature. Most of the other ethers are volutile liquids,Ignition and boiling points are too low. Therefore, they vaporize readily at room temperature . They are colorless and they have pleasant odors. As they don't have hydrogen bonds between their molecules, they have lower boiling points than alcohols. Ethers do not dissolve in water as they cannot form hydrogen bonds with water. But those with small alkyl groups dissolve partially in water.

Note:

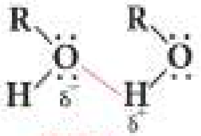
Through reaction of ethers with oxygen in air, epoxides are formed. While distillation ethers, peroxides accumulate somewhere and at the end of the process, this causes explosions with elevated temperatures. Therefore, Ethers must not be distilled to the point of dehydration (dryness).



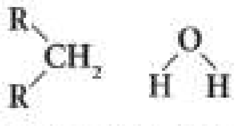
Alkanes
They do not have hydrogen bond between their molecules. They have low boiling point.



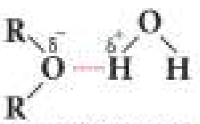
Ethers
They do not have hydrogen bond between their molecules. They have low boiling points.



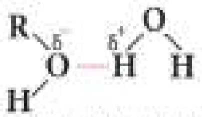
Alcohols
They have hydrogen bond between their molecules. They have high boiling points.



Alkanes -insoluble in water



Ethers partially soluble in water



Alcohols soluble in water

2- Chemical Properties

Ethers are stable compounds, thus they don't react with bases and active metals, they don't undergo oxidation reactions. Ethers can only undergo following reactions:

A- They form alcohols when they are heated with dilute sulfuric acid.

$$\underset{\text{Ethoxyethane}}{CH_3CH_2\text{-}O\text{-}CH_2CH_3} + H_2O \xrightarrow[\Delta]{H_2SO_4} \underset{\text{Ethanol}}{2CH_3CH_2OH}$$

But when they react with concentrated sulfuric acid or HCl, ethers donate a pair of electrons to hydrogen ion and form oxonium salts which can dissolve in acidic solutions. Ethers can be obtained again when oxonium salts are mixed with water. This reaction is used to differentiate alkanes and ethers as alkanes don't react with concentrated acids. For example:

$$CH_3-CH_2-\ddot{O}-CH_2-CH_3 + H_2SO_4 \xrightarrow{\text{cold}} \left[CH_3-CH_2-\underset{\oplus}{\overset{H}{\overset{|}{O}}}-CH_2-CH_3\right] HSO_4^-$$

Ethoxy ethane

oxonium salt of ethoxyethane

Exercise 7-15

How can you differentiate methoxymethane and ethane?
Tip: Consider the reaction of ethers with water in presence of concentrated sulfuric acid.

B- Reaction with PCl_5

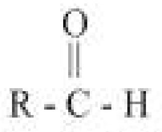
Ethers react with phosphorus pentachloride and form alkyl chloride.

$$R\text{-}O\text{-}R' + PCl_5 \xrightarrow{\Delta} R\text{-}Cl + R'\text{-}Cl + POCl_3$$

$$\underset{\text{Ethoxyethane}}{CH_3CH_2\text{-}O\text{-}CH_2CH_3} + PCl_5 \xrightarrow{\Delta} \underset{\text{Ethyl chloride}}{2CH_3CH_2\text{-}Cl} + POCl_3$$

7-5 ALDEHYDES AND KETONES

Aldehydes and ketones have the same functional group. Its name is carbonyl group. This group is formed by oxygen atom attached with a double bond to carbon atom. Compounds which include this $\overset{O}{\overset{\|}{-C-}}$ functional group are called as carbonyl compounds. Their general formula is $C_nH_{2n}O$. In aldehydes, the carbon of carbonyl is bonded to a hydrogen and an alkyl group, whereas in ketones, carbon of carbonyl group is bonded to the same or different two alkyl groups.



$$R-\overset{O}{\overset{\|}{C}}-H$$

General formula of aldehydes

$$R-\overset{O}{\overset{\|}{C}}-R'$$

General formula of ketones

Do you know that

The substance which is used in autopsy and to preserve bodies is the simplest form of aldehydes that is formaldehyde?

7-5-1 Nomenclature of Aldehydes and Ketones

Aldehydes and ketones are named according to IUPAC nomenclature system as in the following steps:

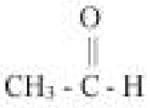
A) Nomenclature of Aldehydes

1- The longest carbon chain is chosen. The carbon atom of carbonyl group is numbered with 1.

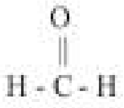
2- -al suffix is added to the end of the name of the corresponding alkane.

3- Alkyl groups are mentioned with their numbers.

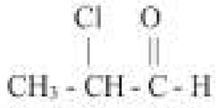
As numbering starts from the side of carbonyl group, the number of carbonyl group doesn't need to be mentioned. For example:


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Ethanal


$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Methanal


$CH_3-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-H$

2-chloropropanal


$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Propanal

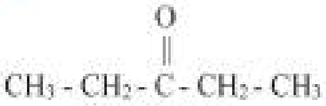
B) Nomenclature of Ketones

Apply the steps in nomenclature of aldehydes.

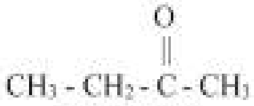
1- choose the longest carbon chain and start numbering from the closest carbon to the carbonyl group.

2- add –one suffix to the end of the corresponding alkane.

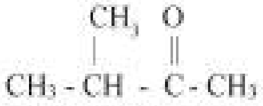
3- If there is branching, alkyl groups are mentioned with their numbers.


$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$

3-pentanone


$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

2-butanone


$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

3-methyl-2-butanone

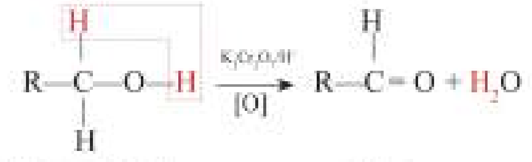
7-5-2 Preparation of Aldehydes and Ketones

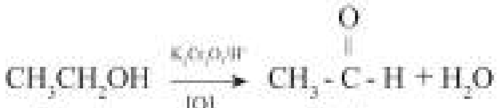
Aldehydes and ketones are synthesized through many methods in industry and laboratories. Here, we will explain one of the laboratory methods.

Oxidation of Alcohols

Aldehydes and ketones are prepared by oxidation of primary (1°) and secondary (2°) alcohols with acidic solution of potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).

Primary alcohols form aldehydes as shown in the following equation.


$$R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-O-H \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} R-\overset{\overset{\displaystyle H}{|}}{C}=O+H_2O$$


$$CH_3CH_2OH \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H+H_2O$$

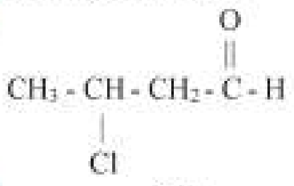
Do you know that

The organic compound used to remove nail polish is the simplest form of ketones that is acetone (propanone)?

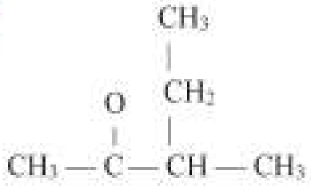
Exercise 7-16

1- Write down systematic names for the following compounds:

a)


$CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

b)


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\overset{\overset{\displaystyle CH_3}{|}}{CH_2}}{|}}{CH}-CH_3$

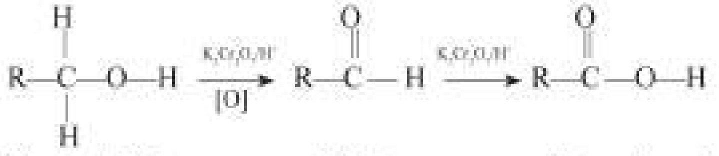
2- Write down formulas for the following compounds.

a) 3-methylbutanal

b) 2-hexanone

The aldehyde remaining in the reaction mixture above is readily oxidized and it forms carboxylic acid.

Therefore, oxidation reaction must be controlled.



$$R-CH_2-O-H \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{K_2Cr_2O_7/H^+} R-\overset{O}{\overset{\|}{C}}-O-H$$

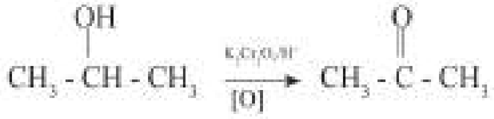
Primary alcohol   Aldehyde   Carboxylic acid

Ketones are prepared through oxidation of secondary (2^0) alcohols.

$$R-\overset{H}{\underset{R}{C}}-O-H \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} R-\overset{R}{C}=O$$

Secondary alcohol   Ketone

For example:



$$CH_3-\overset{OH}{CH}-CH_3 \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

2-propanol   Propanone

Tertiary alcohols cannot be oxidized.

Example7-7

Write down oxidation products of the following compounds.

1) 1-propanol
2) 2-pentanol

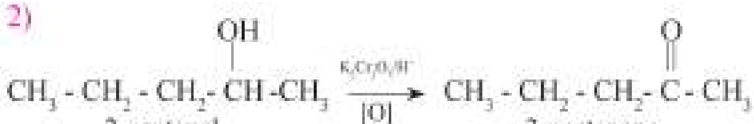
Solution:

1)

$$CH_3-CH_2-CH_2\text{-}OH \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2O \xrightarrow{[O]} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-H$$

1-propanol   propanal   propanoic acid

2)



$$CH_3-CH_2-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

2-pentanol   2-pentanone

Attention

when placing chemical reagents to conduct chemical reactions above the arrow in the chemical equation, this means that the equation can be written regardless of the balance.

Do you know that

Some aldehydes and ketones are obtained from plants.
Benzaldehyde is obtained from almonds and some ketones are obtained from cinnamon.

Exercise 7-17

Prepare the following compounds using suitable alcohols.

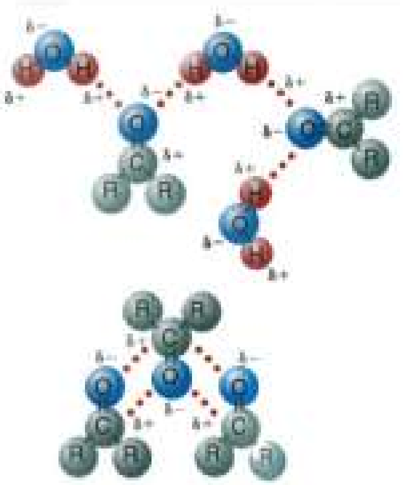
1) ethanal
2) 2-butanone

7-5-3 Properties of Aldehydes and Ketones

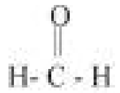
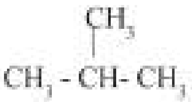
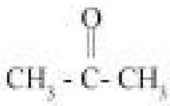
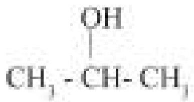
1- Physical Properties

All aldehydes and ketones are in liquid form at room temperature except mathanal (formaldehyde, in gas form).

Although ketones have pleasant odors, aldehydes have unplaeasant odors. Densities of ketones are lower than that of water. Owing to the polar property of carbonyl group, these compounds are accepted as polarized. They can dissolve in water and organic solvents like ether. Boiling points of aldehydes and ketones are higher than those of alkanes, but lower than alcohols which have the same molecular weight with them. For example:



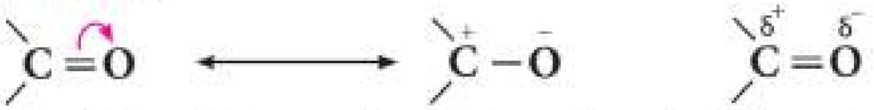
Aldehydes can dissolve in water because of hydrogen ion in their molecules, which form hydrogen bonds with water.

$CH_3 - CH_3$	 $H-\overset{\overset{\displaystyle O}{\|}}{C}-H$	$CH_3 - OH$
Ethane	Formaldehyde	Methyl alcohol
M= 30, bp = -89 °C	M= 30, bp = -21 °C	M= 32, bp = 64.5 °C
 $CH_3-\overset{\overset{\displaystyle CH_3}{\|}}{CH}-CH_3$	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$	 $CH_3-\overset{\overset{\displaystyle OH}{\|}}{CH}-CH_3$
Isobutane	Acetone	Isopropyl alcohol
M= 58, bp = -12 °C	M= 58, bp = 56 °C	M= 60, bp = 82.5 °C

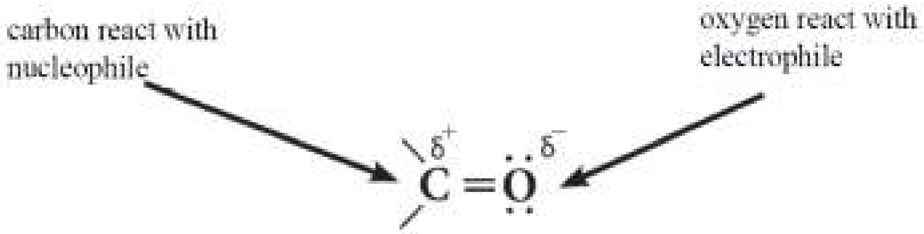
(M = molecular weight and b.p = boiling point)

2- Chemical Properties

The carbonyl group in aldehydes and ketones has high ionization property as shown below:



Carbon in the carbonyl group is positive charged, as nucleophile approaches it, electrophile approaches to negative charged oxygen.



Aldehydes and ketones can undergo two-step nucleophilic reactions. These are:

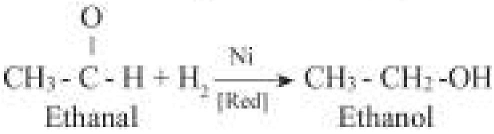
A) 1st step: Nucleophile (Nu:) approaches carbon of carbonyl group and forms a new bond. This bond breaks double bond between oxygen and carbon and pushes a pair of electrons to oxygen atom.

B) 2nd step: approach of an electrophile such as H^+ ion:

Reactions of Aldehydes and Ketones:

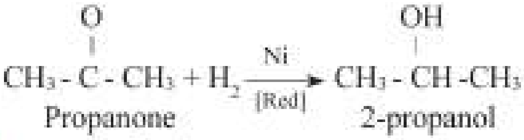
a) Reduction with hydrogen

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols when they react with H_2 with Ni and Pt as catalysts.



$$CH_3-\overset{O}{\overset{|}{C}}-H + H_2 \xrightarrow[\text{[Red]}]{Ni} CH_3-CH_2-OH$$

Ethanal Ethanol



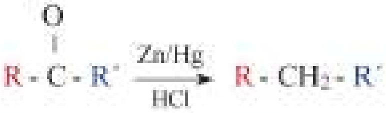
$$CH_3-\overset{O}{\overset{|}{C}}-CH_3 + H_2 \xrightarrow[\text{[Red]}]{Ni} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$$

Propanone 2-propanol

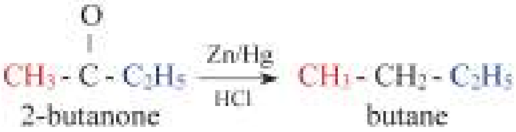
(Red means reduction)

b) Reduction to Alkanes

Aldehydes and ketones are reduced to alkanes via **Clemmensen reduction** method. In this method, solution of zinc and mercury in hydrochloric acid is used as catalyst.

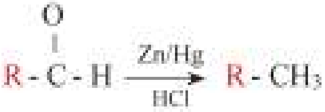


$$R-\overset{O}{\overset{|}{C}}-R' \xrightarrow[HCl]{Zn/Hg} R-CH_2-R'$$



$$CH_3-\overset{O}{\overset{|}{C}}-C_2H_5 \xrightarrow[HCl]{Zn/Hg} CH_3-CH_2-C_2H_5$$

2-butanone butane



$$R-\overset{O}{\overset{|}{C}}-H \xrightarrow[HCl]{Zn/Hg} R-CH_3$$

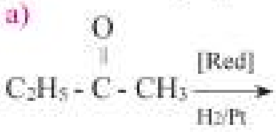
$$CH_3-\overset{O}{\overset{|}{C}}-H \xrightarrow[HCl]{Zn/Hg} CH_3-CH_3$$

Ethanal Ethane

Exercise 7-18

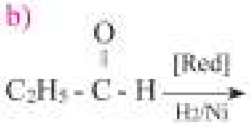
Complete following equations:

a)



$$C_2H_5-\overset{O}{\overset{|}{C}}-CH_3 \xrightarrow[H_2/Pt]{\text{[Red]}}$$

b)



$$C_2H_5-\overset{O}{\overset{|}{C}}-H \xrightarrow[H_2/Ni]{\text{[Red]}}$$

Exercise 7-19

1- Prepare propane from propanal.

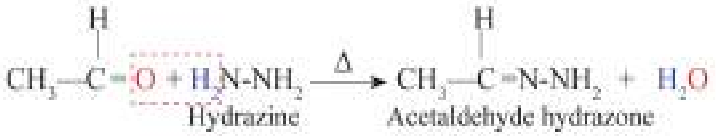
2- Write down the reaction of propanal with hydrazine.

Do you know that

The accumulation of silver on test tube as a result of the reaction of aldehydes with Tollens' Reagent enabled chemists to produce many types of mirrors .

c) Reaction with Hydrazine

Aldehydes and ketones react with hydrazine (H_2N-NH_2) and produce hydrazone which is known as Schiff base.



$$CH_3-\overset{H}{\overset{|}{C}}=O + H_2N-NH_2 \xrightarrow{\Delta} CH_3-\overset{H}{\overset{|}{C}}=N-NH_2 + H_2O$$

Hydrazine — Acetaldehyde hydrazone

$$\underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O} + \underset{\text{Hydrazine}}{H_2N-NH_2} \xrightarrow{\Delta} \underset{\text{acetone hydrazone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=N-NH_2} + H_2O$$

This reaction is used to examine the presence of carbonyl group in aldehydes and ketones. Hydrazone (orange or yellow color) shows the presence of the carbonyl group.

d) Oxidation

Presence of hydrogen bonded to carbonyl group in aldehydes causes some reactions different from those of ketones. The most important reactions of aldehydes and ketones are oxidation reactions.

Aldehydes are oxidized into carboxylic acids by the help of some oxidizing agents. But in ketones, this does not occur. We can differentiate aldehydes and ketones using following reactions:

1-Tollens' Reagent

In order to differentiate aldehydes, silver ammonium hydroxide is used. In this reaction, silver ion is reduced in solution and silver metal covers the tube's surface as mirror showing the presence of aldehyde. This reaction is shown below:

$$\underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{silver ammonium hydroxide}}{2Ag(NH_3)_2OH} \rightarrow \underset{\text{salt of carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-O^-NH_4^+} + \underset{\text{Silver mirror}}{2Ag\downarrow} + H_2O + 3NH_3$$


1


2


3


4


5

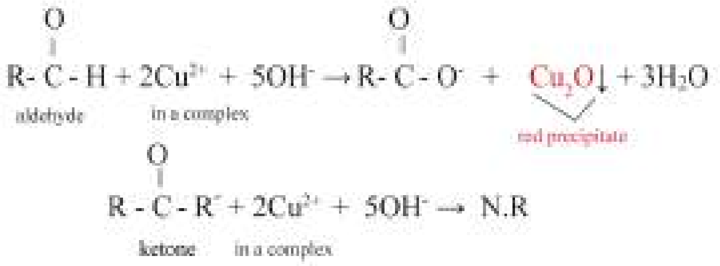

6

Tollens' Reagent

$$R-\overset{O}{\overset{\|}{C}}-R' + 2Ag(NH_3)_2OH \rightarrow N.R.$$

e) Reaction with Fehling's Solution

Fehling's solution is a solution of copper sulfate (II) salt. It's basic and dark blue. it contains negative roots such as citrate and tartrate to prevent the formation of a copper hydroxide precipitate because it always forms stable complexes. It is used in oxidation of aldehydes. In this reaction, copper (II) ions transforms into red copper (I) oxide. This red copper (I) oxide precipitate shows presence of aldehyde in mixture. As shown below, ketones do not react with this reagent.



$$\underset{\text{aldehyde}}{R-\overset{\overset{O}{|}}{C}-H} + \underset{\text{in a complex}}{2Cu^{2+}} + 5OH^- \rightarrow R-\overset{\overset{O}{|}}{C}-O^- + \underbrace{Cu_2O\downarrow}_{\text{red precipitate}} + 3H_2O$$

$$\underset{\text{ketone}}{R-\overset{\overset{O}{|}}{C}-R'} + \underset{\text{in a complex}}{2Cu^{2+}} + 5OH^- \rightarrow N.R$$

7-6 CARBOXYLIC ACIDS

The functional group of all carboxylic acids is carboxyl group (-COOH) or $(-\overset{\overset{O}{|}}{C}-OH)$. This group consists of hydroxyl and carbonyl groups.

The structural formula of carboxylic acids is $R-\overset{\overset{O}{|}}{C}-OH$. (R) represents alkyl group or hydrogen atom. Their general formula is $(C_nH_{2n}O_2)$.

7-6-1 Nomenclature of Carboxylic Acids

Carboxylic acids are named according to IUPAC system as shown in the following steps:

1- The longest carbon chain that includes carboxyl group is chosen and numbered. Carboxyl group is given number 1.

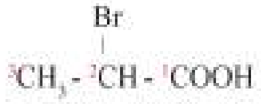
2- Branched groups are written in alphabetical order and with their numbers mentioned.

3- The word "acid" is added.

4- The name of the alkane which corresponds to the longest carbon chain is written and suffix (-oic) is added in the end.

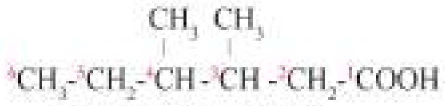
CH_3COOH
Ethanoic acid

$HCOOH$
Methanoic acid



$${}^3CH_3-{}^2\overset{\overset{Br}{|}}{C}H-{}^1COOH$$

2-bromopropanoic acid



$${}^6CH_3-{}^5CH_2-{}^4\overset{\overset{CH_3}{|}}{C}H-{}^3\overset{\overset{CH_3}{|}}{C}H-{}^2CH_2-{}^1COOH$$

3,4-dimethylhexanoic acid

Fehling's Solution

Exercise 7-20

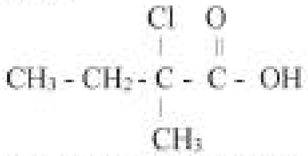
How can you differentiate propanal and propanone compounds using the following practically?

a) Fehling's solution
b) Tollens' Reagent

Ethanoic acid
(vinegar)

Exercise 7-21

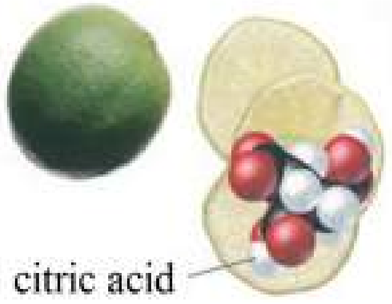
1) Write the name of the following compound.



$$CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$$

2) Write the structure formula of the following compounds.

a) 2- methylbutanoic acid
b) 3-chloropropanoic acid

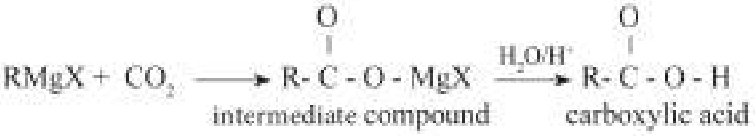


Lemons contain citric acid which is a carboxylic acid.

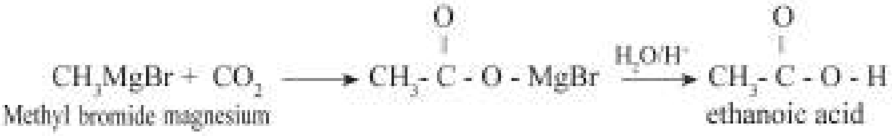
7-6-2 Preparation of Carboxylic Acids

Carboxylic acids are prepared through many methods. As we have mentioned before, they are prepared by oxidation of primary (1^{o}) alcohols or aldehydes. We will explain preparation of carboxylic acids using Grignard reagent. In this reaction, firstly, alkyl halide is used then CO_2. As shown below, in order to prepare wanted carboxylic acid, hydrolysis (reaction with water) in acidic medium is realized.

$$R-X + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{RMgX}$$



$$RMgX + CO_2 \longrightarrow \underset{\text{intermediate compound}}{R-\overset{\overset{O}{|}}{C}-O-MgX} \xrightarrow{H_2O/H^+} \underset{\text{carboxylic acid}}{R-\overset{\overset{O}{|}}{C}-O-H}$$



$$\underset{\text{Methyl bromide magnesium}}{CH_3MgBr + CO_2} \longrightarrow CH_3-\overset{\overset{O}{|}}{C}-O-MgBr \xrightarrow{H_2O/H^+} \underset{\text{ethanoic acid}}{CH_3-\overset{\overset{O}{|}}{C}-O-H}$$

Exercise 7-22

Prepare propanoic acid from the following:

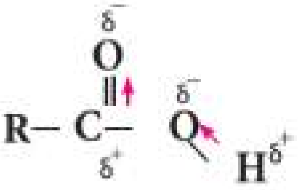
1) ethyl bromide
2) propanal

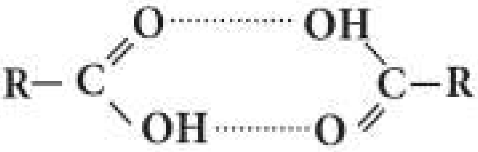
The carboxylic acid prepared through this method has one extra carbon than the alkyl group of Grignard reagent.

7-6-3-General Properties of Carboxylic Acids

1-Physical Properties:

The carboxylic acids with low molecular mass (lower than C_{10}) are liquids with pungent and unpleasant odors. As their molecular mass increase, their boiling points also go up and the boiling points are higher than those of alcohols with the same number of carbons. The reason is that carbonyl and hydroxyl group in acid molecule ionize at a high rate and hydrolysis occurs (more than alcohols) between acid molecules. forming hydrogen bonds.





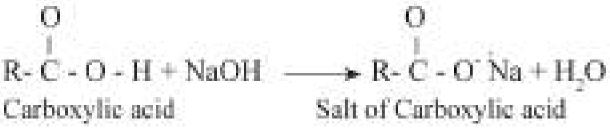
Hydrogen bond

Carboxylic acids with low molecular mass are highly-soluble in water. As their molecular mass increase, their solubilities decrease.

2-Chemical Properties:

A) Acidity of Carboxylic Acids:

Carboxylic acids assume acid property by carboxyl group's donation of proton. Therefore, they react with bases readily and form water and salt.



$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{|}}{C}-O-H} + NaOH \longrightarrow \underset{\text{Salt of Carboxylic acid}}{R-\overset{\overset{O}{|}}{C}-O^-Na^+} + H_2O$$

B) Reactions of carboxylic acid with carbonates and bicarbonates

When carboxylic acids react with carbonates and bicarbonates, CO_2 gas is formed. This reaction is one of the important reactions to differentiate carbonyl group in carboxylic acids.

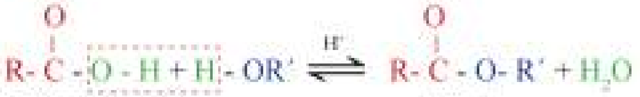
$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2\uparrow + H_2O$$

Exercise 7-23

Write down the reaction equation of acetic acid with sodium bicarbonate, ($NaHCO_3$).

C) Reaction of carboxylic acid with alcohols (esterification reaction)

Carboxylic acids react with alcohols along with HCl or H_2SO_4 catalysts and form esters. This reaction is reversible as seen below and called as **esterification.**



$$\underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{|}{C}}-\boxed{O-H+H}-OR'} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R-\overset{O}{\overset{|}{C}}-O-R'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{|}{C}}-\boxed{O-H+H}}\underset{\text{Ethanol}}{-OC_2H_5} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl ethanoate}}{CH_3-\overset{O}{\overset{|}{C}}-O-C_2H_5} + H_2O$$

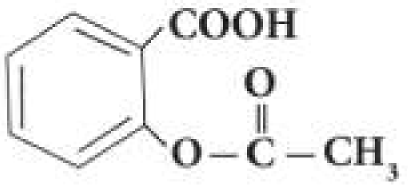
D) Reduction of Carboxylic Acids

Carboxylic acids are reduced by reducing agents such as lithium aluminum hydride ($LiAlH_4$) and form primary alcohols. But they cannot be reduced with H_2/Ni.

$$\underset{\text{Acetic acid}}{CH_3-\overset{O}{\overset{|}{C}}-OH} \xrightarrow[\text{ether}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

Do you know that

Aspirin which has been used as pain killer anticoagulant for patients with heart disease, is one of the most importent drug that contain carboxylic acid.



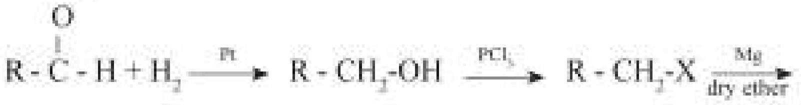
Example 7-8

Prepare propanoic acid starting from ethanal.

$$CH_3-\overset{O}{\overset{|}{C}}-H \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Solution:

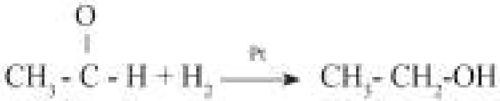
The equations of the reactions are as follows:



$$R-\overset{O}{\overset{|}{C}}-H+H_2 \xrightarrow{Pt} R-CH_2-OH \xrightarrow{PCl_5} R-CH_2-X \xrightarrow[\text{dry ether}]{Mg}$$

$$R-CH_2-MgX \xrightarrow{CO_2} R-CH_2-COOMgX \xrightarrow{HX} R-CH_2-COOH + MgX_2$$

1. step



$$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{|}{C}}-H+H_2} \xrightarrow{Pt} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

Exercise 7-24

Prepare butanoic acid starting from propanal.

Exercise 7-25

Prepare butanoic acid starting from 1-butanol.

Vitamin C is found in many fruits.

2. step

$3CH_3\text{-}CH_2\text{-}OH + PCl_3 \longrightarrow 3CH_3\text{-}CH_2\text{-}Cl + H_3PO_3$

Ethanol → Ethyl chloride

3. step

$CH_3\text{-}CH_2\text{-}Cl + Mg \xrightarrow{\text{dry ether}} CH_3\text{-}CH_2\text{-}MgCl$

Ethyl chloride → Grignard reagent

4. step

$CH_3\text{-}CH_2\text{-}MgCl + CO_2 \longrightarrow CH_3\text{-}CH_2\text{-}COOMgCl$

Intermediate compound

5. step

$CH_3\text{-}CH_2\text{-}COOMgCl + HCl \longrightarrow CH_3\text{-}CH_2\text{-}COOH + MgCl_2$

Propanoic acid

Example 7-9

Prepare propanoic acid starting from ethyl chloride.

Solution:

In this method, a carboxylic acid is obtained with one more extra carbon than the number of carbons of the starting alkyl.

$CH_3\text{-}CH_2\text{-}Cl + Mg \xrightarrow{\text{dry ether}} CH_3\text{-}CH_2\text{-}MgCl$

Ethyl chloride → Grignard reagent

$CH_3\text{-}CH_2\text{-}MgCl + CO_2 \longrightarrow CH_3\text{-}CH_2\text{-}COOMgCl$

Intermediate compound

$CH_3\text{-}CH_2\text{-}COOMgCl + HCl \longrightarrow CH_3\text{-}CH_2\text{-}COOH + MgCl_2$

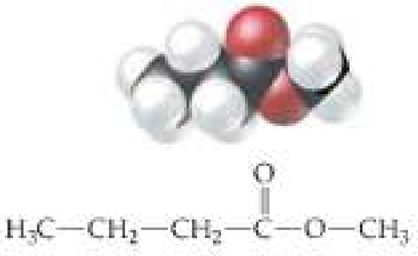
Propanoic acid

(Vitamin C), which is known as ascorbic acid is a carboxylic acid which is found in citrus fruits most. It has an important place in our lives. Vitamin C helps improving defense of body by strengthening immune system. It is given as pills to patients.

7-7 ESTERS

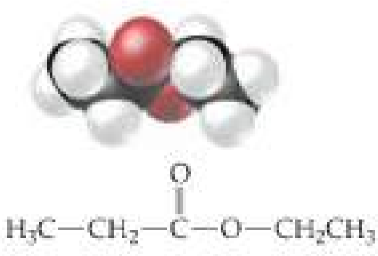
Esters have got the same functional group with carboxylic acids. They both have $(R-\overset{\overset{O}{\|}}{C}-O-)$ molecule. The structural formula of esters is $R-\overset{\overset{O}{\|}}{C}-O-R'$

and general formula is $C_nH_{2n}O_2$. Here R′=R or R′≠R.
Besides, R can never be a hydrogen atom as in carboxylic acids.



$H_3C-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$

Methyl butanoate



$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$

Ethyl propanoate

7-7-1 Nomenclature of Esters

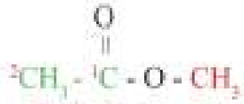
As esters $R-\overset{O}{\overset{\|}{C}}-O-R'$ are made up of two groups, one is from carboxylic acid and the other is from alcohol $R-\overset{O}{\overset{\|}{C}}-OH$, so they are named after they are divided into two groups as follows:

1- The first name of ester belongs to the alkyl group bonded to the oxygen atom in alcohol group.

2- The remaining name is written by adding –oate suffix to the alkane part of the carboxylic acid.

$$\overset{3}{C}H_3-\overset{2}{C}H(Cl)-\overset{1}{C}(=O)-O-C_2H_5$$

Ethyl 2-chloropropanoate

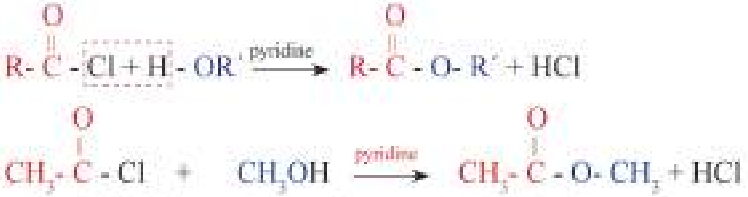


$$\overset{2}{C}H_3-\overset{1}{C}(=O)-O-CH_3$$

Methyl ethanoate

7-7-2-Preparation of Esters

Esters can be synthesized through many methods such as the reaction of alcohols and carboxylic, Besides from the reaction of carboxylic acid chloride with alcohol in the presence of pyridine used to remove the HCl acid that produce, esters are prepared.



$$R-\overset{O}{\overset{\|}{C}}-Cl+H-OR' \xrightarrow{pyridine} R-\overset{O}{\overset{\|}{C}}-O-R'+HCl$$

$$CH_3-\overset{O}{\overset{|}{C}}-Cl + CH_3OH \xrightarrow{pyridine} CH_3-\overset{O}{\overset{|}{C}}-O-CH_3+HCl$$

Acetyl chloride Methanol Methyl ethanoate

7-7-3 General Properties

1- Physical Properties of Esters

Esters can ionize. Its shows apolar characteristic in its molecules, but its effect on the molecule decreases with the increase of non-polar hydrocarbon part . They don't form hydrogen bonds between their molecules.

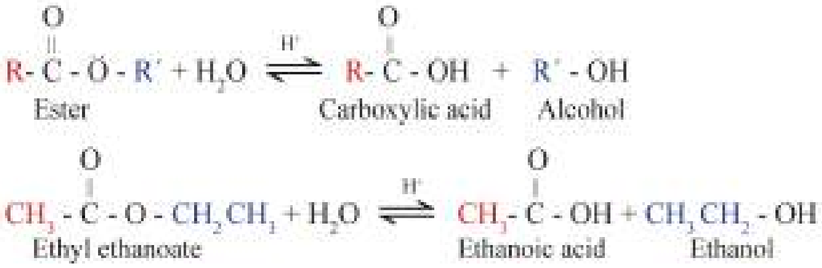
Therefore, their boiling points are lower than those of carboxylic acids with the same number of carbons. Most esters don't dissolve in water but dissolve in many organic solvents. Besides, these substances are used as good solvents for many organic compounds.

2- Chemical Properties of Esters

Esters undergo following reactions.

a) Reaction of Esters with Water in Acidic Medium

This reaction is the opposite of esterification reaction which is synthesis of esters from alcohols and carboxylic acids. Here H_2SO_4 and HCl are used as catalysts. Esters react with water and form carboxylic acids and alcohols.



$$R-\overset{O}{\overset{\|}{C}}-O-R'+H_2O \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{|}{C}}-OH + R'-OH$$

Ester Carboxylic acid Alcohol

$$CH_3-\overset{O}{\overset{|}{C}}-O-CH_2CH_3+H_2O \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{|}{C}}-OH+CH_3CH_2-OH$$

Ethyl ethanoate Ethanoic acid Ethanol

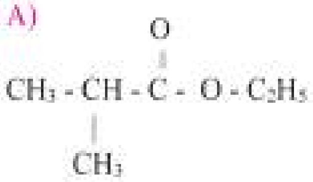
Do you know that

Esters which are found in fruits and vegetables have pleasant odors and therefore they are used as sweetener in foods, perfumes and kids' foods .

Exercise 7-26

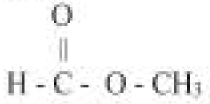
1- Write down systematic names of the following compounds.

A)



$$CH_3-\underset{CH_3}{\underset{|}{C}H}-\overset{O}{\overset{|}{C}}-O-C_2H_5$$

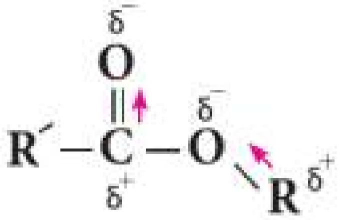
B)

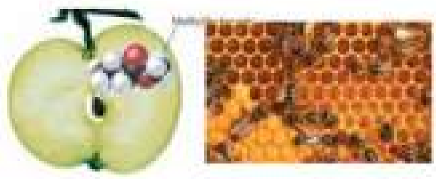


$$H-\overset{O}{\overset{\|}{C}}-O-CH_3$$

2- Write down structural formula for the following compound.

Propyl 2,3-dimethylhexanoate





Apples and beeswax contains esters.

Exercise 7-27

1- Prepare ethyl methanoate starting from methanol.

2- Prepare methyl propanoate starting from ethanol.

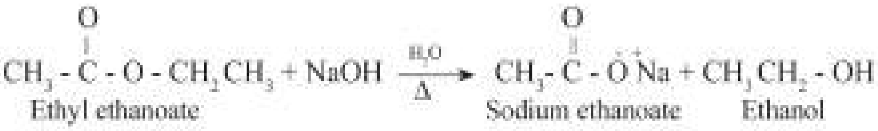
3- Prepare ethyl ethanoate starting from acetyl chloride.

Exercise 7-28

Write down the reactions of ethyl methanoate with water in acidic and basic medium.

b) Reaction of Esters with Water in Basic Medium

Esters react with water molecules in basic medium such as NaOH. At the end of the reaction, sodium salt of carboxylic acid and alcohol are formed. This reaction is very important as it is used in soap production. Therefore, it is also known as saponification reaction. Besides, it is used to differentiate esters as shown in the following reaction:



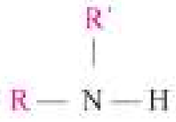
$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + NaOH \xrightarrow[\Delta]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na} + CH_3CH_2-OH$$

Ethyl ethanoate — Sodium ethanoate — Ethanol

7-8 AMINES

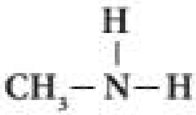
Amines are compounds which are formed by substitution of hydrogen atoms in ammonia NH_3 by one or more alkyl groups. Therefore, amines are named according to the number of alkyl groups they contain. If an alkyl group replaces one hydrogen of ammonia, it is called as a primary amine RNH_2 ; if two alkyl groups replace two hydrogen atoms, it is called as a secondary amine R_2NH ; if three alkyl groups replace three hydrogen atoms, it is called as a tertiary amine R_3N. For example:

Primary amine
(1°)

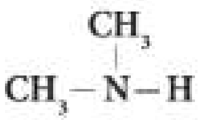


Secondary amine
(2°)

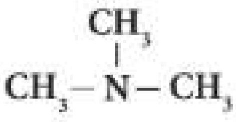
Tertiary amine
(3°)



methyl amine



dimethyl amine



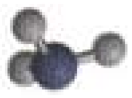
trimethyl amine

ammonia

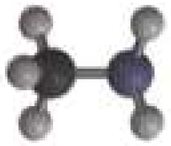
(1˚) primary amine

(2˚) secondary amine

(3˚) tertiary amine

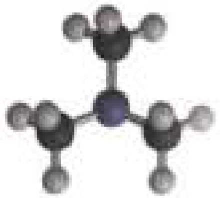


ammonia



methyl amine

dimethyl amine



trimethyl amine

7-8-1-Nomenclature of Amines

a) Special (Common) Nomenclature

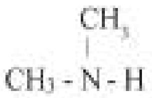
1- In this method, firstly, the alkyl group bonded to nitrogen atom is written then the word amine.

For example:

CH_3-NH_2 Methyl amine $CH_3CH_2-NH_2$ Ethyl amine $CH_3CH_2CH_2-NH_2$ n-propyl amine

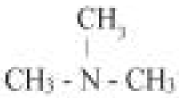
Amines cause odor of rotten fish.

2- If there are two or three alkyl groups bonded to nitrogen atom, di- or tri- prefixes are added to the word amine.



$CH_3-\overset{CH_3}{\overset{|}{N}}-H$

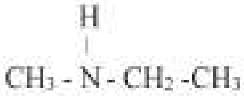
dimethyl amine



$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$

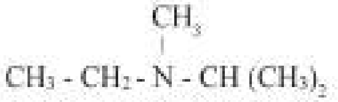
trimethyl amine

3- If the alkyl groups are different, they are written in alphabetical order.



$CH_3-\overset{H}{\overset{|}{N}}-CH_2-CH_3$

ethyl methyl amine



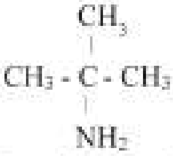
$CH_3-CH_2-\overset{CH_3}{\overset{|}{N}}-CH(CH_3)_2$

ethyl isopropyl methyl amine

b) Amines are named according to IUPAC system as in the following steps:

1- The longest carbon chain which carries the amine ($-NH_2$) group is chosen and numbered. Amine group acts as the functional group.

2- Previous rules are valid in naming amines.



$CH_3-\underset{NH_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

2-amino-2-methylpropane

$CH_3-\overset{NH_2}{\overset{|}{CH}}-COOH$

2-aminopropanoic acid

$CH_3-CH_2-\overset{NH_2}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$

3-amino-5-methylhexane

7-8-2 Preparation of Amines

There are many methods to prepare amines. We will explain only two of them here.

1- Reaction of Ammonia and Alkyl Halide

Using ammonia, we can prepare the three types of amines.
For this, as in the example below, alcoholic ammonia solution and alkyl halide are mixed in asealed test tube.

$$\underset{\text{Methyl iodide}}{CH_3I} + NH_3 \longrightarrow CH_3-\overset{+}{N}H_3\overset{-}{I} \xrightarrow{NaOH} \underset{(1°)\text{ methyl amine}}{CH_3-NH_2} + NaI + H_2O$$

This is not a successful laboratory method as a mixture of primary, secondary and tertiary amines which are difficult to separate are prepared. We only prepare primary amines with this method.

Exercise 7-29

Prepare ethyl amine using suitable alkyl halides.

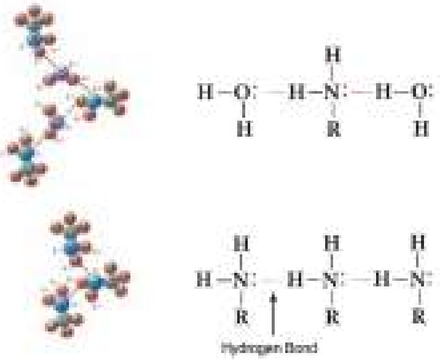


Figure 7-2

a- Hydrogen bonds between water and amine molecules.

b- Hydrogen bonds between amine molecules

Exercise 7-30

Prepare propyl amine using suitable alcohol.

$$R-\underset{\underset{R}{|}}{\ddot{N}}-H$$

Amine is a base.

2- Ammonia-Alcohol Reactions

Primary amines are prepared when ammonia and alcohol vapor passage over aluminum oxide as (catalyst) at 400°C. In this reaction, just like the reaction above, a mixture of primary, secondary and tertiary amines is obtained. But when a great amount of ammonia is used, we get mainly primary amine.

$$\underset{\text{Methanol}}{CH_3OH} + \underset{\text{ammonia}}{HNH_2} \xrightarrow[Al_2O_3]{\Delta} \underset{\text{(1°) methyl amine}}{CH_3\text{-}NH_2} + H_2O$$

7-2-3-General Properties

1- Physical Properties

Molecular mass of amines are small and their odors are like ammonia's. They are in gas and liquid form at room temperature. These compounds form hydrogen bonds due to their ionization property. Therefore, their boiling points are higher than those of compounds which cannot ionize. Figure 7-2

Amines can dissolve in water as they can form hydrogen bonds with water molecules. Besides, they can dissolve in organic solvents such as benzene and ether.

2- Chemical Properties

Amines are considered as bases because nitrogen atom has a pair of electrons which can make bond with protons or Lewis acids. This indicates its ability to react with acids such as HCl as below :

$$\underset{\text{amine}}{R\text{ - }NH_2} + HCl \longrightarrow \underset{\text{amine salt}}{R\text{-}NH_3^+Cl^-}$$

This salt can be transformed into amine again when it reacts with a strong base.

$$R\text{-}NH_3^+Cl^- \xrightarrow{NaOH} R\text{-}NH_2 + NaCl + H_2O$$

Besides, amines form compounds known as amides when they react with acid chlorides.

$$\underset{\text{Acetyl chloride}}{CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl} + \underset{\text{Methyl amine}}{H\text{-}\overset{\overset{H}{|}}{N}\text{-}CH_3} \longrightarrow \underset{\text{N-methylacetamide}}{CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{N}\text{-}CH_3} + HCl$$

QUESTIONS OF CHAPTER-7

7-1- There are two colorless liquids in two different test tubes. One is hexane, the other is 1-hexanol. How can you differentiate these two liquids?

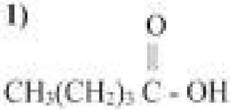
7-2- Write down the preparation processes of the following compounds from the starting substances.

a) 1-propanol from 1-chloropropane
b) ethanol from ethene
c) ethanal from ethanol
d) sodium ethanoate from methyl ethanoate

7-3- We have 1-chlorobutane and 1-butene compounds in laboratory. Which one do you use to prepare 1-butanol?

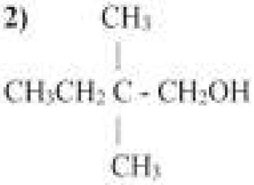
7-4- Supply names for the following organic compounds according to IUPAC system.

1)



$CH_3(CH_2)_3\overset{\overset{O}{\|}}{C}-OH$

2)

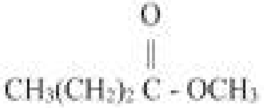


$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$

3) $CH_3CH_2CH_2CH_2CH_2Br$

4) $CH_3CH_2CH_2CH_2NH_2$

5)



$CH_3(CH_2)_2\overset{\overset{O}{\|}}{C}-OCH_3$

6)

$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

7)

$CH_3(CH_2)_4\overset{\overset{O}{\|}}{C}-H$

8)

$CH_3(CH_2)_2\overset{\overset{O}{\|}}{C}-CH_3$

7-5- Supply structural formulas for the following organic compounds.

1) 2,3-dimethylhexanoic acid
2) butyl butanoate
3) 3-ethyl-1-heptanol
4) 3-methyl-4-heptanone
5) 2-methyl-2-pentanol
6) 3-ethyl-2-aminohexane
7) 3-chlorohexane
8) 2-amino-2-methylbutane
9) butoxybutane
10) 3-methylpentanoic acid

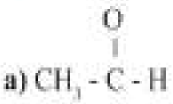
7-6- Write the equations showing the following reactions.

1) Preparation of ethanoic acid starting from methanal.
2) Preparation of ethanol starting from methanol.
3) Preparation of propanoic acid starting from 1-bromopropane.

7-7- An organic compound which has general formula $C_nH_{2n+2}O$ with molar mass of 60 g/mol does not react with Lucas reagent. But it undergoes oxidation completely. Write the molecular and structural formulas of the compound. After that write its reactions and then write general formulas and names of its products.

7-8- Circle the correct answers.

1- Which compound is obtained by heating ethanol and sulfuric acid?



a) $CH_3-\overset{\overset{O}{|}}{C}-H$ b) $CH_2=CH_2$ c) CH_3COOH d) $CH_3\text{-}CH_3$

2- What is the compound obtained from oxidation of 2-propanol with the help of $K_2Cr_2O_7$ in acidic conditions?

a) propanal b) propanone c) propene d) propanoic acid

3- The compound obtained from reduction of propanal by addition of Ni and H_2

a) propanoic acid b) 1-propanol c) 2-propanol d) propane

4- The gas obtained from the reaction of ethanol with sodium metal:

a) CO_2 b) O_2 c) CO d) H_2

5- Addition of amalgam (mercury-zinc) in the presence of HCl and ethanal:

a) Primary alcohols b) Secondary alcohols c) Tertiary alcohols d) Alkane

6- The gas obtained from the reaction of ethanoic acid with sodium hydrogen carbonate:

a) H_2 b) CO_2 c) O_2 d) CO

7- For which of the following is Lucas' reagent ($HCl/ZnCl_2$) used to differentiate?

a) primary, secondary and tertiary alcohols b) aldehydes and ketones c) primary and secondary amines

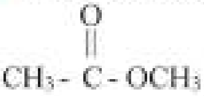
8- The number of structural formulas of $C_3H_6Br_2$ compound:

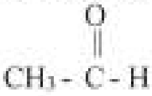
a) 2 b) 3 c) 4 d) 5

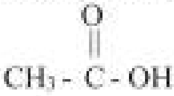
9- In order to form silver mirror, with which of the following should silver ammonium hydroxide react?

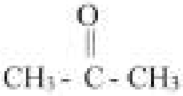
a) ketone b) aldehyde c) tertiary alcohol d) alkane

10- Which of the following compounds reacts with Fehling's solution?

a) 
$CH_3-\overset{\overset{\large O}{||}}{C}-OCH_3$

b) 
$CH_3-\overset{\overset{\large O}{||}}{C}-H$

c) 
$CH_3-\overset{\overset{\large O}{||}}{C}-OH$

d) 
$CH_3-\overset{\overset{\large O}{||}}{C}-CH_3$

11- What is the reaction which transforms propanone to 2-propanol?

a) oxidation **b)** cleavage **c)** reduction **d)** substitution

7-9- Write down the synthesis equation of butanoic acid from suitable alkyl halide with Grignard reagent.

7-10- Write down the names of organic compounds from A to E in the chain reactions starting with ethylene ($CH_2=CH_2$).

$$CH_2=CH_2+HCl\longrightarrow A$$

$$A+KOH\xrightarrow{H_2O}B$$

$$B\xrightarrow{K_2Cr_2O_7/H^+}C\xrightarrow{K_2Cr_2O_7/H^+}D$$

$$D+NaHCO_3\longrightarrow E+CO_2+H_2O$$

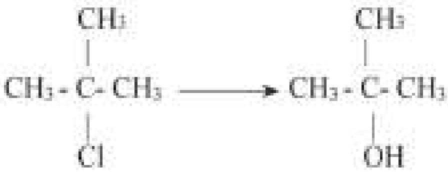
7-11- How can you differentiate the following compound pairs experimentally?

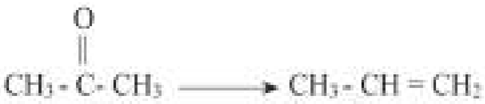
1) propanal and propanone **2)** 1-pentanol and pentane

3) butanal and butanoic acid **4)** 2-methyl-2-propanol and 1-propanol

5) ethanol and ethanoic acid **6)** ethylamine and ethane

7-12- Explain the following changes via chemical equations:

a) 
$$CH_3-\underset{\underset{\large Cl}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3\longrightarrow CH_3-\underset{\underset{\large OH}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3$$

b) 
$$CH_3-\overset{\overset{\large O}{||}}{C}-CH_3\longrightarrow CH_3-CH=CH_2$$

c) 1-butene → 2-butanol

7-13- The following compounds are formed from result of oxidation reactions of alcohols. Write down their reactions and structural formulas and names of alcohols.

a) Ethanal **b)** 2-methylpropanal **c)** 2-butanone

7-14- Study the following equations and answer the questions.

$$C_4H_9Br \xrightarrow[A]{OH^-} C_4H_9OH \xrightarrow[B]{K_2Cr_2O_7} C_4H_8O \xrightarrow[C]{\text{Fehling's Solution}} N.R.$$

a) Write down the structural formulas of A, B and C.
b) Write down the names of A, B and C.
c) Which of B and C has higher boiling point?
d) Write down other structural formulas of compound B which doesn't oxidize with $K_2Cr_2O_7$ in acidic conditions.

7-15- Two of the following compounds were mixed in acidic conditions. At the end of the reaction, pleasant-smelling $C_4H_8O_2$ compound formed. Find out those two compounds and write down the equation:

CH_3CH_3, CH_3CH_2OH, CH_3CHO, CH_3COOH, $CH_3CH_2OCH_3$

7-16- Write down the synthesis equations of the following compounds starting from ethanol.

a) ethanoic acid CH_3COOH **b)** ethyl ethanoate $CH_3COOCH_2CH_3$

c) chloroethane CH_3CH_2Cl **d)** ethyl magnesium chloride CH_3CH_2MgCl

7-17- Obtain the following compounds starting from ethylene ($CH_2=CH_2$). Write down the equations.

a) ethanal **b)** ethyl magnesium chloride **c)** ethyl hexanoate

7-18- As A has three carbon atoms, write down the formulas of the following A, B, C, D, E organic compounds in the following equation chain.

$$\mathbf{A} \xrightarrow{HCl} B \xrightarrow[\text{dry ether}]{Mg} \mathbf{C} \xrightarrow{CO_2} D \xrightarrow{HCl} E$$

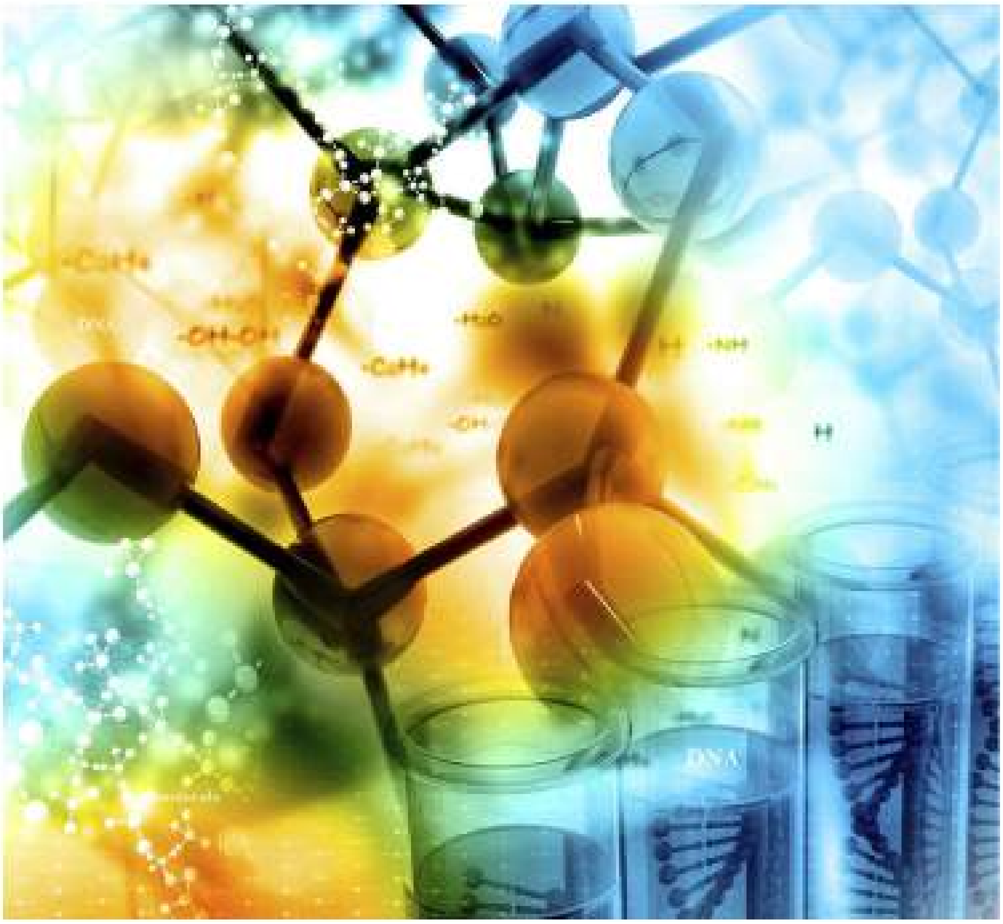
7-19- A is an organic compound which has 3 carbon atoms. It forms compound B when it is oxidized. This substance doesn't react with Fehling's solution. When sodium metal reacts with compound A, compound C is obtained. But when B is reduced, it yields compound A.

a) Write down the structural formulas of A, B, and C.

b) Write down the formation equations of compounds A, B and C.

BIOCHEMISTRY

CHAPTER-8



ACHIEVEMENTS

After completing this chapter, the student is expected to :

* Differentiate different types of carbohydrates.
* Learn types of sugars and their differences.
* Differentiate starch.
* Learn lipids.
* Learn how soap is produced and the ingredients used in soap production.

Carbonhydrates,starch and sugar are fundemental foods for humans.

8-1 PREFACE

Biochemistry is the branch of science which studies chemistry of biosynthesis in living beings. This branch of science explains biological phenomena in bodies of living beings in terms of chemistry by studying chemical changes in human body and in other creatures. In this chapter, we will study the properties and reactions of two important chemical substances which we take into our bodies from foods. These are carbohydrates and proteins.

8-2 CARBOHYDRATES

Have you ever thought about carbohydrates which make up of most of our food as bread and rice?

Do you know why honey, banana, apple, grapes and some other fruits are sweet?

In the structure of these foods, chemical substances as carbohydrates, starch, sugar are found.

What are carbohydrates? What are their properties and how many kinds of carbohydrates are there?

8-2-1- Structure of Carbohydrates

If we examine the structures of the foods mentioned above, we see that they are made up of oxygen, hydrogen and carbon. But the ratio of oxygen is higher than others. In the structural formula of most carbohydrates, carbon atom forms bonds with atoms of water molecule. These are $(CH_2O)_n$ and $C_n(H_2O)_n$. Therefore, this kind of molecules are called as carbohydrates as they originate from hydrate (water) and carbon.

Carbohydrates are divided into two groups as complex and simple carbohydrates. They can be in long carbon chains which can rotate plane polarized light (optically active) or in cyclic structure. Both structures are stable.

8-2-2-Classification of Carbohydrates

Carbohydrates are classified as follows:

1-Monosaccharides: e.g. Glucose and fructose
2-Disaccharides: e.g. sucrose, maltose and lactose
3-Polysaccharides: e.g. Starch and cellulose

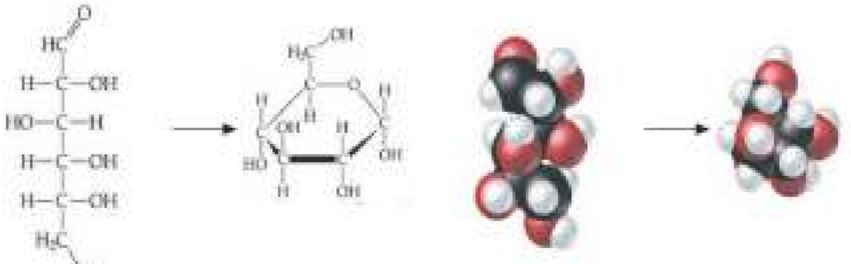
We will mention some important properties of each group.

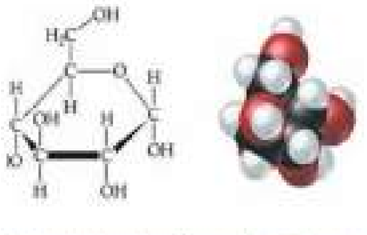
1-Monosaccharides:

They are the simplest form of carbohydrates.as examples, glucose and fructose

a) Glucose (Grape sugar):

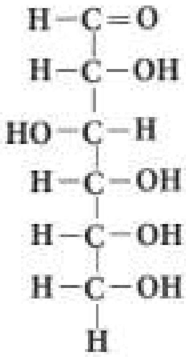
Glucose is found in grapes and blood in nature. It is especially important as a nutrient for patients who cannot be fed through mouth and also in surgical operations. Its molecular formula is $C_6H_{12}O_6$ or $C_6(H_2O)_6$. The molecular structure and geometrical shape of glucose are given below.

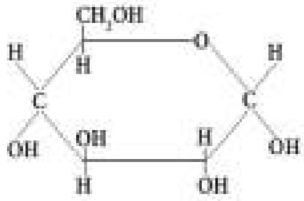




Closed structure formula of glucose

In open structure formula glucose molecule, functional groups are attached to long carbon chain.



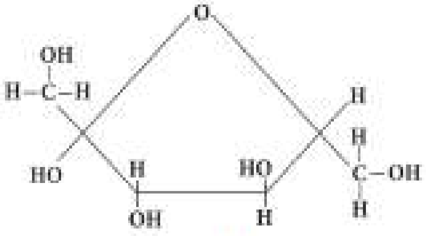


-In cyclic structure, it is an ether containing hydroxyl groups.
-In open structure, it is an aldehyde containing hydroxyl groups.
We can explain the properties of glucose with respect to its molecular structure. The molecular structure also helps us understand its reactions.most of reactions occur in aqueous solution, Glucose has a crystalline structure. Its boiling point is high. It dissolves in water. When we study the structural formula of glucose, we can see that hydrogen bonds form between hydroxyl groups and hydrogen atoms and glucose molecules. These hydrogen bonds cause boiling point elevation.
When we examine the open structural formula of glucose, we see that it is formed from an aldehyde group and many hydroxyl groups. Therefore, it has some properties similar to those of alcohols and aldehydes. Therefore, they are oxidized in Tollens' Reagent and Fehling's Solution.

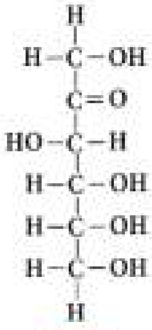
b) Fructose (Fruit sugar)

Fructose is found in honey and most fruits. Its molecular formula is $C_6H_{12}O_6$ and it is same as the molecular formula of glucose. But their structural formulas are different. In Figure(A) and (B)these formulas are shown. ($\overset{O}{\overset{\|}{-C-}}$). As its structure is similar to that of glucose, their physical properties are also similar. They both contain hydroxyl groups (-OH) and carbonyl groups. In their open formulas. In cyclic structure, they have (-OH) and ($-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$) groups which raise both boiling point and water solubility.

In open structural formula, there are numbers of hydroxyl groups in addition to carbonyl ketones which gives similar properties and inter similer reaction to those for Alcohols and ketones. Therefore, fructose can be oxidized. Contrary to ketones, fructose is oxidized with Tollens Reagent and Fehling's Solution. Therefore, although fructose is a ketone, it is accepted as among reducing sugars.



(A)



(B)

A) Cyclic formula of fructose
B) Open formula of fructose

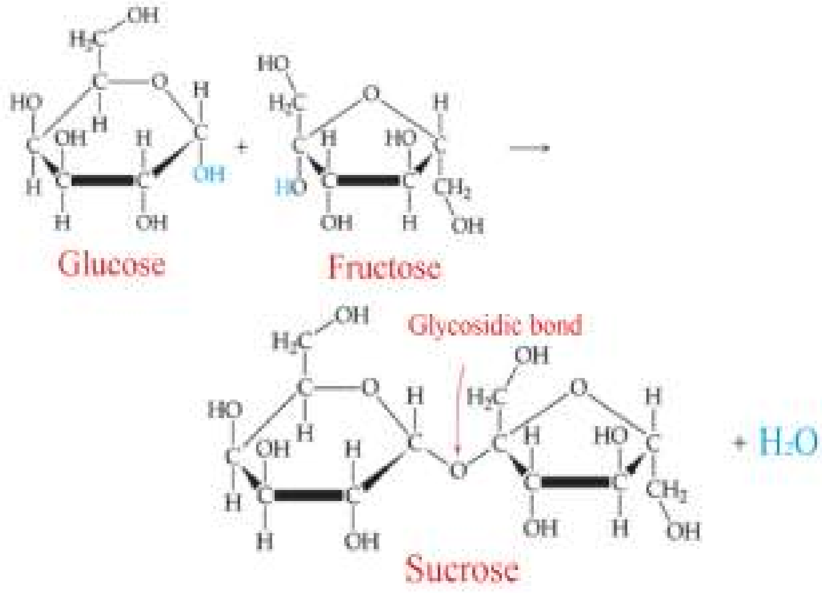
2) Disaccharides

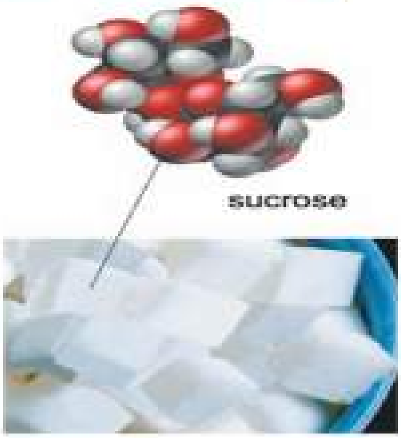
Amolecule of this type consists of two identical or different monosaccharide after losing a water molecule, the most example of this:

Sucrose

Sucrose and sugar cane are examples. Sucrose is sweet. It is produced from sugar cane. After refining, purification and crystallization, we get white sugar. Its molecular formula is $C_{12}H_{22}O_{11}$. In sucrose molecule, through cleavage of one water molecule from one glucose and fructose molecule, glycoside bonds are formed between them. But this bond dissolves during digestion in our bodies.

Sucrose ⟶ Fructose + Glucose





White sugar is disaccharide that is sucrose.

3) Polysaccharides

They are large molecules (polymers) formed through bonding of many monosaccharides together. Starch and cellulose are examples.

a) Starch

When we consume potato, we get carbohydrates formed from small glucose units. This substance is a polymer called as starch. Its basic unit is glucose, which are connected through the decoding of the carbonyl double bond. Foods containing this type of carbohydrate are called (starches)due to the presence of starch in them in a large amount.

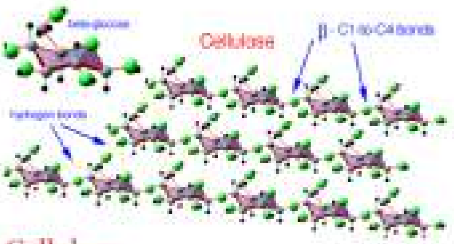
b) Cellulose

Cellulose is a large molecule (polymer) formed from glucose. Although basic units of cellulose and starch are the same, they have different shapes and properties depending on The number of glucose units that make up each of them and the difference in their bonding with each other. The main source of cellulose is wood fibers and besides peel of some fruits as date palm have cellulose.

Some enzymes or some acid solutions dissolve those big molecules. A similar event to this occurs in digestive system in our bodies.

Enzymes or
acid solution

8-2-3- Detection of Starch



Cellulose

Starch molecules form bonds with iodine molecules in iodine solution and produce a compound with blue colour. The iodine solution is obtained by dissolving iodine crystal in potassium iodide with blue colour solution. Thus, to detection of starch, a few drops of iodine solution in potassium iodide is added to starch solution. If blue color is observed, that shows the presence of starch.

8-3 PROTEINS

Starch

The Greek origin of the word protein, the first syllable (pro-) means the (primary), and the second syllable (-teins) means importance or basis.

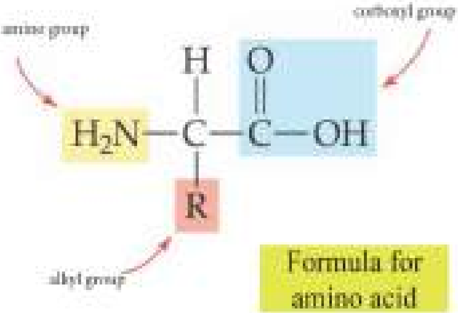
It is the main building block of our bodies. It is found in all living beings.
It carries great importance as it is the biggest source of amino acids which are necessary for growing of living beings.
What are the chemical structures of these substances? What are the similarities and differences between molecules?
What are the shapes of their molecules? Can we prepare them in laboratory?

The main source of any protein is living bodies, but one area of the body may contain multiple types of proteins that must be separated from each other. Due to the similarity of its chemical composition and its physical and chemical properties, it is difficult to separate it by simple chemical methode.

8-3-1 The constituent elements of protein molecules

As a result of many experiments, it is shown that protein is contains of carbon, hydrogen oxygen and nitrogen elements. In addition to those elements, protein may contain sulfur and phosphorus.

8-3-2 Amino acids



$$H_2N-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

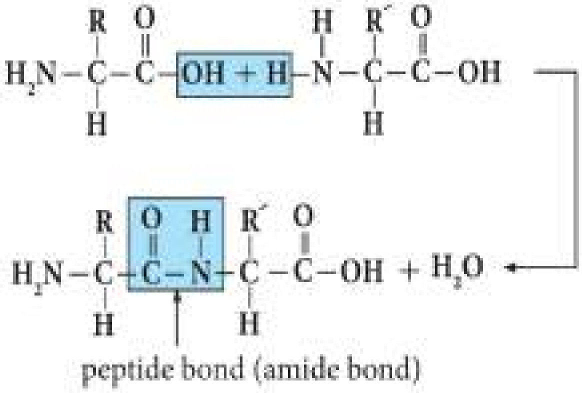
Formula for amino acid

They are the most important units in protein structure. They are shown with the formula below:

Examine general structural formula for amino acids and answer the questions.
1-What is the functional group common in all amino acids?
2-What are the chemical effects of each functional group on the properties of amino acid ?
All differences between amino acids depend on alkyl R groups.

8-3-3-Formation of Proteins

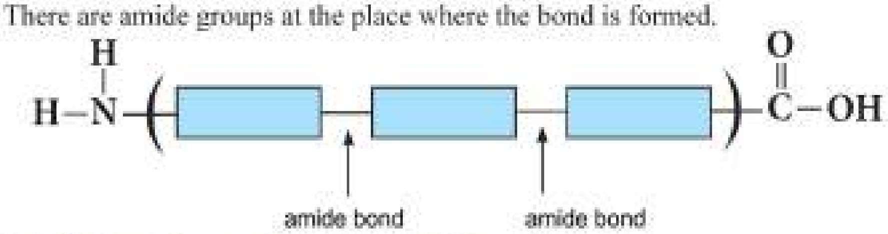
Protein is formed from bonding of many amino acids (after lossing H_2O molecule) when the bond is formed with peptide (amide) bonds.
These bonds make long chains (polymer) with big molecular mass containing from 40,000 to 40,000,000 molecules.



$$H_2N-\underset{H}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-\boxed{OH+H}-\overset{H}{N}-\underset{H}{\overset{R'}{C}}-\overset{O}{\overset{\|}{C}}-OH \longrightarrow H_2N-\underset{H}{\overset{R}{C}}-\boxed{\overset{O}{\overset{\|}{C}}-\overset{H}{N}}-\underset{H}{\overset{R'}{C}}-\overset{O}{\overset{\|}{C}}-OH + H_2O$$

Egg is source of protein.

Protein has a carboxyl group on one side and an amine group on the other side. There are amide groups at the place where the bond is formed.



8-3-4-Significant Reactions of Proteins

The most significant reactions of proteins occur in cells of living beings. At the end of most reactions, protein decomposes to one or more amino acid units.

In laboratories, proteins can be decomposed to amino acids forming them by addition of inorganic acid (HCl). These reactions occur by the breaking of amide bond as in digestion. Besides, by addition of inorganic base (NaOH), proteins can be decomposed to amino acids salts .

Proteins show some differences with respect to the type of amino acids they contain and also with the numbers and order of those amino acids. There are more than 20 amino acids in nature. The functions of protein in body depend on the amino acid and its sequence. Therefore, scientists have tried to produce amino acids in laboratories in order to make use for living beings when necessary and learn their sequence.

Proteins play a vital role in lives of living beings. They have many different types which have the same chemical formula and same bonds but due to their sizes, they have different functions.

For example:

* those in fibrous shape as keratin in hair and wool.

* those in semi spherical shape as in egg.

Proteins assume important roles in bodies of living beings with respect to their shapes. Any effect changing the shapes of proteins interrupts their functions and affects the life of the living being. The most important proteins in our bodies are enzymes, hormones and hemoglobin in blood.

8-4-ENZYMES

They are some kind of proteins. They are found in all cells of living beings. They function independently. They play vital roles in events like digestion and Metabolism and Breathing.

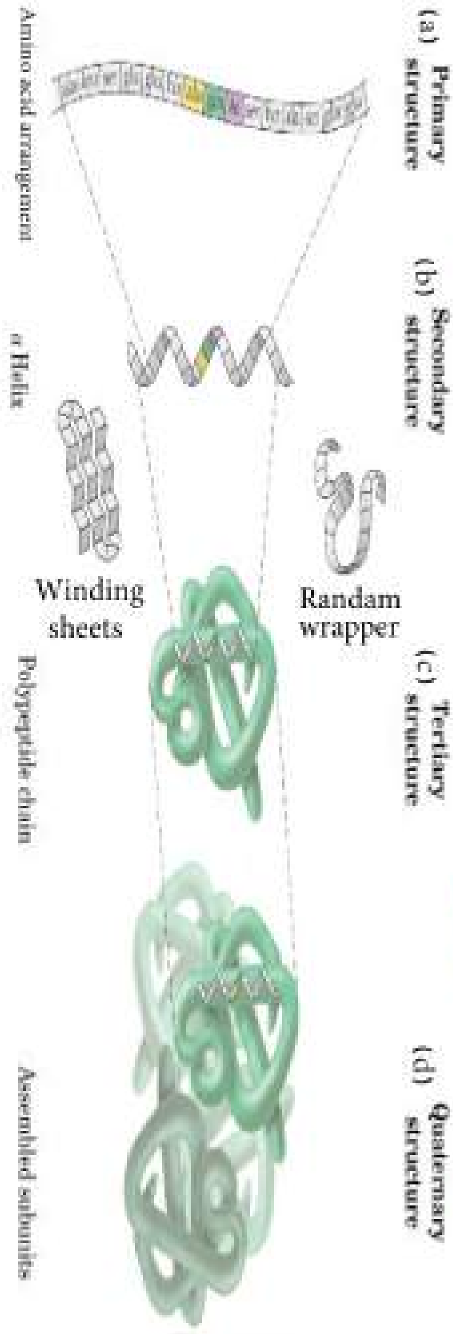
Enzymes are produced in bodies of living beings. They are constantly renewed during vital reactions as they lose their effects by time. They function at a certain pH value. High temperatures disrupts their structures and prevents their functions.

Enzymes supply the necessary energy for reactions.

There are two types of enzymes:

1- Internal enzymes: They enable oxidation reactions inside cells and they don't get out of cell membrane, such as oxidative enzymes.

2- External enzymes: They perform their duties out of cells after they are secreted as digestive enzymes.



Structure of protein

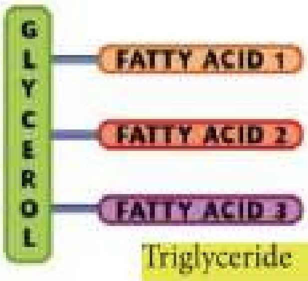
Exercise 8-1

Proteins show either basic or acidic property (amphoteric). Say the reasons for this.

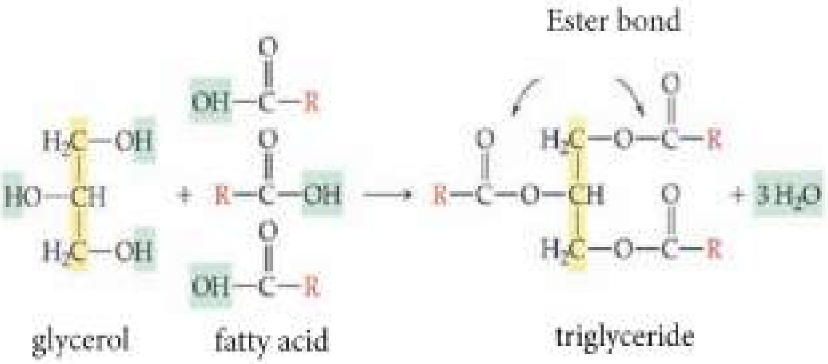
8-5-LIPIDS

There are plenty of lipids in nature. Vegetable oils are found in cores of plants as cotton, corn, and fruits like olive and coconut. Animal fats are found in all cells of animals. They are stored for energy to be used when necessary. In digestion and oxidation reactions, plenty of energy is obtained. Lipids represent energy potential in living beings. They are very important in soap, paint and candle industries. Lipids don't dissolve in water. They dissolve in organic solvents like ether and chloroform. Animal fats are solid at room temperature whereas vegetable oils are in liquid form.

Lipids are formed through esterification reaction of fatty acids with glycerol. They are also called as triglycerides and formed from long hydrocarbon chains (C_{12}-C_{24}) with carboxyl group at one side.



Triglyceride

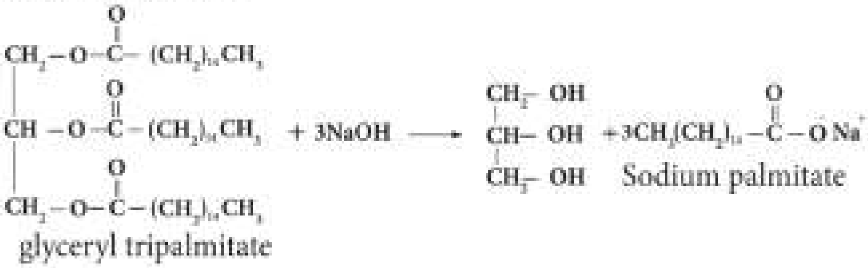


$$\begin{matrix} H_2C-OH \\ HO-CH \\ H_2C-OH \end{matrix} + 3\, R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \begin{matrix} H_2C-O-\overset{O}{\overset{\|}{C}}-R \\ R-\overset{O}{\overset{\|}{C}}-O-CH \\ H_2C-O-\overset{O}{\overset{\|}{C}}-R \end{matrix} + 3H_2O$$

Soap

8-6-SOAPS

Soap production is the oldest industry that humans have been doing. Soap is sodium or potassium salt of fatty acids. Soap is obtained by addition of strong bases as sodium or potassium hydroxide followed by adding sodium chloride solution and finally by precipitating a thick layer on a cloth. The reaction occurs here is called as saponification reaction. At the final step, it is washed with water to remove salt.



$$\begin{matrix} CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{14}CH_3 \\ CH-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{14}CH_3 \\ CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{14}CH_3 \end{matrix} + 3NaOH \longrightarrow \begin{matrix} CH_2-OH \\ CH-OH \\ CH_2-OH \end{matrix} + 3CH_3(CH_2)_{14}-\overset{O}{\overset{\|}{C}}-O^-Na^+$$

Steps of soap production

Shape and quality of soaps depend on the type of base and oil used in saponification. When sodium hydroxide is used as base, we get soap bars we use in daily life. If we use potassium hydroxide, we get soft soaps as liquid soaps and shaving foams.

Similarly, quality of soap depends on the type of oil used.

Exercise 8-2

Why aren't calcium or magnesium hydroxides used instead of sodium and potassium hydroxides in soap production?

QUESTIONS OF CHAPTER-8

8-1- Circle the correct answer in the following questions.

1) Which of the following isn't a protein?

a) A compound which is made up of carbon, oxygen, hydrogen and sulfur.

b) A compound whose molecules are made up of carbon, hydrogen and nitrogen.

c) A compound which reacts with acids and bases.

2) Sucrose molecule consists of units. These are:

a) glucose **b)** fructose **c)** glucose and fructose

3) Which of the following elements isn't found in amino acids?

a) nitrogen **b)** phosphorus **c)** oxygen **d)** carbon

4) Which polymers are formed by fatty acids?

a) proteins **b)** carbohydrates **c)** oils (Lipids)

8-2- Tell reasons for the following:

a) Fructose is assumed as a reducing sugar.

b) Proteins react with acids and bases.

c) Separation of proteins with simple methods isn't easy.

8-3- How can you differentiate starch and glucose?

8-4- Complete the following table:

Subject of comparison	Glucose	Fructose
Molecular formula		
Open Formula		
Functional group in open formula		
Functional group in cyclic formula		

SI Units and Conversion Factors الوحدات وعوامل التحويل الجدول (1)

الطول (Length) SI Unit: meter المتر (m)

1 kilometer(km) =1000 meter(m)
1 mile = 1.61 kilometer (km)
1 meter(m)=100 centimeter (cm)

الحجم (Volume) SI Unit: cubic meter المتر المكعب (m^3)

1 liter (L) = 10^{-3} $meter^3$ (m^3)
1 liter(L) =1000 milliliter(mL)
1 liter(L)= 1000 $centimeter^3$ (cm^3)
1 milliliter (mL) =1$centimeter^3$ (cm^3)

درجة الحرارة (Temperature) SI Unit: Kelvin (K)

T Kelvin(K) =t Celsius (°C) +273
°F Fahrenheit = $\frac{9}{5}$ × t Celsius (°C) +32

الكتلة (Mass) SI Unit: kilogram (kg)

1 kilogram =1000 grams (1 kg = 1000 g)
1 amu(وكذ) = 1.66×10^{-27} kg
amu (وحدة كتلة ذرية)

الزمن (Time) SI Unit: second (s)

1 hour (h) = 60 minutes (min)
1 hour (h)= 3600 seconds (s)

الطاقة (Energy) SI Unit : Joule(J)

1 Joule (J) = 1 kg . m^2/s^2 (exact)
1 calorie (cal)= 4.184 Joules (J)

الضغط (Pressure) SI Unit: Pascal (Pa)

1 atmosphere (atm) = 101.325 Pascal (Pa)
1 atmosphere(atm) = 760 mm Hg = 760 Torr
1 mmHg =1 Torr

Oher Symbols and abbreviations (المختصرات العلمية)

α alpha particals (دقائق الفا)	h hour (ساعة)	mL milliter (volume) (حجم) مللتر
β beta particals (دقائق بيتا)	J Joule(energy)(جول) وحدة طاقة	mm millimeter (length) (طول) ملمتر
γ gamma rays (اشعة كاما)	K Kelvin (temperature) (حرارة)	mole (amount) (مول(كمية
atomic mass unit (amu) (وحدة كتلة ذرية)	kg kilogram (mass) (كتلة) كيلو غرام	(mp) melting point نقطة انصهار
(aq) aqueous solution (محلول مائي)	kPa kilopascal (pressure) (ضغط) كيلو بلسكال	n^{o} neutron نيوترون
(atm) atmosphere (pressure)(وحدة ضغط)	L liter (volume) (حجم) لتر	n number of moles عدد المولات
bp boiling point(نقطة الغليان)	(l) liquid (سائل)	n principal quantum number عدد الكم الرئيسي
°C degree Celsius (temperature)(درجة سيليزية)	M molar mass الكتلة المولية	P pressure ضغط
C Speed of light in vacunm (سرعة الضوء)	m meter (length) (طول)متر	p^{+} proton بروتون
cm centimeter (lenght)(سنتيمتر وحدة الطول)	m mass كتلة	Pa pascal (pressure) بلسكال ضغط
E energy(الطاقة)	V volume حجم	R ideal gas constant ثابت الغاز المثالي
e^{-} electron(الكترون)	$t_{1/2}$ half- life time زمن عمر النصف	s second ثانية
g gram (mass)(غرام (وحدة الكتلة	T temperature درجة حرارة	(s) solid صلب
(g) gas (غاز)	STP Standard Temperature and Pressure الظروف القياسية	SI international System of Units ظام الدولي للوحدات

List of Elements

ATOMIC NUMBER	NAME	SYMBOL	RELATIVE ATOMIC MASS	GROUP	PERIOD
1	Hydrogen	H	1.00794	1 / IA	1
2	Helium	He	4.002602	18 / VIIIA	1
3	Lithium	Li	6.941	1 / IA	2
4	Beryllium	Be	9.012182	2 / IIA	2
5	Boron	B	10.811	13 / IIIA	2
6	Carbon	C	12.0107	14 / IVA	2
7	Nitrogen	N	14.0067	15 / VA	2
8	Oxygen	O	15.9994	16 / VIA	2
9	Fluorine	F	18.9984032	17 / VIIA	2
10	Neon	Ne	20.1797	18 / VIIIA	2
11	Sodium (Natrium)	Na	22.98976928	1 / IA	3
12	Magnesium	Mg	24.3050	2 / IIA	3
13	Aluminium (Aluminum)	Al	26.9815386	13 / IIIA	3
14	Silicon	Si	28.0855	14 / IVA	3
15	Phosphorus	P	30.973762	15 / VA	3
16	Sulfur	S	32.065	16 / VIA	3
17	Chlorine	Cl	35.453	17 / VIIA	3
18	Argon	Ar	39.948	18 / VIIIA	3
19	Potassium (Kalium)	K	39.0983	1 / IA	4
20	Calcium	Ca	40.078	2 / IIA	4
21	Scandium	Sc	44.955912	3 / IIIB	4
22	Titanium	Ti	47.867	4 / IVB	4
23	Vanadium	V	50.9415	5 / VB	4
24	Chromium	Cr	51.9961	6 / VIB	4
25	Manganese	Mn	54.938045	7 / VIIB	4
26	Iron (Ferrum)	Fe	55.845	8 / VIII	4
27	Cobalt	Co	58.933195	9 / VIII	4
28	Nickel	Ni	58.6934	10 / VIII	4
29	Copper (Cuprum)	Cu	63.546	11 / IB	4
30	Zinc	Zn	65.39	12 / IIB	4
31	Gallium	Ga	69.723	13 / IIIA	4
32	Germanium	Ge	72.64	14 / IVA	4
33	Arsenic	As	74.92160	15 / VA	4
34	Selenium	Se	78.96	16 / VIA	4
35	Bromine	Br	79.904	17 / VIIA	4
36	Krypton	Kr	83.798	18 / VIIIA	4
37	Rubidium	Rb	85.4678	1 / IA	5
38	Strontium	Sr	87.62	2 / IIA	5

39	Yttrium	Y	88.90585	3 / IIIB	5
40	Zirconium	Zr	91.224	4 / IVB	5
41	Niobium	Nb	92.906 38	5 / VB	5
42	Molybdenum	Mo	95.94	6 / VIB	5
43	Technetium	Tc	97.9072*	7 / VIIB	5
44	Ruthenium	Ru	101.07	8 / VIII	5
45	Rhodium	Rh	102.905 50	9 / VIII	5
46	Palladium	Pd	106.42	10 / VIII	5
47	Silver (Argentum)	Ag	107.8682	11 / IB	5
48	Cadmium	Cd	112.411	12 / IIB	5
49	Indium	In	114.818	13 / IIIA	5
50	Tin (Stannum)	Sn	118.710	14 / IVA	5
51	Antimony (Stibium)	Sb	121.760	15 / VA	5
52	Tellurium	Te	127.60	16 / VIA	5
53	Iodine	I	126.904 47	17 / VIIA	5
54	Xenon	Xe	131.293	18 / VIIIA	5
55	Caesium (Cesium)	Cs	132.9054519	1 / IA	6
56	Barium	Ba	137.327	2 / IIA	6
57	Lanthanum	La	138.90547	-	6
58	Cerium	Ce	140.116	-	6
59	Praseodymium	Pr	140.90765	-	6
60	Neodymium	Nd	144.242	-	6
61	Promethium	Pm	144.9127	-	6
62	Samarium	Sm	150.36	-	6
63	Europium	Eu	151.964	-	6
64	Gadolinium	Gd	157.25	-	6
65	Terbium	Tb	158.92535	-	6
66	Dysprosium	Dy	162.500	-	6
67	Holmium	Ho	164.930 32	-	6
68	Erbium	Er	167.259	-	6
69	Thulium	Tm	168.93421	-	6
70	Ytterbium	Yb	173.04	-	6
71	Lutetium	Lu	174.967	3 / IIIB	6
72	Hafnium	Hf	178.49	4 / IVB	6
73	Tantalum	Ta	180.94788	5 / VB	6
74	Tungsten (Wolfram)	W	183.84	6 / VIB	6
75	Rhenium	Re	186.207	7 / VIIB	6
76	Osmium	Os	190.23	8 / VIII	6
77	Iridium	Ir	192.217	9 / VIII	6
78	Platinum	Pt	195.084	10 / VIII	6
79	Gold (Aurum)	Au	196.966569	11 / IB	6

80	Mercury (Hydrargyrum)	Hg	200.59	12 / IIB	6
81	Thallium	Tl	204.3833	13 / IIIA	6
82	Lead (Plumbum)	Pb	207.2	14 / IVA	6
83	Bismuth	Bi	208.98040	15 / VA	6
84	Polonium	Po	208.9824*	16 / VIA	6
85	Astatine	At	209.9871*	17 / VIIA	6
86	Radon	Rn	222.0176*	18 / VIIIA	6
87	Francium	Fr	223.0197*	1 / IA	7
88	Radium	Ra	226.0254*	2 / IIA	7
89	Actinium	Ac	227.0277*	-	7
90	Thorium	Th	232.03806*	-	7
91	Protactinium	Pa	231.03588*	-	7
92	Uranium	U	238.02891	-	7
93	Neptunium	Np	237.0482*	-	7
94	Plutonium	Pu	244.0642*	-	7
95	Americium	Am	243.0614*	-	7
96	Curium	Cm	247.0704*	-	7
97	Berkelium	Bk	247.0703*	-	7
98	Californium	Cf	251.0796*	-	7
99	Einsteinium	Es	252.0830*	-	7
100	Fermium	Fm	257.0951*	-	7
101	Mendelevium	Md	258.0984*	-	7
102	Nobelium	No	259.1010*	-	7
103	Lawrencium	Lr	262.1097*	3 / IIIB	7
104	Rutherfordium	Rf	261.1088*	4 / IVB	7
105	Dubnium	Db	262	5 / VB	7
106	Seaborgium	Sg	266	6 / VIB	7
107	Bohrium	Bh	264	7 / VIIB	7
108	Hassium	Hs	277	8 / VIII	7
109	Meitnerium	Mt	268	9 / VIII	7
110	Darmstadtium	Ds	271	10 / VIII	7
111	Roentgenium	Rg	272	11 / IB	7
112	Ununbium	Uub	285	12 / IIB	7
113	Ununtrium	Uut	284	13 / IIIA	7
114	Ununquadium	Uuq	289	14 / IVA	7
115	Ununpentium	Uup	288	15 / VA	7
116	Ununhexium	Uuh	292	16 / VIA	7
117	Ununseptium	Uus	-	17 / VIIA	7
118	Ununoctium	Uuo	294	18 / VIIIA	7

*Relative atomic mass of the isotope of the element with the longest known half-life.

Examples of acids, bases and salts **امثلة عن الحوامض والقواعد والاملاح**

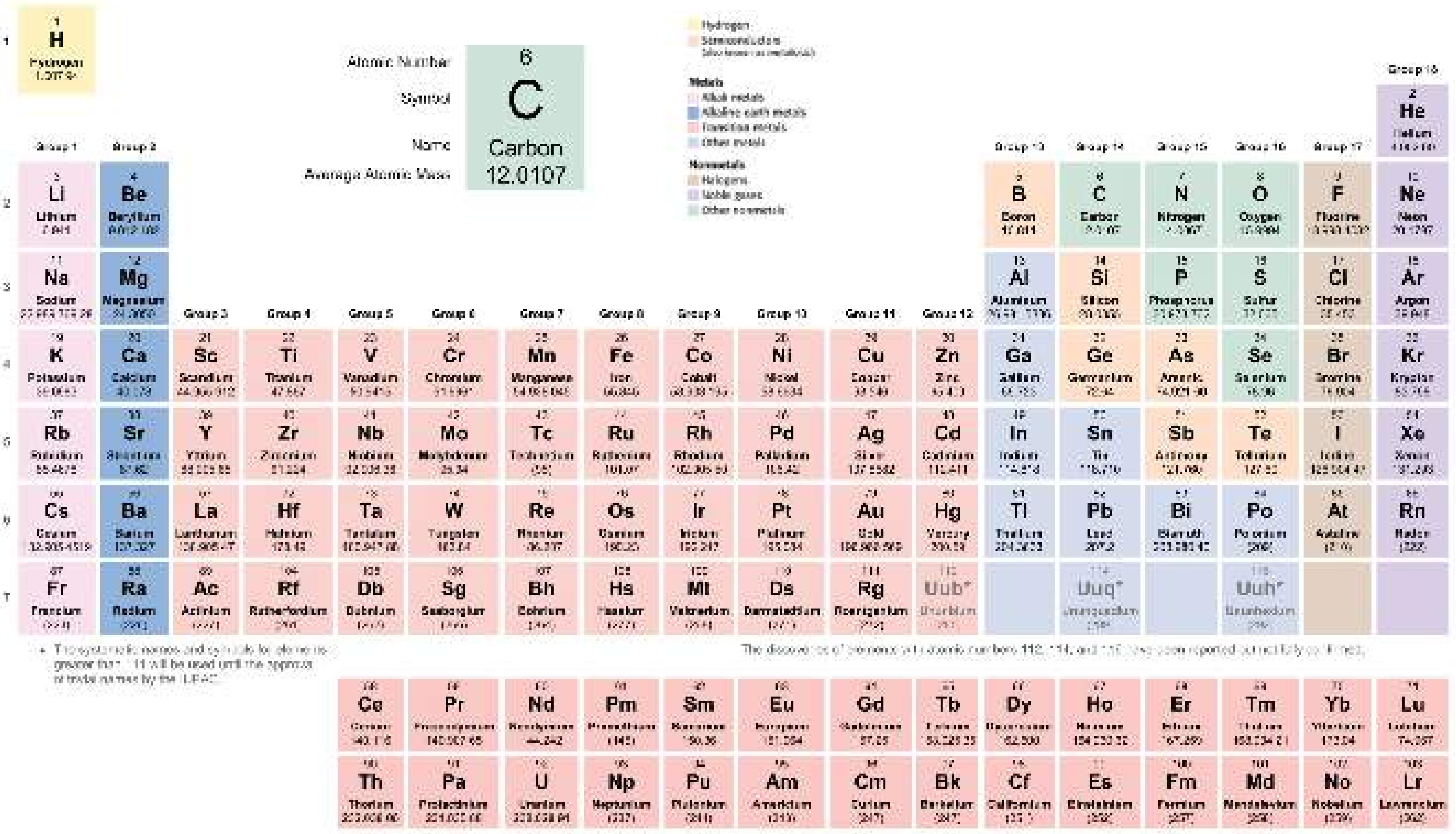
حوامض قوية	قواعد قوية	حوامض ضعيفة	قواعد ضعيفة	مواد شحيحة الذوبان	املاح تامة الذوبان
HCl حامض الهيدروكلوريك	$NaOH$ هيدروكسيد الصوديوم	الحوامض العضوية بصيغة $R\text{-}COOH$ مثل :	NH_3 الامونيا	$AgCl$ كلوريد الفضة	$NaCl$ كلوريد الصوديوم
HBr حامض الهيدروبروميك	$Ba(OH)_2$ هيدروكسيد الباريوم	CH_3COOH حامض الخليك	و الامينات بصيغة $R\text{-}NH_2$	$PbSO_4$ كبريتات الرصاص	KCl كلوريد البوتاسيوم
HI حامض الهيدرويوديك	$Ca(OH)_2$ هيدروكسيد الكالسيوم	$HCOOH$ حامض الفورميك	C_6H_7N الانيلين	$BaSO_4$ كبريتات الباريوم	KNO_3 نترات البوتاسيوم
H_2SO_4 حامض الكبريتيك	KOH هيدروكسيد البوتاسيوم	C_6H_5OH الفينول		CaF_2 فلوريد الكالسيوم	Na_2SO_4 كبريتات الصوديوم
HNO_3 حامض النتريك	$LiOH$ هيدروكسيد الليثيوم	HCN حامض الهيدروسيانيك		$Zn(OH)_2$ هيدروكسيد الخارصين	K_2CrO_4 كرومات البوتاسيوم
$HClO_4$ حامض البيركلوريك		HF حامض الهيدروفلوريك		$Ca_3(PO_4)_2$ فوسفات الكالسيوم	$CaCl_2$ كلوريد الكالسيوم
H_2CrO_4 حامض الكروميك		HNO_2 حامض النتروز		Ag_2CrO_4 كرومات الفضة	NH_4Cl كلوريد الامونيوم
				$Fe(OH)_3$ هيدروكسيد الحديد	CH_3COOK خلات البوتاسيوم
				$Al(OH)_3$ هيدروكسيد الالمنيوم	CH_3COONa خلات الصوديوم
				MgF_2 فلوريد المغنيسيوم	$MgSO_4$ كبريتات المغنيسيوم
				$Mg(OH)_2$ هيدروكسيد المغنيسيوم	

Types of Ligands

انواع الليكندات

اسم الليكاند		صيغة الليكاند	نوعه	عدد المخالب
خلاتو	Acetato	CH_3COO^-	قوي	احادي المخلب
أمين	Ammine	NH_3	قوي	احادي المخلب
اكوا	Aqua	H_2O	ضعيف	احادي المخلب
ازيدو	Azido	N_3^-	ضعيف	احادي المخلب
برومو	Bromo	Br^-	ضعيف	احادي المخلب
كاربونيتو	carbonato	CO_3^{-2}	قوي	ثنائي المخلب
كاربونيل	Carbonyl	CO	قوي	احادي المخلب
كلورو	Chloro	Cl^-	ضعيف	احادي المخلب
سيانو	Cyano	CN^-	قوي	احادي المخلب
ثنائي مثيل كلايكسيماتو	Dimethylglyoximato	dmg^-	قوي	ثنائي المخلب
اثيلين ثنائي امين en	Ethylenediamine	$NH_2CH_2CH_2NH_2$	قوي	ثنائي المخلب
اثيلين ثنائي امين رباعي حامض الخليك	Ethylenediaminetetraacetic acid	EDTA	قوي	سداسي المخالب
فلورو	Fluoro	F^-	ضعيف	احادي المخلب
هايدرازين	Hydrazine	NH_2NH_2	قوي	ثنائي المخلب
هايدرازينيوم	Hydrazinium	$NH_2NH_3^+$	قوي	احادي المخلب
هيدروكسيدو (هيدروكسو)	Hydroxido	OH^-	ضعيف	احادي المخلب
ايودو	Iodo	I^-	ضعيف	احادي المخلب
مثيل امين	Methylamine	CH_3NH_2	قوي	احادي المخلب
نتراتو	Nitrato	NO_3^-	قوي	ثنائي المخلب
نتريتو	Nitrito	NO_2^-	قوي	احادي المخلب
نايتروسيل	Nitrosyl	NO	قوي	احادي المخلب
اوكزاليتو	Oxalato	$C_2O_4^{-2}$	ضعيف	ثنائي المخلب
بيريدين	Pyridine	C_5H_5N	قوي	احادي المخلب
ثايوسياناتو	Thiocyanato	SCN^-	ضعيف	احادي المخلب
يوريا	Urea	$\{(NH_2)_2CO\}$	قوي	احادي المخلب(معقد)

Periodic Table of the Elements



Atomic Number 6
Symbol C
Name Carbon
Average Atomic Mass 12.0107

▨ Hydrogen
▨ Semiconductors (also known as metalloids)

Metals
▨ Alkali metals
▨ Alkaline earth metals
▨ Transition metals
▨ Other metals

Nonmetals
▨ Halogens
▨ Noble gases
▨ Other nonmetals

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	1 **H** Hydrogen 1.00794																	2 **He** Helium 4.002602
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
3	11 **Na** Sodium 22.98976928	12 **Mg** Magnesium 24.3050											13 **Al** Aluminium 26.9815386	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973762	16 **S** Sulfur 32.065	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
4	19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955912	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938045	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933195	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.409	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.64	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.798
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.293
6	55 **Cs** Cesium 132.9054519	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.90547	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.94788	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.084	79 **Au** Gold 196.966569	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98040	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (277)	109 **Mt** Meitnerium (268)	110 **Ds** Darmstadtium (271)	111 **Rg** Roentgenium (272)	112 Uub* Ununbium (285)		114 Uuq* Ununquadium (289)		116 Uuh* Ununhexium (292)		

* The systematic names and symbols for elements greater than 111 will be used until the approval of trivial names by the IUPAC.

The discoveries of elements with atomic numbers 112, 114, and 116 have been reported but not fully confirmed.

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.242	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92535	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.03806	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.02891	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

The atomic masses listed in this table reflect the precision of current measurements. (Each value listed in parentheses is the mass number of that radioactive element's most stable or most common isotope.)